TEXTILE DYEING

Edited by **Peter J. Hauser**

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Contents

Preface

Nearly all textile materials are colored after fabrication and before final finishing. The coloration of fibers and fabrics through dyeing is an integral part of textile manufacturing. This book discusses in detail several emerging topics on textile dyeing.

The pretreatment of textiles prior to dyeing is addressed by several authors. Menezes and Choudhari present chemical alternatives to traditional pretreatment, while Tavcer discusses enzyme pretreatment procedures. Bendak and Raslan review pretreatment methods of protein and synthetic fibers, and Bhatti et al. introduce the concept of radiation induced pretreatment. Control of the dyeing process is discussed by Günay and enhancing the dyeability of fibers is reviewed by Gashti et al. Details for dyeing specific fiber types are given by Gupta et al (polypropylene), Suesat and Suwanruji (polylactic acid), and Giménez-Martín et al (acrylic). Individual dyestuff classes are addressed by Koh (disperse dyes), Rippon et al (vat dyes). The use of cyclodextrins as dye leveling agents is reviewed by Voncina while Durasevic et al. suggest that photochromic dyes can function as useful sensors. The interaction of plasma with textile material prior to dyeing is well represented with chapters by Durasevic et al, Souto et al, Deshmukh and Bhat, and Mokbul and Dirk.

“Textile Dyeing” will serve as an excellent addition to the libraries of both the novice and expert.

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1

Effect of Radiation on Textile Dyeing

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1. Introduction

Love for colours is a natural instinct and every individual has his own choice and liking for colour. The icy appearance of Hamaliyan ranges or lush green forests or fields of agriculture or trees laden with colorful fruits or butterflies moving from flower to flower presents the beauty of nature, generation after generations are being attracted. The choice of beautiful fascinating colours reflects the aesthetic sense of humans that varies.

Colour is visual perceptual property corresponding in humans to the categories called red, yellow, blue and others. It is a sensation that arises from the activity of retina of the eye and its attached nervous mechanism, and results in a specific response to the radiate energy of certain wavelength and intensity. Thus it is a quality of an object with respect to light (Mizzarini *et al.*, 2002).Colorants may be either pigment or a dye which are characterized by their ability to absorb or emit light in the visible range 400-700nm.They may be organic or inorganic depending upon their structure and method of production.

Dyes are the coloured substances which are capable of imparting their colours to the matrix which may be fiber, paper or any object. They must have fixing tendency on a fabric that is impregnated with their solution and the coloured fixed dyes must be fast to light as well as resistant to action of water, dilute acids, alkalies, various organic solvents used in dry cleaning, soap solutions, detergent, etc (Shukla, 1992) . A pigment generally is a substance which is insoluble in the medium in contrast to dye in which it is applied and has to be attached to a substrate by additional compounds e.g. polymer in paints and plastics (Taylor and Nonfiction, 2006)

A compound looks coloured because it has absorbed certain electromagnetic radiation from the visible region. The moieties, present in colouring substance, responsible for the absorption of electromagnetic radiation and reflect in the visible region are called chromophores (Younas, 2006).Ultraviolet radiation constitutes to 5% of the total incident sunlight on earth surface (visible light 50% and IR radiation 45%). Even though, its proportion is quite less, it has the highest quantum energy compared to other radiations. Light is electromagnetic in nature. Within the electromagnetic spectrum, human eye captures visible light in the range between about 380 nm and 700 nm (Mizzarini *et al.*, 2002). Dyes absorb electromagnetic radiation of varying wavelength in the visible range of

spectrum. Human eyes detect the visible radiations only for the respective complementary colours.
Fig.1 shows the different regions of spectrum with their wavelengths.

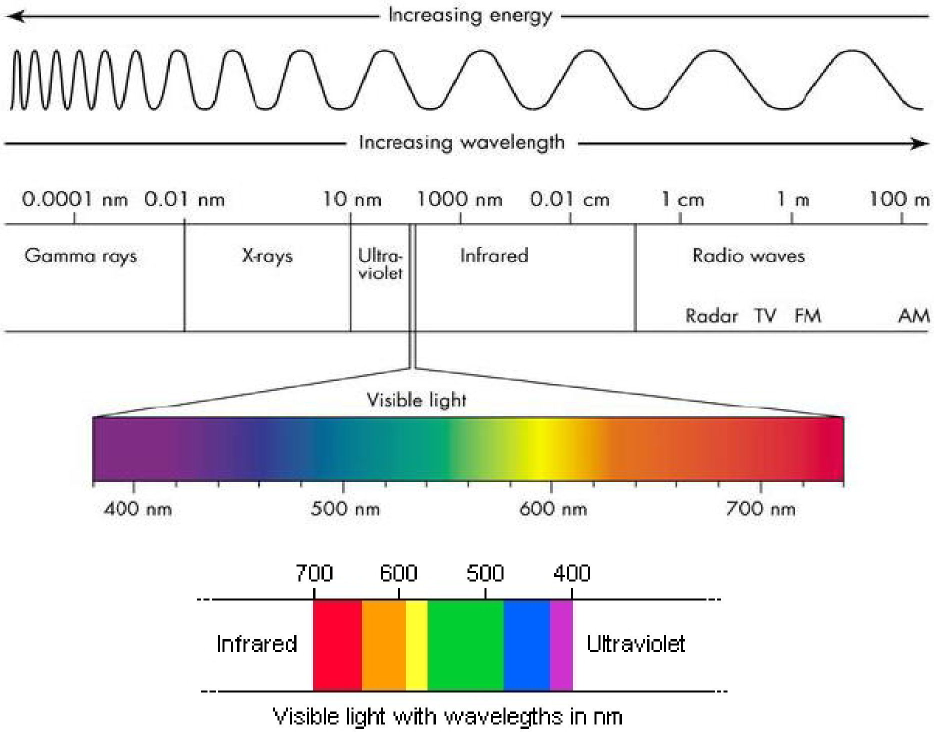


Fig. 1. Regions of electromagnetic spectrum

2. Classification of dyes: Natural & synthetic dyes

All colourants obtained from animals, plants and minerals without any chemical processing are called natural dyes.e.g.Alizarin a pigment extracted from madder, tyrian purple from snail and ochre which is a mineral of Fe_2O_3 (Gulrajani, 1992). Natural dyes may be vat dyes, substantive or mordant dyes as they require the inclusions of one or more metallic salts of tin, chromium, iron, copper, aluminum and other for ensuring reasonable fastness of the colours to sun light and washing. The natural dyes have several advantages such as: these dyes need no special care , wonderful and rich in tones , act as health cure, have no disposal problems, have no carcinogenic effect ,easily biodegradable, require simple dye house to apply on matrix and mild reactions conditions are involved in their extraction and application (Sachan and Kapoor,2004).There are some limitations of natural dyes which includes, lesser availability of colours, poor colour yield, complex dyeing processing, poor fastness properties and difficulty in blending dyes (Pan *et al.,* 2003). Table 1 given below, shows the classification of dyes based upon both colours and structures.

Colours	**Chemical Classification**	**Common Names**
Yellow and Brown	Flavone Dyes	Quercitron, Tesu
Yellow	Iso-quinoline Dyes	Barberry
Orange- Yellow	Chromene Dyes	Kamala
Brown	Naphthoquinone Dyes	Henna , Alkanet
Black	Benzophyrone Dyes	Cochineal , Madder
Blue	Indigoid Dyes	Logwood
Red	Anthraquinone Dyes	Indigo
Neutrals	Tannins	Pomegranate, Eucalyptus

Table 1.

Commercialization of natural dyes can be done successfully by a systematic and scientific approach to extraction, purification and use. Optimization of extraction condition is a must to minimize the investment cost and to avoid discrepancy in the dye shade quality. Natural dyes occur in many plant parts in small quantities and as complex mixtures with many chemical compounds of similar or different structures. These compounds vary considerably with change in general, same genus but different species and ecological conditions of the plant source. So when natural dyes extracted from these sources are used for dyeing and printing, variation in shade, depth and tone, among others, may arise. Further, chemical components of plants change with age and maturity of the parts. Extraction may include drying, pounding, soaking, skimming, crystallizing, condensing, caking and liquidifying, among others, depending on the quality and species of the dye yielding plant, mineral and insect (Shrivastava and Dedhia, 2006; Vankar *et al.,* 2000).

Synthetic dyes are a class of highly coloured organic substances, primarily utilized tinting textiles that attach themselves through chemical bonding between the molecules of dye and that of fiber. The use of natural dyes in textiles was eliminated since synthetic dyes give variety of reproducible shades and colours (Deo and Desai, 1999). Synthetic dyes are classified on the basis of chemical structure or on the basis of methods of application to the material. Dyes are synthesized in many ways by using different chemicals. On the basis of methods of application dyes are categorized as:-

Acid dyes: These dyes are anionic and form ionic bonds with fibers that are cationic in acid solutions. These dyes are applied onto the acrylic, wool, nylon and nylon/cotton blends. These are called acidic because they are normally applied to nitrogenous fibers in inorganic or organic acid solutions.

Azoic dyes: These dyes contain azo component (–N=N-), used for dyeing of cotton fabrics. In the dyeing process fiber is first treated with coupler followed by application of azo dye. This type of dye is extremely fast to light.

Basic dye: These dyes are cationic and form ionic bonds with anionic fibers such as acrylic, cationic dyeable polyester and cationic dyeable nylon. These are amino derivatives used mainly used for application on paper

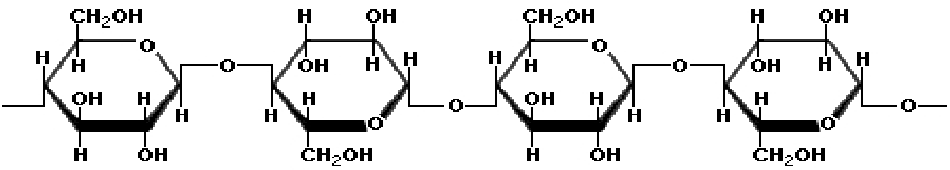
Disperse dyes: These dyes are colloidal and are soluble in hydrophobic fibers. Mostly these dyes are used for coloring polyester, nylon, and acetate and triacetate fibers. They are usually applied from a dye bath as dispersion by direct colloidal absorption method

Direct dyes: These are also azo dyes applied generally on cotton-silk combination from neutral or slightly alkaline baths containing additional electrolyte. These dyes predominantly interact and attach themselves with the Matrix (wool , polyamide fabric) through electrostatic interactions. These dyes are used to color cellulose, wool, nylon, silk etc.

Reactive dyes: Reactive dyes are the best choice and other cellulose fiber at home or in the art studio. Fixation of dye occur onto the fiber under alkaline conditions by forming a covalent bond between reactive group of dye molecule and OH, NH, SH etc groups present in the fibers (Cotton , wool , silk , nylon etc).
Mordant dyes: Applied in conjunction with chelating salts of Al, Cr and Fe. Metallic salts or lake formed directly on the fiber by the use Al, Cr or Fe salts which cause precipitation in situ.
Sulfur dyes: These dyes are used for dyeing cotton and rayon. The application of this dye requires careful process due to its water-soluble reduced form and insoluble oxidized form. These dyes are fast to washing but poorly fast to chlorine and give dark and dull colors.
Vat dyes: These dyes are insoluble in water and cannot be directly applied to textiles. These dyes require oxidation as well as reduction step for its application onto matrix.
Acetate rayon dyes: Developed for cellulose acetate and some synthetic fibers (Kim *et al.*, 2005; Shenai, 1992).
Dyes are synthesized in a reactor, filtered, dried, and blended with other additives to produce the final product. The synthesis step involves reactions such as sulfonation, halogenation, amination, diazotization, and coupling, followed by separation processes that may include distillation, precipitation, and crystallization. In general, organic compounds such as naphthalene are reacted with an acid or an alkali along with an intermediate (a nitrating or a sulfonation compound) and a solvent to form a dye mixture. The dye is then separated from the mixture and purified. On completion of the manufacture of actual colour, finishing operations, including drying, grinding, and standardization, are performed. These steps are important for maintaining consistent product quality.

3. Chemistry of fibers

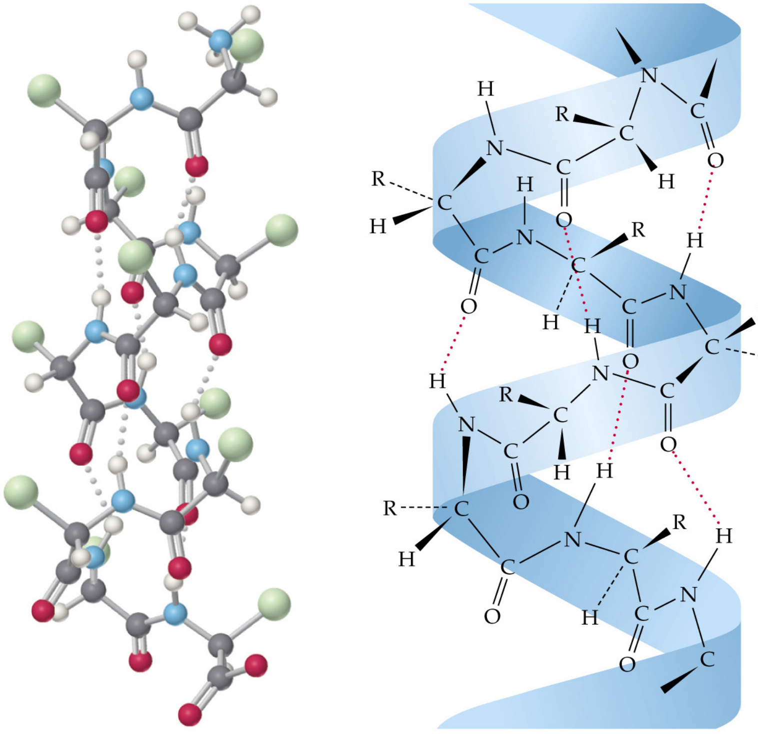
Cotton the most abundant of all naturally occurring substrates and is widely used. For the fabric strength, absorbency quality, capacity to be washed and dyed, cotton has become the principal clothing fabric of the world. The materials characteristically exhibit excellent physical and chemical properties in terms of water absorbency, dye ability and stability and can not be entirely substituted by artificial polymer fibers (Jun *et al.,* 2001).
The cellulose consists of glucose units linked together through oxygen atoms, 30 to several hundred chains from micro fibrils (Foldvary *et al.,* 2003). By dry weight 94% of cotton is made up of cellulose. The remaining constituents include 1.3% protein, 1.2% pectic substances, 0.6% waxes, 1.2% ash, and 4% of other components. Of three hydroxyl groups on the cellulose ring, two are secondary, and one is primary. Most of the reactions with cellulose occur at the primary hydroxyl groups.



When cellulose is chemically modified with the compounds containing cationic and anionic groups, the molecular chains are modified. In the modified fiber surface, the chemical and physical properties of cellulose fiber are changed. Through chemical modification, the reactivity of the cellulose fiber is enhanced. And several classes of dyes such as direct, azo, reactive etc can be successfully applied. The application of the cationic dyes has not gained widespread success. Our study comprises of the treatment method such as high energy radiation treatment which may create the anionic centre in the fabric to transfer the cationic dye onto the physically or chemically modified fabric. The reports of modified cellulose with the compounds containing multifiber cationic and anionic groups are scarce (Kim *et al.*, 2005).

Wool is different to other fibers because of its chemical structure that influences its texture, elasticity, staple and crimp formation. It is composed of keratin-type protein having more than 20 amino acids and very small amount of fat, calcium and sodium. The amino acids in wool linked together in ladder-like polypeptide chain to form a protein/polymer type structure.

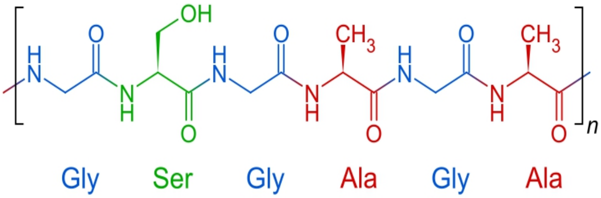
Wool polymer contains some important chemical groups that able to form inter-polymer forces of attraction. These groups are: the polar peptide groups (i.e. -CO-NH-) and the carbonyl groups (-CO-), which forms hydrogen bonds with the slightly positively charged hydrogen of the amino groups (-NH-) of another peptide groups. There are also carboxylate groups (-COO-), and amino groups (-NH3+) present in wool as side groups, between these two groups salt linkages or ionic bonds may be formed. Finally, the existence of the above mentioned inter-polymer forces tends to make the van der Waals` forces rather significant (Tamada, 2004).



Wool is easy to dye since the surface of the wool fiber diffuses light giving less reflection and a softer colour. The proteins in the core of the fiber absorb and combine with a wide variety of dyes and allow the wool to hold its colour (Michael and El-Zaher, 2005).

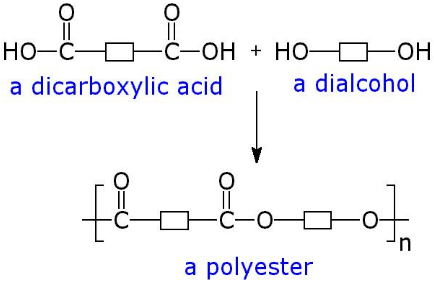
Silk is an insect fiber comes from the silkworm that spins around itself to form its cocoon. A single filament from a cocoon can be as long as 1600 meters. It is considered an animal fiber because it has a protein structure. Like other animal fibers silk does not conduct heat, and acts as an excellent insulator to keep our bodies warm in the cold weather and cool in the hot weather. The flat surfaces of the fibrils reflect light at many angles, giving silk a natural shine.

Natural and synthetic silk is known to manifest piezoelectric properties in proteins, probably due to its molecular structure. Silk emitted by the silkworm consists of two main proteins, sericin and fibroin, fibroin being the structural center of the silk, and sericin being the sticky material surrounding it. Fibroin is made up of the amino acids Gly-Ser-Gly-Ala-Gly-Ala and forms beta pleated sheets. Hydrogen bonds form between chains, and side chains form above and below the plane of the hydrogen bond network (Ellison, 2003).



Silk polymer is composed of sixteen different amino acids where as wool polymer contains twenty amino acids of wool polymer. Three of these sixteen amino acids namely, alanine, glycine and serine, make up about four-fifth of the complete polymer chain The important chemical groupings of the silk polymer are the peptide groups which give rise to hydrogen bonds, the carboxyl and amine groups give rise to the salt linkages. The high proportion (50%) of glycine, which is a small amino acid, allows tight packing and the fibers are strong and resistant to breaking. The tensile strength is due to the many interceded hydrogen bonds, and when stretched the force is applied to these numerous bonds and they do not break (Jun and Chen, 2006)

Polyester was first introduced to the American public in 1951by W.H. Carothers Laboratory. It was advertised as a miracle fiber that could be worn for 68 days without ironing and still look presentable. Polyester was once hailed as a magic fiber capable of being washed, scrunched and pulled on without showing any signs of water or wrinkles.



Now it is remembered for its bright double knit fabrics and comfortable texture. The name "polyester" refers to the linkage of several monomers (esters) within the fiber. Polyester is long chain polymer chemically composed of at leas 85% by weight of an ester and a dihydric alcohol and a terephthalic acid (Kiran, 2009).

Polyester Cotton(PC) is a blend of polyester and cotton in varied proportions. This particular fabric is well received by customers around the world. The yarn is available in single and twisted form. The polyester cotton (PC) fabric yarn commonly has a blend ratio of 50% polyester to 50% cotton. In polyester cotton fabric (PC), polyester provides wrinkle resistance and shape retention while cotton provides absorbency and consequent comfort (Hunger, 2003).

4. Irradiation in textiles

Irradiation processes have several commercial applications, in the coating of metals, plastics and glass, in printing, wood finishing, film and plastic cross linking and in the fields of adhesive and electrical insulations. The advantages of this technology are well known energy saving (low-temperature process), low environmental impact, simple, economical and high treatment speed. Despite these advantages, there have been few applications of radiation curing in the textile industry, such as non woven fabric bonding, fabric coating and pigment printing (Ferrero and Monica, 2011). Radiation treatment on fabric and garments can add value in colouration. Modification of the surface fiber can allow more dye uptake; its fixation at low temperature and increase wettability. Cotton knitwear pilling can be eliminated from the surface of the fabric by radiation treatment without affecting the strength of the fiber (Kim *et al.*, 2005).Effect of UV radiation in natural as well as synthetic dyeing using irradiated cotton fabric has given significant results.

4.1 Effect of UV and gamma radiation on the fabric dyed with natural dyes

There is a remarkable difference in colour strength when different extracts of irradiated and un-irradiated turmeric powder were used to dye the irradiated and un-irradiated fabric (Afifah *et al.*, 2011). The methanol solubilized extract gave more colour strength than aqueous (heat) solubilized and alkali solubilized extract as displayed in Fig. 2. The low colour strength using alkali solubilized extract is due to alkaline degradation of curcumin into products like vaniline, vanilic acid, feruloylmethane, ferulic acid and other fission products, which sorb on the fabric along with colourant and impart dull redder shades(Tonnesen and Karlsen,1985a). While using (heat) aqueous solubilized extract, the colourant being insoluble in water may undergo hydrolytic degradation and the actual colourant concentration becomes low onto the fabric as a result low colour strength is observed (Tonnesen and Karlsen, 1985 b). By using methanol solubilized extract, the actual colourant get significant chance to sorb onto fabric and impart yellow colour with dark shades.

The irradiation of fabric is also another factor which affects the colour strength of the fabric. Previous studies show that UV irradiation adds value to colouration and also increases the dye uptake ability of the cotton fabrics through oxidation of surface fibers of cellulose(Millington , 2000; Javed *et al* ., 2008). The colourants from Methanol solubilized extract reach the vicinities of fibres and upon investigation of colour strength using spectraflash SF 650, dark yellow shade was observed. In the case of un-irradiated fabric, the insoluble impurities get significant chance to sorb on the matrix along with colourant which showed the dull redder shades.

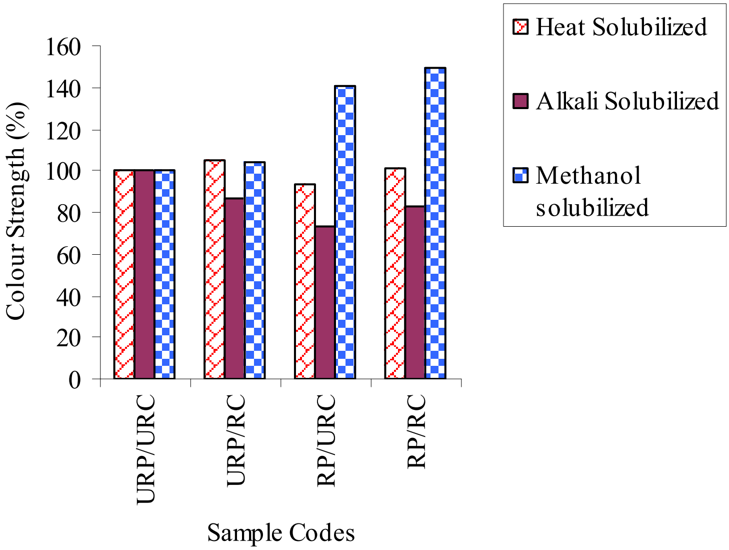


Fig. 2. Effect of UV radiation on the colour strength of the irradiated and un-irradiated cotton dyed with heat solubilized, alkali solubilized and methanol solubilized extract of irradiated and un-irradiated turmeric powder
(Where URP-un-irradiated powder, RP – irradiated powder,
RC- irradiated cotton fabric, URC-un-irradiated cotton fabric)

Gamma rays are ionizing radiations that interact with the material by colliding with the electrons in the shells of atoms. They lose their energy slowly in material being able to travel through significant distances before stopping. The free radicals formed are extremely reactive, and they will combine with the material in their vicinity. Upon irradiation the cross linking changes the crystal structure of the cellulose, which can add value in colouration process and causes photo modification of surface fibers. The irradiated modified fabrics can allow: more dye or pigment to become fixed, producing deeper shades, more rapid fixation of dyes at low temperature and increases wet ability of hydrophobic fibers to improve depth of shade in printing and dyeing (Millington, 2000).

The influence of gamma radiation on the colour strength values of the fabric dyed with natural dyes extracted from eucalyptus bark has been shown in Fig. 3. High colour strengths and dark brown shades of the fabric dyed in ethanolic extract were obtained as compared to aqueous extracts. The low colour strength and un-evenness in shade in aqueous extract is due to presence of insoluble impurities that might come on the fabric along with colourant.(Vankar *et al.*, 2000) The results shown in Fig. 3. demonstrate that irradiated fabric dyed using alcoholic extract gave more colour strength than un-irradiated fabric. Previous studies showed that gamma irradiation causes dislocation and fragmentation of fabric fibers (Foldvary *et al.*, 2003) however, only soluble colourant free from impurities get maximum chances to sorb on the fabric. But un-irradiated fabric contained less dye and yielded greener shade.

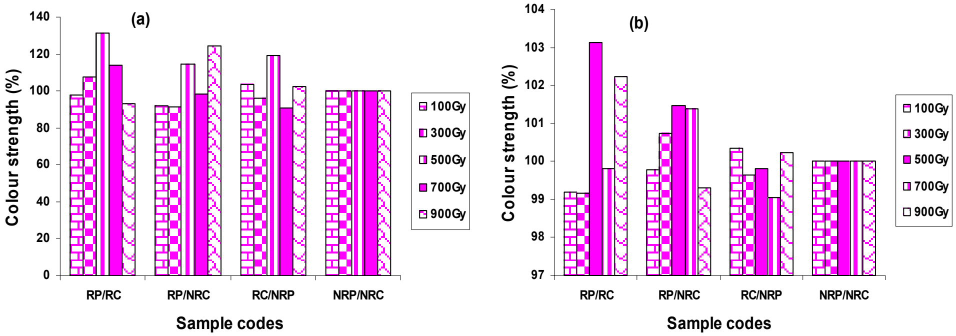


Fig. 3. Effect of gamma radiation on the colour strength of the cotton dyed with (a) ethanolic (b) aqueous extracts obtained form irradiated and un-irradiated Eucalyptus powder. NRP-un-irradiated powder, RP – irradiated powder, RC- irradiated cotton fabric, NRC-un-irradiated cotton fabric

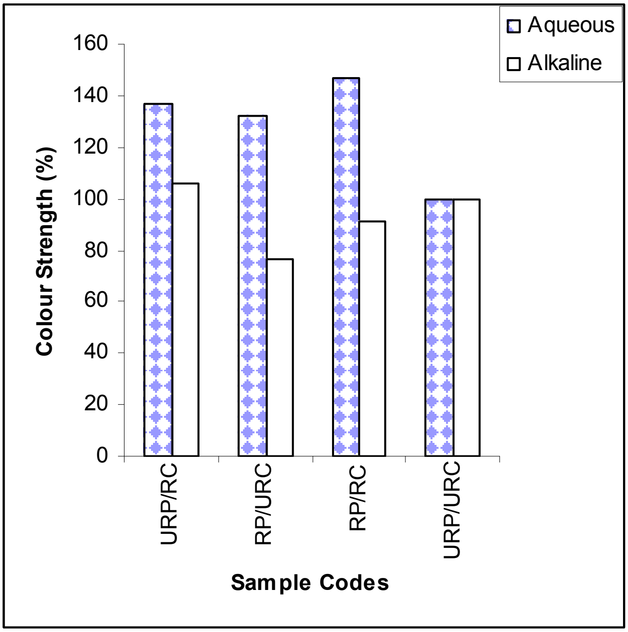


Fig. 4. Effect of gamma radiation on the colour strength of the cotton dyed with extracts obtained form irradiated and un-irradiated turmeric powder using aqueous and alkaline media (Where URP-un-irradiated powder, RP – irradiated powder, RC- irradiated cotton fabric, URC-un-irradiated cotton fabric)

The colour strength changes significantly in aqueous than in alkaline media. The fabrics dyed in aqueous extract of turmeric powder were darker yellow in shades than that of fabrics dyed in alkaline extract. The low colour strength was due to alkaline degradation of curcumin into water-soluble products like vaniline, vanilic acid, feruloylmethane, ferulic acid and other fission products, which gave dull redder shades (Tonessen and Karlsen, 1985a). Tonessen and Karlsen reported that below pH 7, curcumin existed in yellow colour and is insoluble in water (Tonessen and Karlsen, 1985b). Due to insolubility, the colourant might have tendency to get absorbed completely on the fabric without passing through the medium and shows darker yellow shades. Hence irradiated fabrics dyed in aqueous media gave more colour strength than un-irradiated fabrics due to oxidative degradation of cellulose fibres. Treatment of fabric by high-energy radiation causes either dislocation and fragmentation or slight loss in mass of fabric (Foldvary *et al.*, 2003; Takacs *et al.*, 2000). However, only colourants get maximum chance to sorb on fabric than insoluble impurities. So more colour strength is obtained in case of irradiated fabric dyed using aqueous extract of irradiated turmeric powder. Thus it is found that if irradiated fabric dyed with aqueous extract of irradiated turmeric powder, maximum colour strength and darker yellow shade was obtained.

4.2 Effect of UV and gamma radiation on the fabric dyed with synthetic dyes

UV irradiation effects the colour strength values and shades of fabric dyed with synthetic dyes. Using suitable dye and fabric, the process of irradiation can produce large variation in shades.

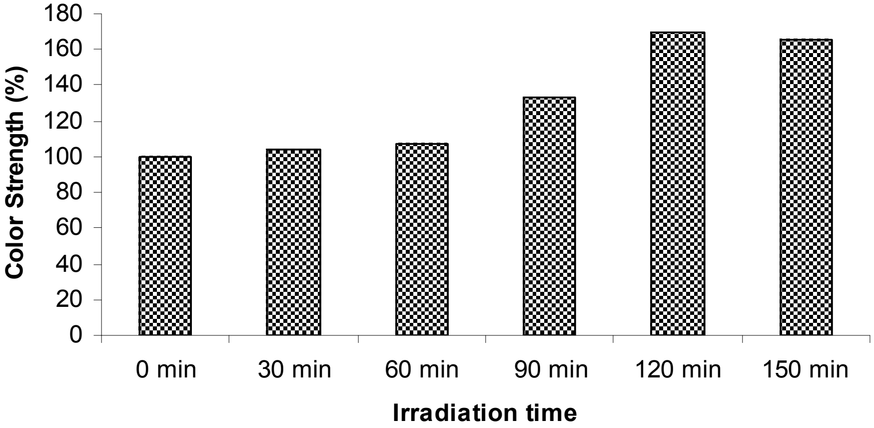


Fig. 5. Effect of UV irradiation time on the colour strength of the irradiated cotton fabric dyed with irradiated stilbene based reactive dye

The data displayed in Fig 5. shows that irradiated fabric for 120 min. gave maximum colour strength as compared to un-irradiated fabric. The fabric irradiated for 120 min. showed even shade with better colour strength. The reason might be the oxidation of cellulose upon exposure to UV radiation. Michael and EL-Zaher in 2005 reported that the UV treatment of cellulose fibre created spaces between fibres which imbibed more dye and as a result the interaction between dye and cellulose fabric becomes more significant. The dye molecules rush rapidly onto the fabric and as a result darker shades were obtained (Tayyba, 2010).

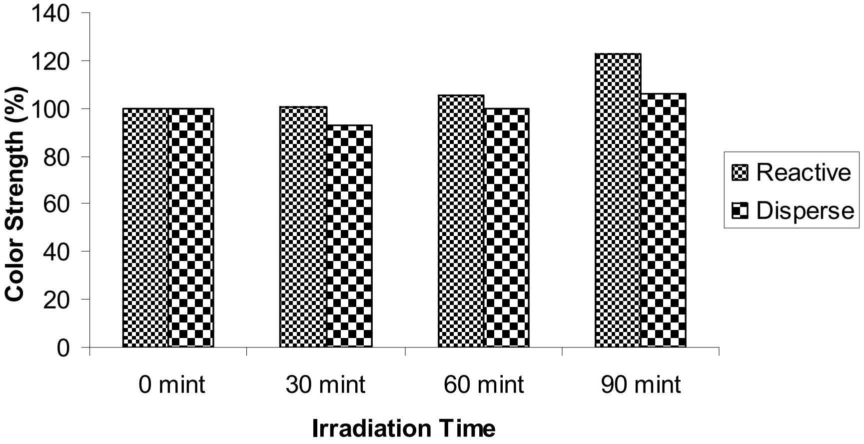
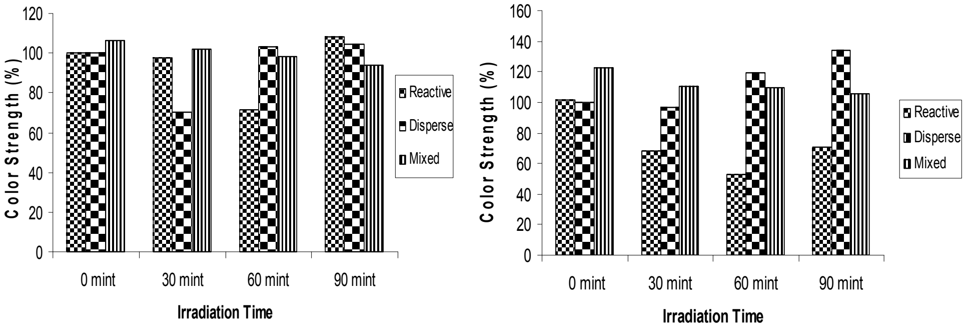


Fig. 6. Effect of UV irradiation time on the colour strength of the irradiated cotton fabric dyed with un-irradiated reactive and disperse dye

The above Fig. 6. shows that the fabric irradiated for 90 min. has maximum affinity for dye substrate to attach. The fabric irradiated for 30 and 60 minutes show even shades having good colour strength. This improvement might be due to the oxidation of cellulose in to carboxylic acid group upon exposure of cellulose to UV radiation which interacts more towards the dye material to form covalent bond.



(a) (b)

Fig. 7. Effect of UV irradiation time on the colour strength of the irradiated cotton fabric dyed with un-irradiated multifunctional triazine (a) and irradiated reactive and dianix disperse and mixed dye (b)

The un-irradiated and irradiated cotton fabric for the period of 30, 60 and 90 min was dyed, the results of fabrics have been shown in Figure 7. (a,b) shows that irradiated fabric and irradiated dyes for 90 min has maximum affinity for dye to attach on it. Oxidation of cellulose upon UV radiation significantly increases the dye uptake in the substrate due to the interstices available in the case of irradiated fabric surface (Michael and EL-Zaher, 2005).

The dye molecules rush rapidly on to the fabric and as a result darker shades were obtained (Sajida Parveen, 2009, Afifah Kausar, 2009; Afifah *et al.*, 2011). Previous study carried out by K.R. Millington suggested that photo modification of surface fiber may attain more dye or pigment to become fixed producing deeper shades. UV radiation causes more rapid fixation of dyes increases wettability of hydrophobic fibers to improve depth and shade in printing. For knitted wool and cotton fabrics, the problem of pilling can be eliminated.

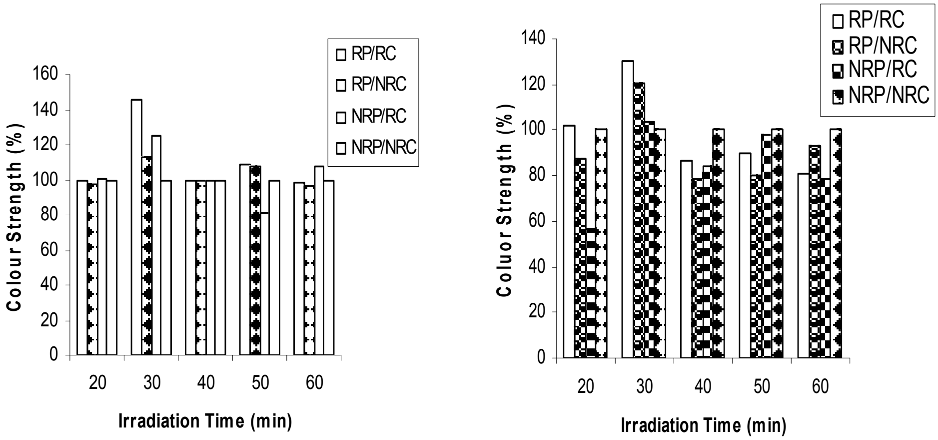


Fig. 8. Effect of UV irradiation time on the colour strength of the irradiated cotton fabric dyed with un-irradiated and irradiated 5 % (a) and 1% (b) Reactive Blue dye

The result shown in Fig. 8. (a & b) indicate that colour strength values of 5% solution of dye powder are more as compared to colour strength values obtained in case of 1 % solution. The optimized time for irradiating cotton fabric is 30 minutes as shown in Fig. 8. (a & b).At this time, oxidation of cellulose generates carboxylic acid group which helps in significant interaction of dye with oxidized a surface and show darker shades. Irradiation for less time does not activate the surface to interact with dye molecules to such an extent. While irradiation for long time may either facilitate insoluble impurities to rush onto modified fabric due to availability of wide interstices /gaps among the fibers which may cause dull and uneven shades having low colour strength (Saddique, 2008).

Gamma radiation shows a promising influence in textile dyeing since irradiated fabric dyed with synthetic dye gave a prominent difference The result shown in Fig. 9. indicate that colour strength values change remarkably using irradiated fabric which results in darker colour strength and more bluer shades than that of un-irradiated fabrics. This low colour strength is due the stuffing of insoluble impurities present in the dye solution on to the fabric.

Results given in Fig. 9. show that the dyeing performed using irradiated fabric treated with 300Gy absorbed dose gave maximum colour strength with darker bluer shades. At higher doses, low colour strength is obtained, which may be due to the degradation or dislocation of crystal moieties on cellulosic material (Foldvary *et al.* 2003; Takacs *et al.*2000). While at low dose, fabric surface does not activate enough to fix dye onto it and does not able to make firm interaction with dye material.

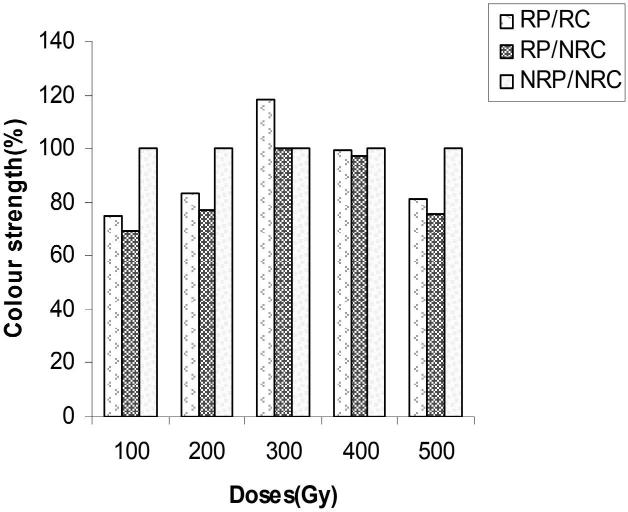


Fig. 9. Effect of gamma irradiation on the colour strength of the irradiated and un-irradiated cotton fabric dyed with Irradiated and un- irradiated reactive blue dye powder

The result displayed in Fig. 10. reveal that colour strength values decrease with increase in absorbed doses. The more colour strength is because of photo modified surface of cellulose which may have more affinity for dye substrate (Mughal *et al.*, 2007). The results show that the dyeing performed using 200Gy dose gives maximum colour strength with darker shades. At sufficient higher dose insoluble impurities along with dye molecule become fixed and causes uneven shades, while below optimum dose, surface of cellulose do not stimulate much to interact significantly with dye material. Thus dyeing performed using cotton fabric irradiated to an absorbed dose of 200Gy gave better colour strength (Toheed Asghar, 2009).

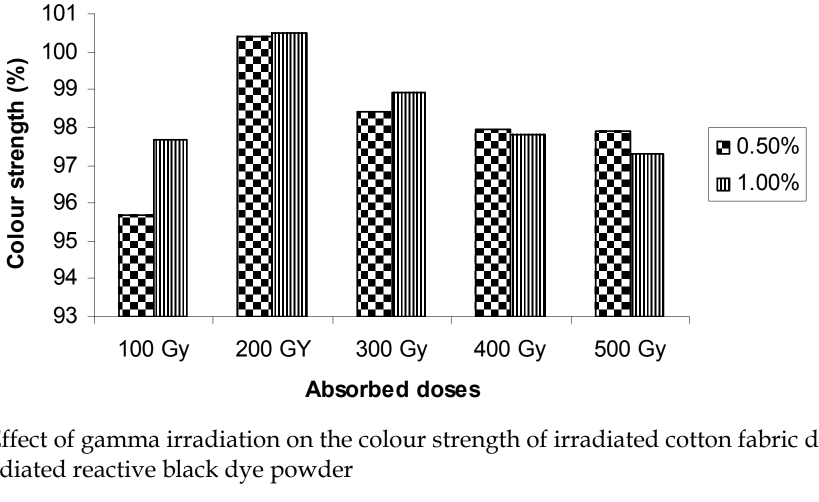


Fig. 10. Effect of gamma irradiation on the colour strength of irradiated cotton fabric dyed with Irradiated reactive black dye powder

4.3 Effect of UV and gamma radiation on wool and silk and polyester

Studies on wool keratin have been previously performed in order to evaluate the effect of UV radiation. Chemical changes induced by short term UV radiation are confined to fibers at surface where as it is unable to penetrate into the fabric. The colour changes i.e. green followed by yellow in wool keratin due to UV radiation have been observed also (Millington, 2000).There are several processes to reduce the pilling yet no process can guarantee the zero pilling in wear. But Millington reported that it is only UV radiation which can reduce the pilling through siro flash technology followed by oxidation with hydrogen peroxide in germicidal UV Tubes. After using such techniques and then dyeing with UV irradiated wool fabric, the characterization of wool fabric meets standard marks by ISO. Thus the continuous UV reduction of the fabric followed by batch oxidation is of great commercial value. (Millington, 1998a; Millington, 1998b; Millington, 1997).

When wool fabric is exposed to UV radiation, it exhibits some physical and chemical changes on its surface. This interaction not only modifies the fabric of wool but also improve the shades particularly grey and black. It also helps in even dyeing, deeper shades, chlorine free printing and improve the photo bleaching of wool (Millington, 1998c). Now a days, UV curing technology is being used for the modification of wool surface that helps in finishing as well as deepening the shades of wool when dyed using reactive dyes. By using UV curing technology, there are no risks involved to any loss of fabrics fibers in weight as well as in its physical appearance. This technology also do not cause any hazardous use of chemicals, smoothness of surface, unpilling as well as deep hues (Ferrero and Periolatto, 2011; Abdul Fattah *et al.*, 2010).

5. Conclusion

Radiation processes has several commercial applications starting from curing of fabrics, finishing, improvement of shades and characterization of dyed fabrics. The advantage of this technology are well known such as improvement in shades , enhanciong colour fastness , colour stregnth , low cost effective and reduction of the concentration of the dye. All these results have been seen from our above experiments. Radiation curing of silk, wool and cotton fabric to reduce pilling , their finishing and mercerization processes has also been improved. Thus both UV and gamma radiation has improved the textile sttuff according to standards of ISO , EPA and FAO.

The use of eco-friendly technnology giving eco–label products under the influence of high energy radiations that may give new orientation for other dyes such as vat, reactrive azo and other brands. Similarly improvement of fibers of wool , silk , nylonn , Polyester cotton (P.C). etc., for dyeing to get good shades, even and lavelled dyeing, accepatable fastness properties yet are underway.So the dyers and colourists should try such techniques inorder to get better results and alternating methods for any risks related to human health.

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2

Dyeing Wool with Metal-free Dyes – The Use of Sodium Borohydride for the Application of Vat Dyes to Wool

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1. Introduction

Vat dyestuffs are pigments that must be pre-treated with a reducing agent, such as sodium hydrosulphite, to make them water-soluble immediately before they are used for dyeing (Latham, 1995; Trotman, 1984). The reduction step converts the pigment form into a leuco compound. This owes its name to the Greek word for colourless, because many vat dyes are very pale in colour when in the reduced state, due to the lower level of conjugation of double bonds. A schematic of this reaction for the dyestuff Vat Red 1 is shown in Figure 1.

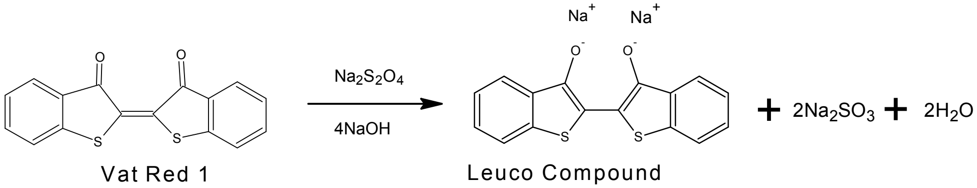


Fig. 1. Structure of Vat Red 1 and formation of the sodium salt of the leuco compound.

In strongly alkaline conditions, the leuco forms of vat dyestuffs are anionic and soluble in water. They can be exhausted onto cotton from long liquors under alkaline conditions in the presence of an electrolyte, such as sodium chloride or sodium sulphate (Latham, 1995; Trotman, 1984). After adsorption by the substrate, the leuco form of the dye is oxidised back to the insoluble coloured pigment inside the fibre. This can be done by exposure to air, or with an oxidising agent such as hydrogen peroxide. Wool is usually dyed with anionic dyestuffs from acidic dyebaths, where the amphoteric wool fibres are positively charged as a result of protonation of amino and carboxyl groups. Under alkaline conditions, however, fewer amino groups are protonated and, depending on the pH, the net charge on the fibres may be neutral or even negative. The effect of this is that conventional acid, premetallised and reactive wool dyes have a lower substantivity for wool under alkaline conditions than under acidic conditions. In contrast to this behaviour, however, even under strongly alkaline conditions, the anionic leuco form of a vat dyestuff has a relatively high substantivity for wool (Bird, 1947; Hug, 1948; Luttringhaus, Flint & Arcus, 1950; Weber, 1951) and wool/cotton blends (Lemin & Collins, 1959). This results in high levels of dyebath exhaustion at pH values as high as pH 9 and above.

Vat dyes are amongst the oldest colouring materials used for textiles, and for many years selected vat dyes were used on both cotton and wool for products requiring very high levels of wet fastness and light fastness. Vat dyes are still used on cotton, where the highly alkaline conditions employed in their application do not damage the fibre. In the case of wool, however, the propensity for alkaline damage during dyeing makes their use less attractive. This resulted in them being replaced by chrome and premetallised dyes, which also give high levels of fastness. Furthermore, chrome and premetallised dyes are applied under pH conditions where fibre damage is less likely to occur. The more recent introduction of reactive dyes for wool also enables excellent wet fastness properties to be achieved with little fibre damage.

Pressure from environmental lobby groups and some major retailers has raised the possibility that wool products that are coloured with metal-containing dyestuffs may become increasingly unacceptable because of concerns about the possible effects of heavy metals on the environment. Although metal-free reactive dyes can be used on wool to give products with high wet fastness, with some shades lightfastness can be a problem. Furthermore, heavy black and navy shades are difficult for many mills to achieve with reactive dyes. This paper investigates the feasibility of using vat dyes as alternatives to reactive dyes to obtain shades with high fastness properties on wool.

The traditional method of preparing the leuco form of a vat dye employs the reducing agent sodium dithionite (sodium hydrosulphite; $Na_2S_2O_4$) and sodium hydroxide. Sodium hydrosulphite has a sufficiently negative reduction potential for it to effectively reduce all vat dyes. Other reducing agents have also been used, but these have not found wide acceptance. Sodium borohydride has been evaluated but, on its own, reacts too slowly with vat dyes for practical usage (Latham, 1995). It has been claimed, however, to improve the stability against atmospheric oxidation of vat dyes reduced with sodium hydrosulphite (Neale, 1961; Harrison & Hinckley, 1963; Medding, 1980; Vivilecchia, 1966), but other workers have disputed this claim (Baumgarte & Keuser, 1966; Nair & Shah, 1970).

A technique has recently been developed for producing sodium hydrosulphite in situ by mixing sodium borohydride and sodium bisulphite (Rohm and Haas Technical Information, 2007) (Figure 2).

$$NaBH_4 + 8NaHSO_3 \longrightarrow 4Na_2S_2O_4 + NaBO_2 + 6H_2O$$

Fig. 2. Reaction between sodium borohydride and sodium bisulphite

Sodium borohydride is supplied commercially as an aqueous solution containing sodium borohydride (12%), stabilised with sodium hydroxide (NaOH). It has been found that a mixture of sodium bisulphite and the sodium borohydride solution in the ratio 4:1 is suitable for the application of indigo to cotton under alkaline conditions (Rohm and Haas Technical Information, 2007; Schoots, 2007). Hydrosulphite produced in this way is claimed to be virtually free of the by-products that result from its decomposition during storage (Rohm and Haas Technical Information, 2007). Furthermore, this reducing system has been found to be more efficient than hydrosulphite alone and it has been claimed to give a dyestuff saving of around 15% in the application of indigo to cotton warps (Schoots, 2007).

A borohydride/bisulphite mixture has also been found to be very effective for the reductive bleaching of wool under acid to neutral conditions (Technical Manual, Australian Wool Innovation, 2010; Schoots & Stevens, 2007).

Based on the findings on cotton, it was considered that this reducing system may provide the basis of a new method of dyeing wool with vat dyes. This study describes an evaluation in which results obtained with a borohydride/bisulphite reducing system are compared with those obtained with a method based on the application of vat dyes using the traditional method with sodium hydrosulphite.

2. Experimental

2.1 Fabric

A 100% wool, plain weave fabric (weight 193 g/m^2) was used in this study.

2.2 Dyes and chemicals

Commercial samples of the following nine vat dyes were used:

- Vat Red 1
- Vat Red 10
- Vat Red 45
- Vat Green 1
- Vat Green 3
- Vat Yellow 5
- Vat Orange 5
- Vat Violet 18
- Vat Brown 24

A commercial sample of sodium borohydride (SBH) was supplied by Rohm and Haas as a 12% solution in sodium hydroxide. Other chemicals were of laboratory grade.
The following dispersing agents were used:

- Kieralon DB (nonionic/anionic mixture; Dyechem);
- Albigen A (solution of polyvinylpyrrolidone; BASF);
- polyvinylpyrrolidone (Mol Wt 44000; BDH Chemicals);
- Detergent NA-B (blend of anionic and nonionic surfactants: APS/Nuplex).

2.3 Equipment

Two types of laboratory machines with different methods of liquor circulation were used to dye samples of wool fabric. The details are described below.

Ahiba Turbomat.

Fabric samples were wound onto perforated spindles. The dyebaths were circulated by pumping the liquor through the fabric tube (in to out).

Mathis Labomat

With this machine, the fabric samples and dye liquors were sealed inside pots. Circulation was achieved by tumbling the pots inside a heated box. This resulted in both fabric and liquor moving together. As the pots were not completely filled with liquor, the air in the pot was mixed with the liquor.

2.4 Preparation of the dye vat by reduction

The vat pigments were converted to the water-soluble leuco form by the following methods.

2.4.1 Hydrosulphite method

The various amounts of sodium hydrosulphite and sodium hydroxide were dissolved in 250 mL of water at room temperature and the solution stirred while the powdered vat dye was slowly added. Stirring was continued while the mixture was heated at 2°C /min to the vatting temperature (usually 60-70°C), where it was maintained for 30 minutes.

2.4.2 Sodium borohydride/bisulphite method

Sodium bisulphite was dissolved in 250mL of water at room temperature, followed by the addition of the aqueous solution of sodium borohydride (SBH) diluted with ten times its volume of water. After 2 minutes, an aqueous solution of sodium hydroxide (320 g/L or 38°Bé) was added and the mixture stirred until the effervescence had ceased (usually 5-10 minutes). Stirring was continued while the vat dye was added slowly and also while the mixture was heated at 2°C/min to the vatting temperature, where it was maintained for 30 minutes.

2.5 Fabric dyeing

After diluting to the required volume, the vatted liquor was added to the dyeing pot containing the fabric. The liquor ratio was 20:1 The liquor was heated at 1.5°C per minute to the required temperature (usually 60°C or 70°C), where it was held for 30 minutes. The fabric was overflow rinsed (cold) for one minute, followed by two five minute rinses at 40°C. Oxidation of the leuco compound to the vat pigment was carried out by treatment with hydrogen peroxide (1g/L) for 10 minutes at 50°C. The fabric was then soaped off (the normal procedure with vat dyes (Latham, 1995; Trotman, 1984; Bird, 1947)) with Detergent NA-B (2g/L), adjusted to pH 9.5 with ammonium hydroxide, for 20 minutes at 98°C. After cooling, the fabric was rinsed and removed from the dyeing machine. It was then rinsed, with hand stirring, for 5 minutes in a beaker containing a solution of Detergent NA-B (1 g/L) at 50°C (liquor ratio 50:1). This treatment was considered to simulate the process of washing-off a fabric in a scouring machine or back-washing wool top after dyeing. It was noted that the gentle mechanical action involved in this step removed a small amount of oxidised, insoluble pigment from between the fibres and yarns in the fabric.

2.6 Measurements

Dyebath exhaustion levels were determined by measuring the absorbance of the dyebath on a Jasco V530 UV-Vis Spectrophotometer at the wavelength of maximum absorbance of the dye. Colour yields were determined by measuring the K/S values of the dyed samples on a Datacolor Texflash Spectrophotometer at the wavelength of maximum reflectance of the dye.
Dry and wet rubbing fastness was assessed by *IWS Test Method 165 – Fastness to Rubbing*.
Alkaline perspiration was assessed by *ISO-105-EO4 – Fastness to Perspiration.*
Washing fastness was assessed by ISO-105-CO2 – Colour Fastness to Washing.
Grey scale staining and colour changes were measured on a Datacolor Texflash Spectrophotometer. The software supplied with the instrument (Datacolor Iris Version 2.3) enabled ratings to be quoted to 0.1 of a greyscale unit.
Wet burst strength was measured according to *Australian Standard AS2001.2.4A-90, Determination of Burst Pressure of Textile Fabrics, Hydraulic Diaphragm Method* (which is equivalent to ASTM D3787-01 but also includes procedures for wet testing).

3. Results and discussion

3.1 Determination of optimum concentration of SBH/bisulphite

Important requirements for a satisfactory vat dyeing are:

i. complete reduction of the dye to the leuco compound during vatting;
ii. prevention of premature oxidation of the leuco compound;
iii. maintaining the leuco compound in a soluble form during the dye exhaustion phase.

A conventional vat dyeing system uses a mixture of sodium hydrosulphite and sodium hydroxide to reduce the dyestuff to its leuco compound. It has been estimated that the stoichiometric relationship between sodium hydrosulphite and SBH is that 1g/L hydrosulphite is equivalent to 0.44 g/L of solid SBH (Rohm and Haas Technical Information, 2007). This, however, provides only an approximate guide to the amount of SBH required for vat dyeing, as the dye manufactures' pattern cards contain only general information on the amount of hydrosulphite required (Weber, 1951).

Reagent/Conditions	A	B	C	D
SBH solution (12%) (g/L)	1	2	4	5
Sodium Bisulphite (g/L)	4	8	16	20
NaOH solution (38° Bé) (ml/L)	3	6	12	15
Vatting conditions	30 min at 60°C			
Colour of vat	Purple	Purple	Purple	Purple
pH after fabric added (40°C)	11.4	11.4	11.5	11.5
Dyebath pH at end of dyeing	8.8	8.8	9.5	10.2
Colour of dyebath after 30 min at 60°C	Purple	Purple	Purple	Purple
Absorbance of dye liquor after 30 min at 60°C	0.15	0.16	0.27	0.36
pH of oxidation liquor	9.5	9.2	9.9	9.9
Final soap off pH	9.9	9.9	9.9	9.9

Table 1. Effect of Concentration of Sodium Borohydride and Sodium Bisulphite in the Application of Vat Red 45 (1% oww) to Wool (Dyed in the Turbomat for 30 mins at 60°C)

The optimum concentrations of SBH, sodium bisulphite and sodium hydroxide required to produce a satisfactory dyeing were, therefore, determined experimentally. A ratio of sodium bisulphite to SBS solution of 4:1 was used because, as discussed previously, this has been found to be suitable for the application of indigo to cotton. Table 1 shows the various concentrations of SBH, sodium bisulphite and sodium hydroxide used to reduce the dye Vat Red 45 to its leuco compound prior to exhaustion onto wool. The samples were soaped off after dyeing with 2g/L Detergent NA-B at pH 9.5 (obtained with ammonium hydroxide) for 20 min at 98°C. Although all the formulations reduced the dye to its purple, soluble leuco form, the three mixtures containing the highest concentrations of reagents gave solutions that were more stable than the one containing the least amounts of the chemicals. The stability was judged by observing the formation of partially oxidised (green) pigment on the liquor surface, after stirring had been stopped. The fully oxidised pigment was red in colour. Other experiments with the lowest concentration of chemicals (i.e. 1 g/L SBH and 4 g/L sodium bisulphite) showed some variability in the reproducibility of the vatting process, in particular with respect to the sensitivity to stirring rate. Furthermore, with liquors vatted with 1g/L SBH and 4 g/L sodium bisulphite, there was a tendency for slight oxidation to occur during the dyeing cycle.

Table 2 shows data for colour yield (K/S) and fastness to dry and wet rubbing. There was no significant difference in rubbing fastness between any of the samples (rubbing fastness gives an indication of the amount of oxidised dye remaining on the fibre surface). There was also no significant difference between the K/S values obtained with the two lowest concentrations of SBH and bisulphite. However, the K/S values decreased with increasing concentration of chemicals above these levels. This was possibly caused by destruction of the chromaphore by over-reduction of the dye. The highest colour yield consistent with good stability of the vatted liquor was obtained with a concentration of 2g/L SBH and 8g/L sodium bisulphite.

Conc. SBH (12%) (g/L)	Conc. Sodium. Bisulphite (g/L)	Final Dyebath pH	K/S Value at 520 nm	Rubbing Fastness	
				Dry	Wet
1	4	8.8	6.6	4.7	4.3
2	8	8.8	6.5	4.6	4.6
4	16	9.5	5.2	4.6	4.3
5	20	10.2	4.1	4.5	4.8

Table 2. Colour Yield (K/S Values) and Rubbing Fastness of Wool Fabrics Dyed with Vat Red 45 (1% oww) by the Sodium Borohydride/Bisulphite Method

The combination of 8 g/L sodium bisulphite and 2 g/L SBH, found to be the optimum amounts to effectively reduce Vat Red 45, was used with the dyestuff Vat Green 1. The data in Table 3 show that the blue leuco form of the dye was maintained until the end of the exhaustion phase. This confirmed that these concentrations of SBH and bisulphite were also satisfactory for this dyestuff.

Conc. Dispersing Agent NA-B (g/L)	Dyeing Temp (°C)	Vat Colour	Dyebath pH with Fabric (40°C)	Final Dyebath pH	Final Dyebath Colour	Absorb-ance of final dyebath	K/S at 640 nm
None	60	Blue	11.0	9.5	Blue	0.68	11.0
None	60	Blue	10.8	9.1	Blue	0.21	6.0
None	70	Blue	10.7	9.1	Blue	0.18	7.8
None	80	Blue	11.0	9.0	Blue	0.21	4.8
None	90	Blue	10.9	9.1	Blue	0.08	4.0
0.25	70	Blue	11.2	8.6	Blue	0.70	10.9
0.25	70	Blue	11.0	11.6	Blue	1.66	10.9
Vatted with : 2 g/L SBH; 8 g/L sodium bisulphite; 6 ml/L caustic soda (38°Bé). The dyebaths contained sodium sulphate (5% oww). The samples were soaped off for 20 min at 100°C with 2g/L Detergent NA-B at pH 9.5.							

Table 3. Vat Dyeing with Vat Green 1 (1% oww) by the SBH Method (Dyed for 30 mins in the Turbomat at various temperatures)

Table 3 shows, however, that in contrast to the result obtained with Vat Red 45, the colour yield for Vat Green 1 was dependent on the final dyebath pH, with the highest value obtained when the pH was greater than 9.5. Diffusion into the fibre did not appear to be a factor, as increasing the dyebath temperature above 60°C did not improve the colour yield. It is also unlikely that this effect was due to premature oxidation of the dyebath, because all the liquors remained blue (indicative of the reduced leuco form) throughout the whole exhaustion stage. Furthermore, the poor colour yields cannot be explained by lower levels of dyebath exhaustion, because the absorbance values in Table 3 show that the samples with the lower colour yields had higher dyebath exhaustions. A possible explanation is that the aggregation state of the leuco compound is an important factor; and that with some dyes

this is very sensitive to pH within the range used in these experiments (in this study we tried to minimise alkaline damage to the wool by keeping the pH as low as possible).
In order to test this hypothesis, fabric samples were dyed with Vat Green 1 in the presence of a dispersing agent. Detergent NA-B was used because it was considered that this compound would be an effective dispersing agent for vat dyes as it is recommended for soaping off vat-dyed cotton after oxidation. Table 3 shows that in the presence of 0.25 g/L of Detergent NA-B, a high colour yield was obtained, even when the pH of the dyebath had dropped to pH 8.6 at the end of the dyeing cycle. The results also show that, with a dispersing agent in the dyebath, maintaining the pH to a high value (pH 11.6) by alkali addition had little effect on colour yield. Following these results, the effect of Detergent NA-B and other dispersing agents was examined further.

3.2 Effect of dispersing agent in the dyebath

Table 4 shows the effect of various dispersing agents added to the dyebath on the colour yield of Vat Green 1. Polyvinylpyrrolidone (PVP) was included in the evaluation because it is the main constituent of the commercial product Albigen A. The results from Table 3 for two samples dyed without a dispersing agent are included for comparison purposes.

Dispersing agent (g/L)	Initial Dyebath pH	Dyeing Temp.	Sodium Sulphate in dyebath (% oww)	Final Dyebath Colour	Absorbance at 552 nm	Final Dyebath pH	K/S (at 640 nm)
None	11.0	60	5	Blue	0.68	9.5	11.0
None	10.8	60	5	Blue	0.21	9.1	6.0
0.05 A	11.1	70	0	Blue/Green	0.82	9.0	12.3
0.1 A	11.0	70	0	Blue/Green	1.29	8.9	11.2
0.1 A	11.1	70	5	Blue	0.88	8.7	10.1
0.2 A	11.0	70	0	Blue/Green	1.72	8.9	9.7
0.25 A	11.0	70	0	Blue/Green	1.67	8.9	10.3
0.5 A	11.0	70	0	Blue/Green	3.11	8.8	8.3
0.05 PVP	11.1	70	0	Blue	1.40	8.7	10.6
0.1 PVP	11.1	70	0	Blue	2.24	8.6	10.0
0.1 PVP	11.2	70	5	Blue	2.25	8.7	9.5
0.15 PVP	11.0	70	0	Blue	2.73	8.5	8.3
0.20 PVP	11.0	70	0	Blue	3.30	8.4	7.1
0.25 NA-B	11.0	70	0	Blue/Green	0.96	8.9	13.2
0.25 NA-B	11.2	70	5	Blue	0.70	8.6	10.9
0.5 NA-B	11.5	70	0	Blue	1.05	9.1	10.7
1.0 NA-B	11.5	70	0	Blue	0.53	9.2	6.1
0.25 KDB	11.0	70	0	Blue/Green	0.53	8.9	8.6
0.5 KDB	11.6	70	0	Blue	1.51	9.4	8.6
0.5 KDB	11.1	70	5	Blue	0.68	8.7	7.1
1.0 KDB	11.5	70	0	Blue	3.16	9.2	7.1

(Dyed for 30 mins in the Turbomat at various temperatures).
A is Albigen A; KDB is Kieralon DB; NA-B is Detergent NA-B; PVP is polyvinyl pyrrolidone.

Table 4. Effect of Various Dispersing Agents Added to the Dyebath (1% oww Vat Green 1)

Of the four dispersing agents tested, Kieralon DB gave the worst results and was not investigated further. The other three products gave similar results. For these, only a very small concentration of dispersing agent was required in order to counteract the adverse effect of a low final dyebath pH. High concentrations of dispersing agent tended to reduce the colour yields. The optimum concentrations of Albigen A and PVP were 0.05 g/L, whereas for Detergent NA-B, the highest colour yields were obtained with 0.25g/L.

For all the dispersing agents studied, addition of sodium sulphate (5% oww) to the dyebath slightly decreased the colour yield. It appears, therefore, that with the SBH reducing system, there is a marked benefit with some vat dyes in using a small concentration of dispersing agent in the dyebath, in order to avoid the necessity of maintaining a high liquor pH throughout the dyeing cycle. The pH always dropped to some extent when the dyebath, set with the vatted dye, contacted the wool fabric. It was observed that the amount the pH changed varied from dye to dye. Although the reason for this variability is not known, it is possible that the finishing agents used in the formulation of the dyes give a buffering effect, in some cases. It was found that not all vat dyes showed this pH sensitivity when applied to wool. However, in order to offset any adverse effects caused by unpredictable pH changes, a dispersing agent was added to all dye liquors, as a standard part of setting the dyebath.

3.3 Application of vat dyes to wool by the conventional sodium hydrosulphite/sodium hydroxide method

In order to compare the SBH/bisulphite method with the conventional vat dyeing procedure, a series of fabric samples were dyed with either Vat Red 45 or Vat Green 1 (1% oww), following reduction to the respective leuco compound with sodium hydrosulphite and sodium hydroxide. As the dyestuff manufacturers' pattern cards give only very general information on the amounts of sodium hydrosulphite and sodium hydroxide required for effective reduction, the dyes were vatted by the method described in Section 2.2.1 with the two concentrations of the chemicals shown in Table 5. All the dye liquors contained sodium sulphate (5% oww), in accordance with normal practice on wool. Two sets of fabric samples were dyed with each formulation: one without a dispersing agent and one containing 0.25g/L Detergent NA-B. All the samples were soaped off in a similar manner with Detergent NA-B and ammonia.

It can be seen from Table 5 that all the concentrations of sodium hydrosulphite and NaOH reduced Vat Red 45 to the purple leuco compound. However, although the two dyebaths set with the lower concentrations of these chemicals remained purple up to the end of the exhaustion phase, the fabrics changed to a pink/purple during the dyeing cycle. This showed that some oxidation of the leuco compound to the pigment form of the dye had occurred during dye exhaustion, which indicates that insufficient hydrosulphite had been used. The results show that the most stable system regarding resistance to premature oxidation was the one containing 5 g/L hydrosulphite and 12 ml/L of the sodium hydroxide solution. This was considered to be the optimum concentrations of these chemicals for Vat Red 45, because in this case the dye was not oxidised until after the end of the exhaustion/fibre penetration phase of the dyeing cycle. These concentrations are very similar to those recommended for the application of vat dyes to wool/cotton blends (Lemin & Collins, 1959).

Reagent/Conditions	**A**	**B**	**C**	**D**
Sodium hydrosulphite (g/L)	3	3	5	5
Sodium hydroxide solution (38°Bé) (ml/L)	7	7	12	12
pH of vat	12.2	12.2	12.3	12.3
Colour of vat	Purple	Purple	Purple	Purple
Dispersing agent (Detergent NA-B) (g/L)	0.25	nil	0.25	nil
pH after fabric added (40°C)	11.8	11.8	11.9	11.9
pH after 30 min at 60°C	11.3	11.2	11.5	11.5
Colour of fabric after 30 min at 60°C	Pink/Purple	Pink/Purple	Purple	Purple
Colour of liquor after 30 min at 60°C	Purple	Purple	Purple	Purple
Absorbance of final dyebath at 548 nm	1.08	0.88	0.43	0.71
Water rinse pH	11.0	11.0	11.1	11.2
Soap off	2g/L Detergent NA-B pH 9.5 ammonia 20 mins at 100°C			
Final soap off pH	10.0	9.9	10.0	10.0

Table 5. Vat Dyeing with Vat Red 45 (1% oww) by the Conventional Hydrosulphite/NaOH Method (Dyed in Turbomat 30 mins at 60°C)

Table 6 shows K/S and rubbing fastness data for samples dyed with Vat Red 45 and various concentrations of hydrosulphite and sodium hydroxide. The best results were obtained with the highest concentrations of chemicals (5g/L hydrosulphite and 12 ml/L NaOH solution) without a dispersing agent. Table 6 also shows that when Vat Red 45 was applied to wool by the optimised SBH method, the colour yield and rubbing fastness were superior to the values obtained by the conventional hydrosulphite procedure. Another advantage of the SBH method was the lower pH of the dye liquors at the end of the dyeing cycle (pH 8.5 - 9.0 compared with pH 11.5 for the hydrosulphite/NaOH method). This would be expected to result in a lower level of fibre damage, as discussed later.

Conc. Sodium Hydrosulphite (g/L)	Conc. NaOH (ml/L of 38°Bé)	Dispersing Agent (Detergent NA-B) (g/L)	Final pH of Dyebath	K/S Value at 520 nm	Rubbing Fastness	
					Dry	Wet
3	7	Nil	11.3	3.4	4.4	4.3
3	7	0.25	11.2	4.0	4.4	4.3
5	12	Nil	11.5	4.3	4.3	4.1
5	12	0.25	11.5	3.9	4.4	3.7
Dyed with 2g/L SBH; 8 g/L Bisulphite; 6 ml/L 38°Bé NaOH		0.25	9.5	6.5	4.6	4.6

Table 6. Comparison of Colour Yield (K/S Values) and Rubbing Fastness of Samples Dyed with Vat Red 45 (1% oww) by the Hydrosulphite/NaOH and SBH Methods at 60°C (Dyed for 30 mins in the Turbomat)

The results obtained when Vat Green 1 was applied by the conventional hydrosulphite/NaOH method are shown in Tables 7 and 8.

Reagent/Conditions	**A**	**B**	**C**	**D**
Sodium Hydrosulphite (g/L)	3	3	5	5
NaOH (38°Bé) (ml/L)	7	7	12	12
pH of vat	11.9	11.9	12.0	12.0
Colour of vat	Blue	Blue	Blue	Blue
Dispersing agent (Detergent NA-B) (g/L)	0.25	Nil	0.25	Nil
pH After fabric added (40°C)	11.4	11.4	11.5	11.5
Final dyebath pH	11.0	11.0	11.5	11.5
Colour of fabric after 30 min at 70°C	Green	Green	Blue	Blue/Green
Colour of liquor at after 30 min at 70°C	Green	Green	Blue	Green
Absorbance of final dyebath at 558 nm	1.09	0.63	2.87	1.16
Water rinse pH	10.5	10.6	10.8	10.9
pH of Oxidation	9.5	9.2	9.9	9.9
Soap off	2g/L Detergent NA-B pH 9.5 ammonia 20 mins at 100°C			
Final soap off pH	9.9			

Table 7. Vat Dyeing with Vat Green 1 (1% oww) by the Hydrosulphite Method (Dyed for 30 mins in the Turbomat at 70°C)

Conc. Sodium Hydrosulphite (g/L)	Conc. NaOH (ml/L of 38°Bé)	Dispersing Agent (Detergent NA-B) (g/L)	Final pH of Dyebath	K/S Value at 640 nm	Rubbing Fastness	
					Dry	Wet
3	7	Nil	11.0	7.9	4.4	3.4
3	7	0.25	11.0	5.1	3.8	2.6
5	12	Nil	11.5	7.5	4.2	3.2
5	12	0.25	11.5	9.8	4.4	3.5
Dyed with 2g/L SBH; 8 g/L /Bisulphite; 6 ml/L 38°Bé NaOH		0.25	8.6	11.3	4.6	3.8

Table 8. Comparison of Colour Yield (K/S Values) and Rubbing Fastness of Samples Dyed with Vat Green 1 (1% oww) by the Hydrosulphite and SBH Methods at 70°C (Dyed for 30 mins in the Turbomat)

Table 7 shows that all the concentrations of hydrosulphite and NaOH reduced Vat Green 1 to the blue leuco compound. However, as discussed above for Vat Red 45, the dyebaths set with the two lowest concentrations of these chemicals were oxidised to some extent during the exhaustion phase of the dyeing cycle. This again indicated that insufficient hydrosulphite had been used. The results show that the most stable system regarding resistance to premature oxidation was again the one containing 5 g/L hydrosulphite and 12 ml/L NaOH. In contrast to the finding for Vat Red 45, in this case, the addition of a dispersing agent produced better results for colour yield and rubbing fastness (Table 8). This is similar to the finding for this dye applied with SBH/bisulphite.

Table 8 compares results for Vat Green 1 applied by the hydrosulphite/NaOH method with results obtained by the optimised SBH method. Thus, as found for Vat Red 45, the SBH method gave a much better colour yield and slightly better rubbing fastness than the conventional procedure using hydrosulphite and NaOH. Again, it should be noted that the final liquor pH of the SBH dyebath was significantly less than for the hydrosulphite/NaOH system.

3.4 Effect of using a buffered dyebath

Results discussed above show that with some dyes (e.g. Vat Green 1) the colour yield can be adversely affected if the pH of the dyebath falls below a certain value during the exhaustion stage. Despite this effect being decreased by addition of a selected dispersing agent to the dyebath, it was considered that the reproducibility/robustness of the system would be improved by buffering the pH of the dyebath. After examining possible alternatives, trisodium phosphate was selected for further study. This compound has been claimed to produce less fibre damage than other alkalis (Bird, 1947). Table 9 shows the colour yields and rubbing fastness results obtained by adding three concentrations of trisodium phosphate to the dyebath. A concentration of 2g/L trisodium phosphate maintained the pH slightly above pH 9.5 and gave the best colour yield. This amount of trisodium phosphate was used in all further dyeings.

Reagent/Conditions	**A**	**B**	**C**	**D**
pH of vat	11.9	11.9	11.9	11.9
Colour of vat	Blue	Blue	Blue	Blue
Conc. trisodium phosphate in dyebath (g/L)	1	2	3	4
pH After fabric added (40°C)	11.2	11.2	11.2	11.2
pH after 30 min at 60°C	9.6	9.7	10.1	10.3
Colour of liquor after 30 min at 60°C	Blue	Blue	Blue	Blue
Absorbance of final dyebath at 620 nm	1.5	1.6	2.2	2.4
Water rinse pH	10.5	10.5	10.6	10.7
Soap off	2g/L Detergent NA-B pH 9.5 ammonia 20 mins at 100°C			
Final soap off pH	9.5	9.5	9.4	9.5
K/S at 640 nm	8.8	11.3	9.4	10.2
Dry Rubbing	4.5	4.6	4.5	4.5
Wet Rubbing	4.0	3.8	4.0	3.8

Table 9. Effect of Buffering the Dyebath with Trisodium Phosphate on the Colour Yield and Rubbing Fastness of Vat Green 1 (1% oww) Applied to Wool by the SBH Method (2g/L SBH; 8g/L sodium bisulphite; 6 ml/L of 38° Bé NaOH) (Dyed in Turbomat for 30 min at 60°C; 0.05 g/L Albigen A added to dyebath)

3.5 Optimisation of dye fastness

When cotton is dyed with vat dyes, the dyed samples are soaped off to remove oxidised pigment from the fibre surface and to aggregate the pigment particles inside the fibre. Both these effects improve overall fastness properties (Latham, 1995; Trotman, 1984; Bird, 1947; McNeil et al, 2005). It was observed during the early part of this work that some loose pigment remained on the fabric surface, even after wool fabrics had been soaped off for 20 minutes at 98°C. It was also found that this had an adverse effect on fastness properties. Unlike normal wool dyes, vat pigments are insoluble in water after they have been oxidised. It is suggested that a dyeing machine such as the Turbomat is not very effective in removing surface pigment, because its circulation action, which involves pumping liquor through the fabric, will tend to filter any pigment particles removed in the wash off. Washing-off in equipment such as a scouring machine would be expected to be more effective in removing pigment particles trapped within the yarns. In the present study, in order to produce dyed fabrics with optimum fastness properties, after soaping-off in the dyeing machine, all fabrics were rinsed with hand stirring in a beaker containing 1 g/L Detergent NA-B, as described in Section 2. This treatment was considered to provide a laboratory simulation of fabric scouring for piece goods, or backwashing in the case of wool that had been top dyed. Such a treatment should be part of any procedure for applying vat dyes to wool by the new SBH method.

Vat Dye (Colour Index Number)	Method	K/S	Washing Fastness				Rubbing Fastness		Alkaline Perspiration Fastness			
			SC	W	C	N	Dry	Wet	SC	W	C	N
Red 1	Hydrosulphite	5.3	3.7	5.0	4.8	4.9	4.2	3.4	All Rated 5			
	SBH	5.7	4.4	5.0	4.7	4.8	4.6	3.9				
Red 10	Hydrosulphite	4.5	4.2	4.9	4.7	4.8	4.3	3.5				
	SBH	5.5	4.3	4.9	4.7	4.7	4.5	4.0				
Red 45	Hydrosulphite	3.9	4.7	4.9	4.7	3.3	4.4	3.7				
	SBH	6.5	4.8	4.9	4.6	3.8	4.6	4.6				
Green 1	Hydrosulphite	9.8	2.4	4.9	4.8	4.8	4.4	3.5				
	SBH	11.3	3.0	4.9	4.8	4.9	4.6	3.8				
Green 3	Hydrosulphite	1.9	4.5	4.9	4.8	4.8	4.4	4.1				
	SBH	2.9	4.1	4.8	4.8	4.8	4.5	4.3				
Yellow 5	Hydrosulphite	1.5	2.8	4.9	4.8	4.9	4.5	4.3				
	SBH	7.6	3.1	4.9	4.8	4.9	4.4	4.3				
Violet 18	Hydrosulphite	8.8	2.9	4.9	4.8	4.9	4.5	3.9				
	SBH	12.9	2.7	4.8	4.7	4.6	4.6	4.0				
Orange 5	Hydrosulphite	6.1	3.5	4.9	4.8	4.9	4.3	3.8				
	SBH	12.4	4.2	4.9	4.8	4.9	4.4	3.4				
Brown 24	Hydrosulphite	0.75	3.4	4.9	4.8	4.7	4.4	4.1				
	SBH	2.2	3.9	4.9	4.7	4.6	4.5	4.3				

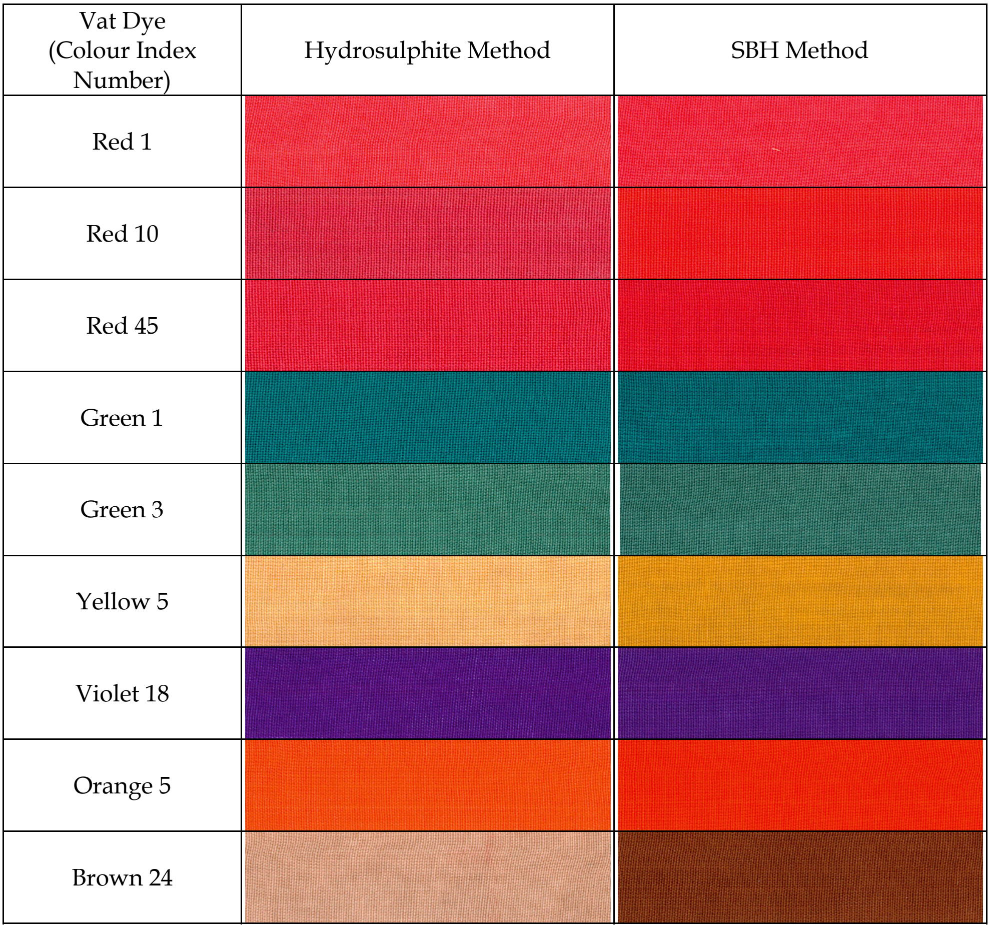
SC- Shade Change; W – Stain on Wool; C – Stain on Cotton; N – Stain on Nylon

Table 10. Colour Yield and Fastness to Wet Treatments and Rubbing of Vat Dyes Applied by the SBH and Hydrosulphite/NaOH Methods at 60°C (1% oww dye).

3.6 Colour yield and fastness of vat dyes applied by the SBH and hydrosulphite methods

The data in Section 3.3 for Vat Red 45 and Vat Green 1 show that the SBH method gave better colour yields and better, or similar rubbing fastness than the conventional method using sodium hydrosulphite and sodium hydroxide. Table 10 presents results for colour yield and fastness to washing, alkaline perspiration and rubbing for 9 vat dyes applied by the optimised SBH method. For comparison, results are also shown for the dyes applied to wool by the hydrosulphite/caustic soda method.

The data in Table 10 confirm the results obtained with Vat Red 45 and Vat Green 1, discussed above. Thus, for all nine dyes, the SBH/bisulphite system gave better colour yields than were obtained by the conventional method using sodium hydrosulphite and sodium hydroxide. The differences in colour yields can also be seen in Table 11. Furthermore, Table 10 also shows that accompanying the higher colour yields, the SBH/bisulphite system gave similar or slightly better overall fastness properties than hydrosulphite.



Vat Dye (Colour Index Number)	Hydrosulphite Method	SBH Method
Red 1	🟥	🟥
Red 10	🟥	🟥
Red 45	🟥	🟥
Green 1	🟩	🟩
Green 3	🟩	🟩
Yellow 5	🟨	🟨
Violet 18	🟪	🟪
Orange 5	🟧	🟧
Brown 24	🟫	🟫

(Table 11 is shown in colour in the on-line version of the paper)

Table 11. Wool Fabrics Dyed with Vat Dyes (1% oww dye) by the SBH and Hydrosulphite Methods

3.7 Effect of type of dyeing machine

In a long liquor dyeing process, interchange of the dyebath liquor with the substrate is important in order to ensure a constant supply of dyestuff molecules to the fibre surface. This can be achieved either by pumping the liquor through a stationary material, moving the substrate though the liquor, or moving both the liquor and material through the machine. Anionic wool dyes applied under acidic conditions have a high substantivity for wool as a result of ionic attraction between the anionic dye molecules and protonated amino groups in the fibre. For this reason, the type of liquor circulation used in the dyeing machine is not an important factor in the uptake of most types of wool dyes. Vat dyes, however, are applied to wool at a relatively high pH, where the fibre is negatively charged. Thus, in this case the substantivity of the dye will be dependent largely on non-polar/hydrophobic interactions rather than on ionic attraction. It is possible, therefore, that the more efficient liquor interchange in the Turbomat, involving pumping the liquor through the fabric, may result in better dyebath exhaustion than in a machine such as the Mathis Labomat, where liquor and fabric are tumbled around together. Another factor that may be important in the Mathis machine is that the constant mixing of air with the liquor could result in premature oxidation of the leuco compound. This could result in precipitation of the dyestuff in the dyebath and, consequently, a lower colour yield.

In order to compare the effects of the SBH vat dyeing system in machines with different actions, fabric samples were dyed with Vat Green 1 by the optimised SBH method in both the Turbomat and Mathis laboratory dyeing machines. The first two sets of data in Table 12 show that the colour yield of the sample dyed in the Mathis was much lower than the one dyed under similar conditions in the Turbomat. Although the exhaustion was slightly better in the Turbomat than in the Mathis, the difference was not great enough to account for the large difference in colour yield. A second possibility, discussed above, is that the reducing power of the SBH system had been adversely affected by oxidation resulting from mixing the dyebath with air during agitation in the Mathis machine. In order to test this possibility, two further samples were dyed in the Mathis machine. Extra SBH, sodium bisulphite and caustic soda were added to one of the pots when the vatted dye liquor was diluted immediately before the fabric was added. This technique, called “sharpening the bath”, is used when concentrated stock vats are prepared and then diluted for use over a few days. The extra reducing agent replaces losses due to air oxidation.

Dyeing Machine	Extra SBH/bisulphite and NaOH added	Final Dyebath pH	Absorb. at 558 nm	K/S at 640 nm	Rubbing Fastness	
					Dry	Wet
Mathis	None	9.6	1.03	1.6	4.2	2.5
Turbomat	None	9.0	0.82	12.3	4.5	3.7
Mathis	Yes (a)	9.9	1.37	16.1	4.5	3.2
Turbomat	Yes (a)	8.6	0.57	14.3	4.4	3.3

(a) Bath Sharpened with 1 g/L SBH / 4 g/L sodium bisulphite / 3 ml/L caustic soda (38°Bé)
All samples soaped off for 20 mins at 98°C in 2 g/L Detergent NA-B

Table 12. Effect of Dyeing Machine Type and of Sharpening the Bath on Dyeing Vat Green 1 (1% oww) by the SBH/Bisulphite Dyeing System (Dyed for 30 min at 70°C; Liquor ratio 25:1; 5% oww Sodium sulphate; 0.05 g/L Albigen A added to the dyebath).

As can be seen from Table 12, the addition of extra reducing agent improved the colour yield of samples dyed in the Mathis machine. The significance of this result is that it provides an indication of the possible behaviour of the SBH system when wool is dyed with vat colours in different types of machines. Thus, the results obtained in the Turbomat can be considered to relate to the behaviour of top, loose stock, package and beam dyeing equipment, where liquor is pumped through the substrate and very little mixing with air occurs. The action of the Mathis, however, can be considered to simulate that of a jet, winch or hank dyeing machine, all of which allow a high degree of contact between the dyebath and atmospheric oxygen. It is clear from these results that when this type of equipment is used, the bath sharpening technique should be employed. It is inadvisable to use extra reagents during the dyestuff vatting step, because with some vat dyes the chromophore can be destroyed by over reduction.

3.8 Wool fibre damage caused by SBH and hydrosulphite/NaOH vat dyeing methods

Wool fibre damage was assessed by comparing the wet burst strength (Lewis, 1989) of fabrics after dyeing with vat dyes, by either the optimised SBH or optimised hydrosulphite/NaOH methods, with the values for the undyed fabrics. In a wet wool fabric, ionic interactions (salt linkages) and hydrogen bonds within fibres are largely disrupted and their stabilising effect on wool structure is considerably diminished. Wet burst strength is, therefore, particularly useful because it provides an indication of cleavage of both disulphide and peptide covalent bonds (Lewis, 1989).

The data in Table 13 show that at dyeing temperature of 60°C and 70°C, the optimised SBH method produced less fibre damage than the standard procedure using hydrosulphite and NaOH. This can be attributed largely to the much lower final dyebath pH obtained with SBH. Fibre damage is, however, determined by both temperature and pH; and at a dyeing temperature of 70°C, the difference in fibre damage was lower than at 60°C. As it has been shown that dyed fabrics with good colour yield and fastness properties can be obtained at 60°C, it is concluded that this temperature should be used for the application of vat dyes to wool by the SBH/bisulphite system. For comparison purposes, a fabric sample was also dyed with a pre-metallised dye (1% oww) at pH 5 for 45 minutes at 98°C. The dyed fabric had a bursting force of 286N (equivalent to a strength retention of 86%).

Dyeing Method	Dyeing Temp. (°C)	Final Dyebath pH	Wet Burst Strength	
			Bursting Force (N)	Strength Retention (%)
Undyed	----	----	330	100
Hydrosulphite	60	11.5	193	58
SBH	60	8.9	256	78
Hydrosulphite	70	11.5	223	67
SBH	70	8.9	242	73

Table 13. Wet Burst Strength of Wool Fabrics Dyed with Vat Dyestuffs by Hydrosulphite/NaOH and SBH Methods

4. Conclusions

The feasibility of using a reducing system based on sodium borohydride and sodium bisulphite to apply vat dyes to wool has been demonstrated. For a range of nine vat dyes, better colour yields and overall better fastness properties were obtained by the borohydride/bisulphite method, compared with the conventional procedure involving sodium hydrosulphite/NaOH. Furthermore, the SBH/bisulphite procedure produced less fibre damage than the conventional method.

Sodium borohydride is more expensive than sodium hydrosulphite. However, the cost difference between the auxiliaries is likely to be offset by the better colour yield and, for an expensive substrate such as wool, by the lower fibre damage produced by the SBH/bisulphite reducing system, compared with sodium hydrosulphite/NaOH.

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3

Pretreatments of Textiles Prior to Dyeing: Plasma Processing

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1. Introduction

Synthetic fibres have acquired an important part of the current textile industry. A great disadvantage of some of the synthetic fibres is their low surface energy. This causes poor wettability and dyeability. Surface modification techniques are mainly carried out to remove loosely bound materials, foreign particles/impurities and to improve hydrophilic nature and thereby improving dyeability. Manipulation of surface characteristics of textile materials is of fundamental importance in the production of advanced functional textiles. Textile fibres can be classified in two main groups: Natural and Synthetic. Natural fibres are of animal origin or plant origin such as silk, wool, hair, jute, cotton, cellulose etc. whereas there are a number of manmade/synthetic fibres such as viscose, polyester, polypropylene, nylon, PLA fibres, polyamide and acrylic fibres. Natural fibres are limited and are not sufficient and not always suitable for many applications. Hence synthetic fibres have acquired greater importance in the present era. Synthetic fibres form an important part of the textile industry, with the production of polyester alone surpassing that of cotton. Improving the surface properties suitably is a very important aspect of the textile processing. Low surface energy of the synthetic fibres affects the processing of the fibres, especially during wet treatments. The surfaces are not easily wetted, thus impeding the application of finishing compound and colouring agents. In addition, a hydrophobic polymer hinders water from penetrating into the pores of the fabric. For a number of applications it is necessary to modify surface properties of textiles from hydrophobic to hydrophilic and vice versa. Plasma processing has a potential to render and change such surface properties. Recent advances in textile chemistry have resulted in imparting various functional properties such as decreased skin irritations, enhancing antimicrobial activity and fragrance to the textile material. The surface composition and structure of a textile material plays an important role in the textile's performance in specific applications. E.g. The surface of apparel / textile garment that is in contact with human skin could be modified to absorb the body moisture while the outside surface could be modified to repel water. Several studies showed that properties of polymeric substrates could be altered through surface modification (Deshmukh and Bhat, 2003 (a); Deshmukh and Shetty, 2007; Jahagirdar and Tiwari, 2004; Navaneetha P., et al., 2009; Yen et al., 2006).

In the history of dyeing, right from early days, when natural dyes derived from extracts of trees, leaves, roots and flowers were used till the modern concept with the use of several synthetic dyes, it can be seen that each one has its own peculiarities. An efficient dyeing process needs good adhesion and penetration of dye molecule into the fibre structure. Thus the structure of the fibre – both Physical and Chemical – becomes important. If not found to be suitable, these need to be modified. Various pretreatments such as chemical, enzymes, plasma, irradiation have been tried.

Textile technology deals with several processes such as desizing, scouring, bleaching, calendaring, singeing, dyeing, printing etc. During each of these stages the structure, properties and behavior of fibres undergo many changes. The assembly of the fibres and fabrics as well as bulk of each fibre undergoes transformations. Of these changes, the surface modifications of the fibres is of profound importance as it improves properties such as softness, adhesion, wettability, dyeability, printability etc. Apart from clothing, textiles find use in a variety of applications such as furnishing, carpets, medical, automobile, geo-textile etc. Each of these can benefit from specially designed characteristics which are governed by surface properties. Wettability, adhesion, friction, biocompatibility, absorption, all begin at surface and thus surface composition is more important than bulk. The properties depend on surface chemical and physical structures which vary according to types of fibres, polymers and the assemblies. The surfaces offer a platform for functional modifications to meet specific needs. The surface modification can be achieved by various techniques such as traditional wet solution treatment, physical treatment, biological approach etc. New technologies using high energy beam process, vapour deposition, nano-particles etc. can have potential for modification of surfaces.

Textile industry is one of the most pollutant industries because of the various processes involved such as singeing, desizing, scouring, bleaching, mercerization, dyeing etc. These processes pollute the environment and water resources. Economical and ecological pressure on textile industry requires the development of economic and environment friendly "green" processes. So one has to select a proper pretreatment for the modification of surfaces amongst the available processes.

2. Surface modification techniques

Wettability and adhesion of polymers / films can be controlled by using surface modification techniques such as exposure to plasma, flame, chemicals, enzymes etc. Wettability can also be regulated by changing chemical composition of the surface. In addition surface roughness can be an important factor for enhancing the adhesion and wettability. Wettability is governed by molecular interaction of the outermost surface layer of a few angstrom units. Therefore the forces dictating the wetting behavior of organic substances do not originate from the organic molecule as a whole, but rather from the outermost surface group. Further interfacial energy minimization needs molecules to arrange themselves in such a way that only the low energy portions come in contact with surrounding phase. As a result wettability depends on the chemical nature of energetically favoured functional groups and the extent to which these are exposed. Several surface modification techniques have been developed to improve wetting, adhesion, dyeing, feel and other properties of textile surfaces by introducing a variety of reactive functional groups. Few important techniques are described below.

2.1 Wet chemical processing

In this surface modification technique, the textile surface is treated with liquid reagent to generate reactive functional groups onto the surface. Chemical agent penetrates in the textile material / substrate, thereby damaging the bulk property. The commonly used chemical processing agents are chromic acid and potassium permanganate which introduce oxygen containing functional groups on synthetic fibres such as PET, PP, Nylon and PE. The degree of functionalization is therefore not repeatable between the polymers of different molecular weight and crystallinity. The another disadvantage is that it can lead to the generation of hazardous chemical waste and can cause skin irritation, even with very small amount of residual on the textile material. The effect of pretreatment of polyester with DMF, DCM and PCE on dyeability of polyester fabric was studied for disperse dyes (Jahagirdar and Tiwari, 2004; Patel and Bhat, 1986). The dye uptake depended on the solvent and the temperature and duration of pretreatment. All the pretreated samples showed a higher dye uptake than the untreated one. The temperature close to the boiling point of the solvent was found to be the best temperature for increased dyeing. The enhanced dyeability was associated with the plasticization and reduction in glass transition temperature of polyester. Similar studies on effect of swelling treatments with benzyl alcohol and formic acid was carried out for nylon-6 filaments. When the pretreated filaments were dyed with disperse dye, a considerable increase in the equilibrium dye uptake was observed. Although these filaments showed increase in lateral order (as evident from X-ray diffraction), the increase in dye uptake was explained due to structural rearrangement creating larger voids (Subramanian et al., 1982).

In the chemical grafting, the first step is to create radicals on the textile to initiate copolymerization reactions with different monomers. Deo and Gotmare have carried out grafting of acrylonitrile monomer on grey cotton to impart high water absorbency (Deo and Gotmare, 1999). They have used $KMnO_4$ as an initiator. Tsukada et al. have used ammonium peroxysulfide as an initiator to graft benzyl methacylate on wool fibres (Tsukada et al., 1997). They have also reported that the tensile strength of grafted fibres increases while elongation and breaking strength decreases.

2.2 Mechanical abrasion

It also leads to non uniform and non repeatable surface modification. We do not have good control over the process as in wet processing. This in turn hampers mechanical properties of the materials under process.

2.3 Flame treatment

The reactive oxygen is generated by burning an oxygen rich gas mixture. It incorporates hydroxyl, aldehyde and carboxylic acid functional groups onto the surface and is utilized to enhance surface properties for better printability, adhesion and wettability. Flame treatment is non-specific surface funcationalization technique that bombards the polymer surface with ionized air generating large amounts of surface oxidation products. One drawback of flame treatment is that it can reduce the optical transparency of polymers. It depends upon flame temperature, contact time and composition that must be accurately controlled to maintain uniform and reproducible treatment and to avoid burning.

2.4 Enzymatic surface modification

Enzymatic surface modification of textile material involves processing of fibres to modify physical and chemical surface properties or introduction of functional groups on the surface.

Research on the enzymatic surface modification of textiles contributes to environment friendly processes through the sustainable development of novel processes for textile. While much research focuses on chemical modification or structuring of the surfaces, the introduction of functionalities using enzymes is relatively unexplored scientific area. The advantage of enzyme technology over the other technologies is their high specificity towards a certain reaction and / or substrate. Review articles (Araujo et al., 2008; Cavaco and Gubtz, 2003; Lenting, 2004) describe importance and potential of enzyme technology in textiles. Enzyme technology has already been proven to be very profitable in industrial pre-treatment processes of natural fibres predominantly. Taking into account the current international state of art, bio processes are getting more and more important. Over the past two decades, much research has been carried out on reactions catalyzed by enzymes that are relevant for the textile industry such as desizing of cotton, depilling of cotton, enzymatic ageing of denim fabric, enzymatic scouring of grey cotton fabric, shrink- resistant treatment of wool and enzymatic degumming of silk (Nierstrasz, 2009). These studies clearly indicate that the surface modification of textiles with enzymatic treatment has the potential to replace conventional wet treatment. Conventional wet processes requires long residence time, high concentrations of harsh chemicals, large amount of water and are generally carried out at high temperatures leading to high energy consumption.

2.5 Sonication

Ultrasonic waves are acoustic waves with frequencies between 20 KHz to 20 MHz. When ultrasonic waves are communicated through media, several effects occur such as mechanical, thermotic and cavitation. These effects are recognized as beneficial to physical and chemical processes (Liu et al., 2007). It has been known that ultrasonic waves in liquids are used to clean surfaces. They produce bubbles in liquids and when the bubbles burst substantial amounts of energy is released. When compared with hand washing, ultrasonic agitation has many advantages. It has negligible effects on the strength and colour of fabrics and causes less fibre migration (Hurren et al., 2008). Vankar and Shankar have carried out dyeing in Ultrasonic bath of cotton fabric pretreated with enzymes (Vankar and Shankar, 2007). Their results show better and faster dye uptake after enzyme pretreatment on cotton fabric and results of dyeing are better than those obtained using metal mordanted fabric. They also observed considerable improvement in wash fastness and light fastness. The improved properties were observed without using metal mordants thereby proving ultrasound to be an effective tool in textile dyeing for cleaner production.

2.6 Surface modification using nano-particles

Nanotechnology has touched every nook and corner of the life and textiles cannot remain aloof. Nanotechnology deals with materials having at least one dimension less than 100 nm. It includes nano-particles, nanorod, nanowires, thin films and bulk materials made of nanoscale structures (Cao G, 2004). Application of nanotechnology on textile materials could lead to the addition of several functional properties. Deposition of silver nano-particles can be used to create shiny metallic yellow to dark pink colour while simultaneously imparting antibacterial properties to the fabric. Gold nano-particles allow the use of molecular ligands so that the presence of biological compound surroundings is rapidly detected. Metal oxide nano-particles such as TiO_2, Al_2O_3, MgO and ZnO possess photo-catalytic and antibacterial activity and UV absorption properties. More often these nano-particles can be impregnated onto textile materials without significantly affecting their texture or comfort. It is reported that the padding of colloidal silver solution onto textile fabric made from cotton, polyester, cotton/polyester and cotton/spandex blended fabrics shows efficient antibacterial activity with good laundering stability (Lee and Yeo, 2003; Lee and Jeong, 2005). Silver nanoparticles coated fabric exhibited better antibacterial properties and protection against UV radiation owing to nano-silver absorption in the near UV region (Vigneshwaran et al., 2007). Super hydrophobic (water repellent), dirt repellent nano-structured surfaces of textiles having self cleaning property have attracted attention of scientists. It is also called the lotus effect. Bozzi et al. have reported on RF plasma, MW plasma, and UV irradiation as pretreatments for synthetic textile surfaces, allowing the loading of TiO_2 by wet chemical techniques, in the form of transparent coatings. These materials show a significant photocatalytic activity (Bozzi et al., 2005). Various functional properties such as comfort and easy care can be imparted with the advent of nano-technology, which otherwise were difficult. Though many people are working in this area of nanofinishing of textiles, their commercial exploitation has only just begun.

2.7 Radiation induced surface grafting

It is relatively a new technique that offers a variety of ways to alter the surface morphology and chemical composition of textile substrates and, thus imparts new or improved functional properties. The surface grafting can be achieved by a) light (generally UV light) induced grafting, b) plasma induced grafting and c) irradiation (γ-rays, electron beam) induced grafting. These three methods share the same objectives i.e. creating free radicals onto the polymeric substrates and then these radical sites are used as initiators for copolymerization reactions with vinyl monomers present in the grafting solution. Various parameters such as concentration of the monomer, time of treatment, radiation dose, type and concentration of catalyst used, if any, could greatly affect the grafting efficiency and need to be optimized.

Radiation induced grafting involves the use of high energy radiation to create free radicals onto the textile substrates. It can be carried out in two ways: in-situ grafting and post exposure grafting. Compared with chemical grafting, radiation-induced grafting has many advantages such as no chemical initiators are used and grafting yield can be controlled by controlling dose and the time of irradiation. Shao et al. used an electron beam to induce grafting of 2-hydroxyethyl methacrylate (HEMA) on silk fabric (Shao et al., 2001). They showed that the degree of grafting was related to the irradiation dose. Uyama et al. have given excellent review on the subject (Uyama et al., 1998).

Plasma induced grafting is another important techniques and the details of it are described in a book (Yasuda, 1984). Plasma-induced grafting has emerged as an alternative and attractive method for surface modification of textiles. Under this technique, first radicals are created by exposing fabric in the gaseous plasma such as O_2, N_2, NH_3, Ar, air etc. and then fabric is immerged in the monomer bath followed by washing. Similarly *in situ* polymerization is also carried out, in which fabric is treated with gaseous plasma followed by plasma polymerization of monomer vapour onto the fabric surface in the plasma reactor. Bhat and Benjamin have successfully grafted acrylamide onto cotton and polyester fabrics using RF plasma (Bhat and Benjamin, 1999). They have observed that the crease recovery angle increases and tensile strength decreases slightly. Abidi and Hequet have studied graft copolymerization of vinyl laurate monomer on gaseous microwave plasma processed cotton fabrics (Abidi and Hequet, 2004, 2005). The grafted cotton fabric showed excellent water repellency properties. Repeated home laundering of the treated cotton fabrics revealed no significant effect on the water contact angle or on the quantity of grafted vinyl laurate monomer as determined by universal attenuated total reflectance Fourier transform IR, demonstrating the good durability of the treatment that was applied. Graft copolymerization of various monomers onto variety of fibres was carried out by means of RF plasma (Zubaidi and Hirotzu, 1996). The monomers used were HEMA, Acrylamide (AAm), N-isopropyl AAm, acrylic acid, 2-methoxyethyl acrylate and 2-hydroxyethyl methacrylate. The textile fibres used were cotton, cellulose acetate, rayon and cupraammonium cellulose. Authors have reported that HEMA monomer was graft polymerized more readily than other monomers investigated and cotton fabrics were shown to be more reactive than other fabrics. Oktem et al. have incorporated acrylic acid onto the surface of polyester fabric to impart soil resistance and improve dyeability using two approaches (Oktem et al., 1999). In the first approach, *in-situ* polymerization of acrylic acid monomer was achieved in a glow discharge reactor. In the second approach, the fabric was first treated in Ar plasma, followed by immersion in an aqueous bath containing different amounts of acrylic monomers. The advantage of plasma treatment over the wet chemistry technique is that the effects of plasma do not penetrate more than few 100 Å from the surface and hence bulk properties of the substrate remains unaltered.

Light induced grafting basically uses, UV light energy for creation of free radicals onto the textile surfaces. UV radiation induced surface grafting of textiles is another technique that has attracted attention because of its simplicity. Radicals thus generated onto the surface are used to initiate copolymerization reactions with various monomers. UV radiations are not as penetrating as high-energy gamma (γ) radiations, free radicals thus produced mainly close to the surface rather than uniformly distributed throughout the fibres (Reinhardt and Harris, 1980). Radiation induced grafting using high energy sources such as UV radiation or electron beams has been explored as an alternative to chemical grafting. However, if the conditions are not controlled, radiation grafting may result in deterioration of physical properties of the substrate and may lead to photo-degradation of the substrate (Abidi, 2009). Shulka and Athalye have successfully grafted HEMA onto the Polypropylene staple fabrics using UV radiation (Shukla and Athalye, 1994). The choice of grafting with HEMA was based on its hydrophilic properties. They used three different photo-initiators. They observed that the moisture regain of the PP fabric was increased and build-up of static electricity was diminished. The parameters affecting the efficiency of grafting, such as time and temperature of the reaction as well as concentrations of the initiators, were optimized in this study to maximize the amount of grafted monomer on the PP fabric surface. UV induced grafting of water soluble monomers onto the surface of polyester fabrics was performed by Uchida et al. to permanently change the surface properties from hydrophobic to hydrophilic (Uchida et al., 1991). UV grafting technique was also used to impart water repellency. Ferrero et al. have reported the use of silicone containing monomer with different formulations on cotton fabrics in order to impart water repellency (Ferrero et al., 2008).

2.8 Plasma processing

The above mentioned methods particularly chemical wet processing have disadvantages that they require the disposal of polluted water and the treatments are non uniform. Plasma treatment of textiles is attractive in that it is clean, dry technology and much less energy is consumed than equivalent conventional treatments. Gas plasma treatments are highly surface specific; they do not affect the bulk properties of the textile fibres. Plasma processing is environmentally friendly, since no wet chemistry is involved. It does not produce any waste/ load on the environment. Therefore, low temperature plasma treatments are set to revolutionize textile processing technology. Although gaseous plasmas have been known for several decades, it is only recently, after the introduction of equipments on an industrial scale, the commercial interests have began. Nowadays, textile fabrics of breadth >1 m can be successfully treated on a commercial scale with low pressure plasma, in a roll to roll manner. The technology is widely perceived as being confined to batch processing. The book edited by Shishoo highlights the huge potential of plasma treatment for textile processing (Shishoo, 2007). An overview of the literature on potential uses of non-thermal plasmas for the modification of textile products and benefit from the plasma treatment is given by Morent et al. (Morent et al., 2008).

Plasma treatments of textiles alter surface morphology and chemical composition without affecting their bulk properties. The depth of surface modification is of the order of few hundred angstroms. Plasma treatment can alter hydrophobic surface to hydrophilic and vice-versa, depending upon the type of gas / monomer used for the generation of plasma. Thus plasma treatment can lead to improved wettability or water repellency, depending on whether greater chemical affinity or inertness has been conferred / transformed on the textile surfaces. Similarly, other properties that can be improved are bio-compatibility, adhesion, resistance to wear and tear, rate and depth of dyeing, cleaning of fibre surfaces, and desizing.

Low temperature glow discharge consists of high energetic electrons, positive and negative ions, free radicals, excited atoms and molecules, neutrals and UV radiation. The mixture of species composing plasma is therefore highly complex and in general all these species can interact with textile surfaces during the plasma treatment. There are basically two kinds of plasmas that can be produced in laboratory, hot plasma and cold plasma. Hot plasmas are thermally in equilibrium and the temperature is of the order of 1000 K. Therefore, hot plasmas are not suitable for polymers and textiles treatments. Whereas, the electrons in the cold plasma acquire energies in the range of 0.1 to 10 eV, much higher than the energies of ions and molecules, so equilibrium between all the species is far from equilibrium. Cold plasma temperature is around room temperature or slightly above, so it can be successfully applied for the surface modification of textiles. Plasma can be generated by applying electric fields of low frequency (50 KHz. to 500 KHz.), radiofrequency (13.56 MHz.) or microwave (915 MHz. or 2450 MHz.). The extent and nature of the modification of a textile surface by plasma treatments is governed by / depends upon several parameters such as, working pressure, power, distance between two electrodes, time of treatment, type of gas / monomer, the type of textile, used etc. In spite of the complexity of all these factors, several effects can be broadly identified. One is cleaning or etching of substrate surface. This process involves removal of tiny amount of contaminant, process aids, adsorbed species etc. So cleaning of surfaces is regarded as first step of plasma processing. After this step actual deposition / etching of the material starts. It is associated with the changes in surface properties and wetting behavior. In general, polymers containing oxygen groups are more sensitive to etching than polyolefins. Under the same conditions of plasma treatment, polyester fibres are more prone to etching than nylon 6 fibres, which in turn are more prone than polypropylene (Radu et al., 2000). An enormous variety of plasma treatments are now available, and so the changes that can be brought to textile surface characteristics are numerous. Plasma treatments are therefore, capable of giving rise to innovative type of textile and moreover on a commercial scale.

2.8.1 Atmospheric pressure plasmas

There are three types of atmospheric pressure plasmas: a) Corona Discharge, b) Dielectric Barrier Discharge (DBD), and c) Atmospheric pressure glow discharge (APGD).

a. Corona Discharge: It is the oldest type of plasma treatment employed for modification of polymeric surfaces. It consists of two parallel electrodes, one of which is cylindrical in shape while other one is knife shaped. A very high voltage 10 to 15 kV is applied between the two electrodes separated by ~1 mm distance. Corona discharges are weak and too inhomogeneous for plasma treatments for textiles. The density of the plasma falls dramatically with the distance from the point of generation, a factor that accounts for smaller gap between the two electrodes. Thicker fabric therefore cannot be treated by corona discharge.
b. Dielectric Barrier Discharge (DBD): It consists of two parallel plate electrodes separated by narrow gap and around 20kV potential difference applied between them. In order to prevent arcs and short circuit between the electrodes, one or both the electrode plates are covered with suitable dielectric material such as ceramic or glass. Therefore it is called as dielectric barrier discharge. The DBD is powered by AC with a frequency of 1-20KHz. DBD is homogeneous as compared with corona discharge.

Olievera et al. have shown the effectiveness of Dielectric Barrier Discharge for the surface modification of Polyamide (PA) fibres (Olievera et al., 2010). PA fibres contain amines and carboxylic acid terminal groups, therefore, both anionic and cationic dyes can be used for dyeing. However, dyeing conditions needs to be controlled properly for better and uniform dyeing. The physical and the chemical changes imparted by DBD plasmas on the PA fabric show excellent dyeing properties. The process of surface modification using DBD plasma can also be used to improve hydrophilic properties of naturally coloured cotton fabric. Atmospheric plasma treatments could influence not only the chemical properties but also the physical properties of naturally colored cotton fibers (Demir et al., 2011). The degree of modification of plasma treatments are influenced significantly by the duration, power, and plasma type. In general, the argon-plasma treatment showed more effective results than the air-plasma treatment.

c. Atmospheric Pressure Glow Discharge (APGD): APGD is generated at much lower voltages and at high frequencies (MHz, RF) as compared with DBD. RF source is connected between two parallel plate electrodes, which are separated from each other by just few millimeters. Therefore, APGD is relatively uniform and stable as compared with DBD. APGD has many advantages over DBD. It does not require electrode(s) to be covered / coated with dielectric layer. However, the discharge is generated in helium (other gases are used with helium), which on commercial scale becomes expensive, unless helium is substantially recovered.

The atmospheric-pressure He and He + O_2 plasma treated nylon 6 films showed increased surface roughnesses, increased surface oxygen contents, and hydrophilic polar groups; this led to lower water contact angles and improved bonding strength (Gao et al., 2011). They have further observed that, when the amount of oxygen increased from 1 to 2% in the plasma-gas mixture, all of these favorable effects were further enhanced.

2.8.2 Low temperature plasma processing

The relative advantages of low pressure and atmospheric pressure plasma treatments on textile substrates are still the subject of considerable debate. Both the treatments have their merits and demerits therefore, final selection of the process will be decided by the requirement of the process speed and the extent of modification. Low pressure equipments are equipped with vacuum pumping system, which consumes more electricity/energy than atmospheric pressure equipment but low pressure equipments require less power to generate and sustain plasma as compared to atmospheric pressure equipment. On the other hand, low pressure equipment requires much smaller quantities of gases / monomer(s), a particularly important consideration where expensive gases / monomers are used. The modifications achieved by low pressure plasma are more uniform than atmospheric plasma. One has a better control over the surface modifications achieved by low temperature plasma. Atmospheric pressure equipment can be utilized as part of an overall continuous process (which industry prefers), whereas low pressure equipment is restricted to batch-to-batch processing.

Gawish et al. have studied the effect of low temperature plasma for improving wool fabric properties (Gawish et al., 2011). They have used plasma treatment to modify the surface properties of wool fabrics by partial removal of the scales and the lipid layer. They have discussed dyeing behavior of untreated and pretreated wool fabrics. Three dyes were used, namely acid dye, 1:2 metal complex dye and reactive dye. Different exposure times (1-5 min) of oxygenated plasma treatment were effected to improve the hydrophilicity, wettabillity, dyeability and the washing and light fastness properties of the dyed wool fabrics (which were increased by increasing the plasma exposure time). Wool has some technical problems that affect the quality and performance of the finished fabric such as felting, shrinkage, handle, luster, pilling and dyeability. These problems are mainly due to scales on the fibres and lipid layer. They act as barriers for diffusion processes, which adversely affects sorption behavior of fibres. Oxygenated plasma treatment of wool fabrics results in removal of the lipid layer and scales from the fibres leading to the improved wetting, dyeing and shrink resistance (Hartwig Höcker, 2002; Hesse 1995; Meade et al., 2008; Rakoweski, 1997). The effect of plasma of non-polymerizable gases on wool fabric is discussed quantitatively (Kan et al., 1999). Three different nonpolymerizing gases—oxygen, nitrogen, and a 25% hydrogen/75% nitrogen gas mixture, were used to study the influence of the nature of each gas on the properties of wool substrates. The properties which include fiber-to-fiber friction, feltability, fabric shrinkage, surface structure, dyeability, alkali solubility, and surface chemical composition depend on the nature of the plasma gas used. Shahidi et al. have studied the effect of low temperature on dyeing properties of PP fibres (Shahidi et al., 2007). PP fibres were subjected to O_2 and N_2 plasma. It was found that after the plasma treatment, PP fabrics achieve necessary hydrophilicity because of incorporation of polar functional groups such as hydroxyl, carbonyl, ester and carboxyl. Similarly, improvement of dye adsorption on polyester fibres by low temperature plasma pre-treatment is demonstrated (Lehockey and Mracek, 2006). Low temperature plasma of two gases mixture particularly ammonia and acetylene was used by Hossain et al. to modify polyester fabric (Hossain et al., 2009). They have observed some deposition which contains amine groups as evident from XPS studies. The plasma treatment significantly improved the dyeability and colorfastness properties of dyed polyester fabric with an acid dyestuff. The acid dye molecules were found to diffuse into the amine-functionalized nano-porous film and formed ionic bonds with amine end groups. The dye uptake was strongly correlated with the plasma process time, that is, with the deposited film thickness, and this indicated that only the plasma coating on the polyester fibers was dyed, not the fibers themselves. The K/S values could be controlled by the adjustment of the film thickness during plasma polymerization. Because K/S values are enhanced with the number of incorporated accessible amine groups, the surface hydrophilicity does not strongly influence the dyeability. It is obvious that the entire dyeing process is independent of the substrate material because merely the functional film is dyed. Hence, the same dyeing principle can also be applied to all hydrophobic synthetic textiles. Low temperature DC glow discharge plasma was used to modify / improve hydrophilicity of grey cotton fabric (Navneetha and Selvaraj, 2008). The fabrics were treated for different exposure times, discharge potentials and pressure levels. Effect of plasma treatment on the wettability of the fabric was studied by measuring contact angle. The changes in surface energy were estimated using contact angle measurements. Dyeability of the fabrics was determined by computer colour matching procedure. It was observed that DC glow discharge plasma is useful technique for the improvement in wettability and hence Dyeability.

It is observed that the improvement in wettability / hydrophilicity achieved by gaseous plasma treatment changes with time. This phenomenon is commonly called ageing, which takes place possibly due to surface contamination, orientation of polar groups, blooming of additives, or adsorption of ubiquitous contaminants. In many applications a hydrophobic polymer is converted into a hydrophilic one by suitable treatment and when a sample is stored in air, a driving force exists to restore the original structure or at least lower the surface energy (SE) of treated surface. As a result the high energy polar groups can be lost. It is shown that the hydrophobic recovery depends on the polymer and on treatment (Morra et al., 1989). This ageing itself can be considered as one of the steps of the treatment in the sense that influences the outcome as determined by the properties imparted to the polymer surface. Our previous studies shows that though there is a decrease in surface energy (SE) because of ageing, it is clear that the SE value of aged samples is still sufficiently high in comparison with the untreated one. Hence such polymer films can be suitable for further applications (Deshmukh and Shetty, 2007; Bhat et al., 2003). In order to avoid the effect of ageing, it is necessary to use freshly prepared (gaseous plasma processed) polymer / textiles for the best results of dyeing. However, plasma polymerized and plasma surface grafted polymers do not show much decrease in surface energy and the modifications thus achieved are comparatively permanent. Plasma polymerization and plasma grafting is already covered in **2.7** of this article. Efforts have been made to control / manipulate the chemistry of plasma polymerized films by varying plasma process parameters such as monomer flow rate, distance between two electrodes, working pressure and plasma power. However the success in controlling film chemistry is limited. Timmons and Griggs have showed that by using RF pulsed plasma polymerization technique, a wide range of plasma film chemistry can be achieved in comparison with conventional continuous wave (CW) RF plasma (Timmons and Griggs, 2004). Recently, such pulsed plasma polymerization technique was successfully used to control film chemistry and found useful in bio-logical applications (Bhattacharyya et al., 2010, Xu et al, 2011). So far this technique has not been used for the modification of textile surfaces. There is tremendous scope in this area.

3. Experimental

A tubular type of plasma reactor was used in the present experiment and is shown in the Fig.1 given below.

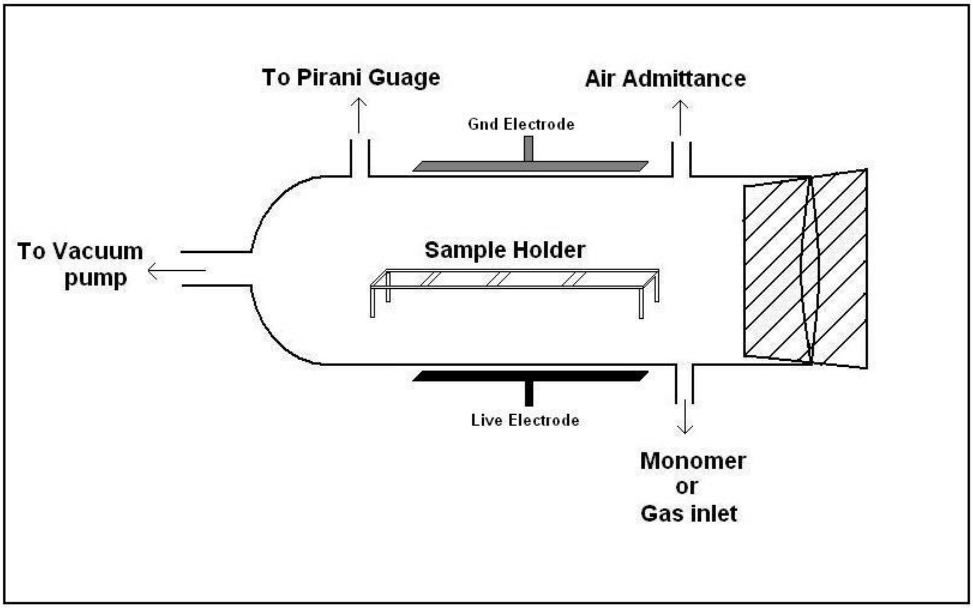


Fig. 1. Schematic of Plasma Unit.

It consists of a glass tube having diameter 8 cm. and length 30 cm. The length and the breadth of the electrode was 25 cm and 3 cm respectively. The sample was kept at the centre of the reactor on a glass stand as shown in Fig 1. The reactor has an inlet for monomer and / or gas. A Pirani gauge was fitted to the reactor to monitor pressure in the reactor. The aluminum electrodes were kept outside the glass tube and were connected to RF (13.56 MHz.) power supply capable of delivering 100W power. The system was evacuated to 0.05 mtorr with rotary pump before inserting the gas / monomer vapours. The system was purged three times with the relevant gas / monomer vapours and the desired working pressure 0.2 mtorr was obtained with the help of fine control needle valve. The sample was mounted on a glass sample holder inside the chamber as shown in Figure 1 above. The gases and the monomer used were of AR grade.

Dyeing Procedure: Acid Dye (Blue coloured) supplied by Clarient India Ltd was used. 1% shade was prepared and its pH. was adjusted to 4.8 by adding formic acid. The liquor to fabric ratio was maintained at 50:1. The temperature of the dyeing bath was adjusted to 85 ^{0}C. The nylon fabric (untreated and plasma processed) were immersed in dye-bath for 15 min. Then the fabric was washed in the soda soap solution with 5gpl soap and 2 gpl soda for 30 min. followed by distilled cold water wash (three times) and then the samples were dried in air. Such samples were used for colour measurement. Colour measurements were performed on Spectra-flash SF 3000 (Datacolour International). Dye Exhaustion was measured using UV visible spectrometer.

The amount of dye absorbed by the sample was determined by measuring the optical densities of the initial solution and also the exhausted one by using an ultraviolet/visible (UV/Vis) spectrophotometer. The percentage dye absorption was calculated as,

$$\% \text{ Dye exhaustion} = \frac{(\text{O.D. of original solution}) - (\text{O.D. of exhausted solution})}{\text{O.D. of original dye bath}} \times 100 \quad (1)$$

Where, O.D. is the optical density at the maximum absorption wavelength.

Nylon fabric was treated in O_2 and N_2 plasma for different durations of time. Similarly plasma polymerization of acrylic acid was carried out onto the nylon fabric for different durations of time. These samples were tested for their hydrophilicity, FTIR, dyeabilty and surface morphology. In order to study the characteristics of plasma polymerized acrylic acid film, KBr disc was kept in the plasma chamber while carrying out deposition onto the fabrics. Such deposited film was used for FTIR study. The wettability of the untreated fabric was measured by contact angle measurement with respect to water and for treated samples; the time required for water drop to disappear was measured and recorded as wetting time. Average of 5 readings is reported here. The shorter is the average wetting time, better is the fabric wettability. The surface energy of untreated sample was calculated from the contact angle data using the equation given by Deshmukh and Shetty (Deshmukh and Shetty, 2008). Surface morphology was studied using SEM.

4. Results and discussions

4.1 Morphological studies

Nylon fabric was treated with nitrogen and oxygen plasma. It can be seen from Figure 2 that the surface morphology changed after the plasma treatment. The untreated nylon fibres are smooth as shown in Fig. 2 (a) and (b). The etching, roughening effect of oxygen plasma on the surface (Fig. e and f) is more as compared with the nitrogen plasma as shown in Fig. 2 (c) and (d). It is probably due to oxygen is more reactive than nitrogen. The treated surfaces look damaged or abraded. This is due to the removal of some material by etching. Similar abraded surface topography for plasma processed wool and cotton fibers, respectively, was observed by Karahan and Ozdogan (Karahan et al., 2009; Ozdogan et al., 2009). In the case of wool fibers this helped to impart anti-felting properties to the fabrics due to loss of the scales. Significant fiber surface roughness was also observed by McCord et al. for nylon and polypropylene fibers with He and He+O_2 atmospheric plasmas (McCord et al.,2002). It may be of interest to try to understand the morphology and mechanism of the etching process. It has been confirmed through various studies that only the amorphous portion gets degraded and etched away in the initial stage (Bhat and Deshmukh, 2002; Thomas et al., 1998; Yoon et al.,1996). The plasma process is such that the electrons and ions attack the amorphous portion, as it is loosely bound. On the other hand, the crystalline regions are more compact and hard as compared to amorphous regions and therefore the amorphous region gets removed easily in the plasma etching. As a result, the percentage crystallinity increases to some extent. This has been concluded by previous studies using X-ray diffraction (XRD) and Fourier transform infrared (FTIR) for silk (Bhat and Nadiger, 1978). Navaneetha and Selvaraj have also observed that the effect of plasma on the amorphous zone is more predominant than the crystalline zone of the cotton fabrics (Navaneetha and Selvaraj, 2008.).

Similarly when nylon fabric was subjected to the plasma polymerization of acrylic acid (PPAA), we observed deposition as shown in Fig. 2 (g) and (h). This deposition leads to decreased capillaries present in the texture. The choice of acrylic acid monomer was based on its hydrophilic properties.

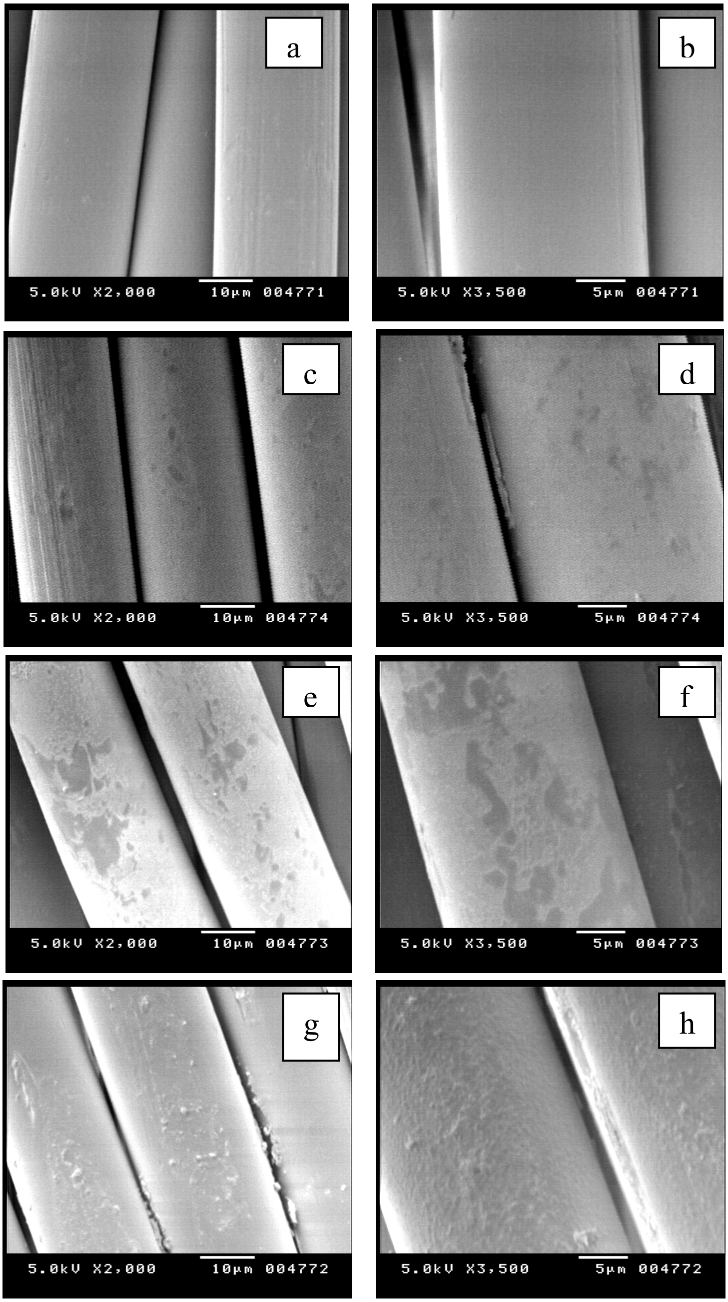


Fig. 2. SEM micrograph of (a) and (b) Untreated Nylon fabric, (c) and (d) 4 min. N_2 plasma treated Nylon fabric, (e) and (f) 4 min. O_2 plasma treated Nylon fabric, (g) and (h) 4 min. PPAA deposited on Nylon fabric.

4.2 FTIR study

Polar functional groups are incorporated onto the polymer film during the plasma treatment. These polar groups are readily detected by ESCA (XPS), but are often missed by ATR-FTIR spectroscopy (Wu S, 1982). XPS is the best technique to study such modified surfaces. Several studies showed that air, N_2, O_2, NH_3, etc. plasma incorporates hydrophilic functional groups onto the polymer surfaces thereby increasing wettability and surface energy (Bhat et al., 2011; Navaneetha et al., 2010; P´ıchal and Klenko, 2009). It has been reported that the treatment carried out in inert gases like Ar introduces oxygen moieties onto the polymer surface because of post plasma exposure of samples to atmosphere (Deshmukh and Bhat, 2003(b); Gupta et al., 2000). Therefore, IR spectra of N_2 and O_2 plasma treated nylon samples is not given here. The IR spectra of plasma polymerized acrylic acid (PPAA) is given in Fig. 3 below.

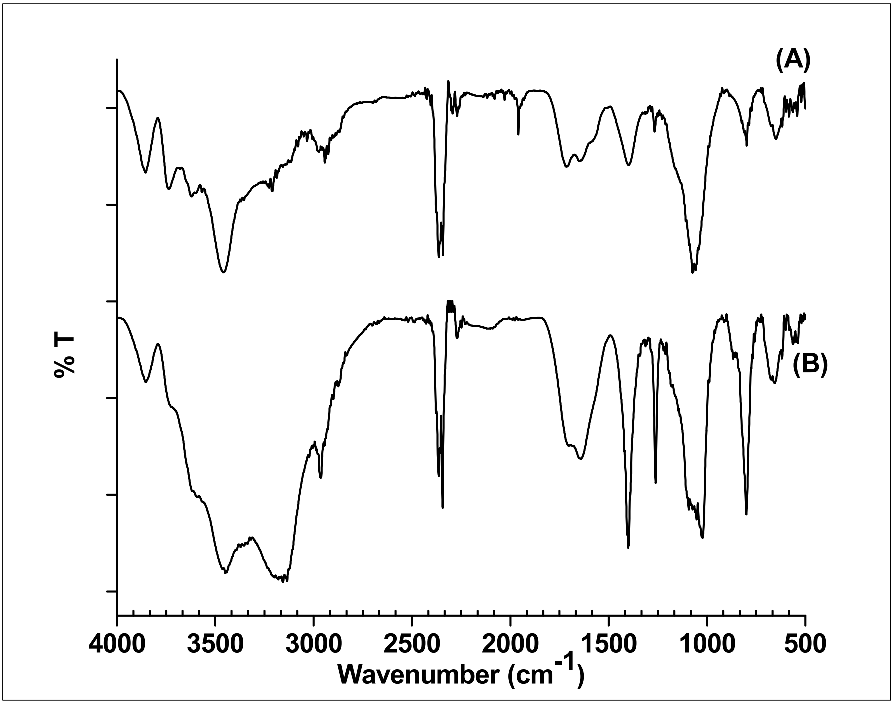


Fig. 3. FTIR spectra of PPAA (A) 2min. deposition, (B) 4min. deposition.

The FTIR spectrum of a PPAA film prepared using the technique of plasma polymerization was very similar to the spectrum of Poly (acrylic acid) prepared by conventional polymerization techniques and it shows all the characteristic bands. In particular, the FTIR spectrum shows that the film contains a high density of C(O)OH groups. The absorption peaks assignment is given in table below (Alaa et al., 2011; Cho et al., 1990; Chilcoti and Ratner, 1993; Eun-Young Choi and Seung-Hyeon Moon, 2007; Jafari et al., 2006; Mirzadeh et al., 2002).

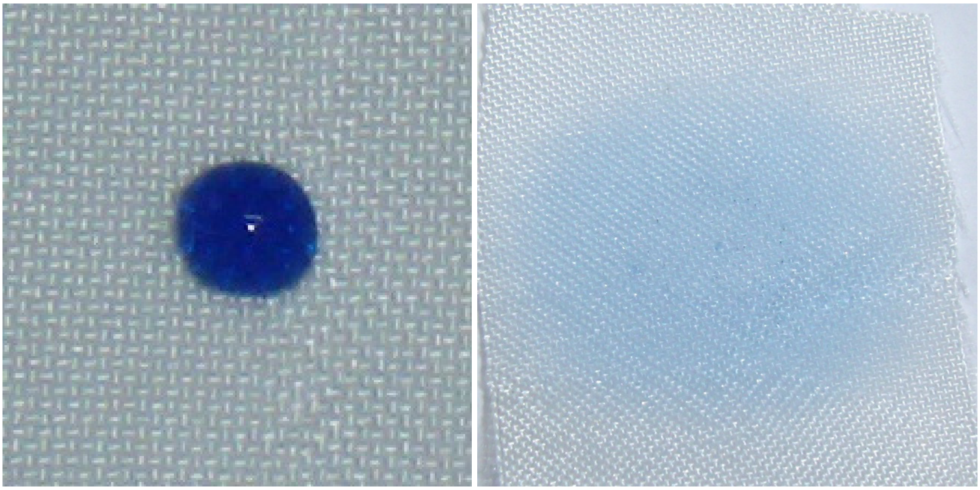
Frequency, cm-1	Peak Assignment
814	O-H out of plane bending vibration of carboxylic acid
1265	C-O stretching of carboxylic acid
1425	O-H bending of carboxylic acid
1710	carbonyl group of acrylic acid, C=O stretching absorption band between 1828 to 1559 cm^{-1} with maximum at ~1710 cm^{-1}
2800 to 3800	a broad OH stretching absorption band due to monomeric and dimeric C(O)OH

Table 1. IR peak assignment of PPAA

It has been observed that our result of plasma polymerization of acrylic acid is in relevance with the literature. PPAA incorporates considerable amount of polar functional groups such as hydroxyl, carbonyl, carboxylic acid, etc. The peak intensity increases with the deposition time.

4.3 Wettability study

The contact angle of untreated nylon fabric was observed to be 83^0 (±2). Its surface energy comes to be 33.6 mJ/m^2. Fig. 4 shows the photograph of water droplet taken on untreated and 4 minute oxygen plasma treated nylon fabric.



(a) (b)

Fig. 4. Water droplet on the nylon fabric. (a) untreated, (b) Oxygen plasma treated.

However, we could not measure contact angle for any plasma processed samples. It shows that the surface energy of all the samples increases rapidly after the plasma processing. Therefore we have measured wetting time of the samples as given in Table 2.

Treatment Time (min.)	Time to absorb water droplet on the Plasma Processed Nylon Fabrics (in Sec.)		
	N_2 Plasma	O_2 Plasma	PPAA
0	112	112	112
0.5	18	12	20
1	15	9	16
2	8	6	14
4	4	3	19

Table 2. Wetting time of untreated and plasma processed nylon samples.

It may be noted from Table 2 that the wetting time of the untreated nylon fabrics was 112 seconds, which dramatically decreases after N_2, O_2 and acrylic acid plasma treatment. The decrease is more significant in case of O_2 plasma treated samples as etching action and oxidation reaction is predominant. On the other hand, the decrease in the wetting time of PPAA treated sample is rather slow. It may be also be noted from the SEM micrographs that the formation of etch-pits and voids is very predominant for O_2 plasma treated nylon fabrics, whereas PPAA treated samples reveal coating on the surface due to formation of PPAA. Due to such thin film formation on the surface the water drop may not easily reach the fabric and as a result the capillary action is reduced.

4.4 Dyeing studies

Plasma processed samples were dyed using acid dye-blue. The dye absorption was determined spectroscopically by measuring the absorption band maximum of the dye-bath solution before starting and after exhaustion. In addition, the amount of dye uptake was also determined from the color matching instrument. The color values are expressed in terms of K/S as the ratio of reflectivity to absorptivity. For each kind of plasma processing, the dye uptake of plasma-treated sample was compared with the untreated sample of the same variety.

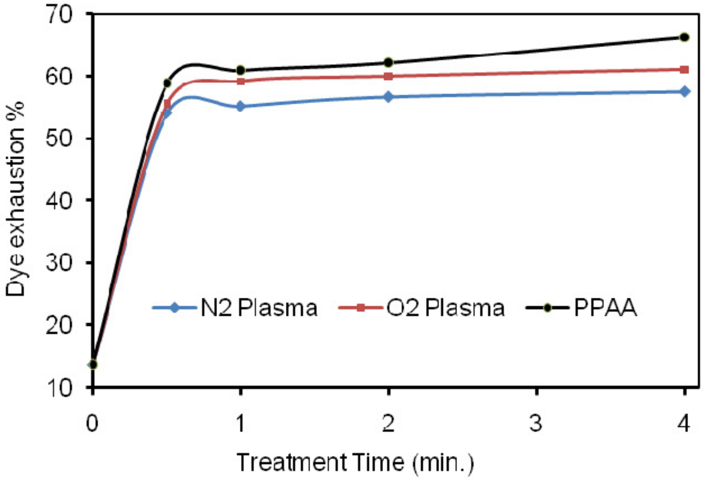


Fig. 5. Relation between the dye bath exhaustion and plasma processing time.

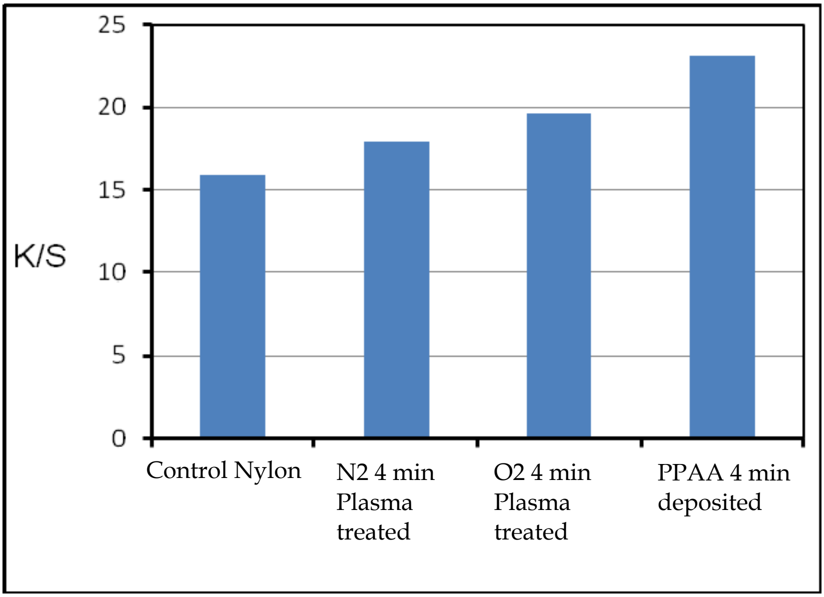


Fig. 6. K/S values of nylon fabric subjected to RF plasma treatment.

The increase in the dyeing in the initial stage could be due to the fact that gaseous plasma etches out the surface of the nylon fibers, creating a rougher surface with irregularities as discussed earlier. The effective surface area increases after the plasma treatment. Thus the interaction and diffusion of the dye molecules is facilitated. The etching of the surface has been confirmed by other researchers (Karahan et al., 2009; Ozdogan et al., 2009). The chemical changes in the nylon fiber surface can lead to the possibility of the formation of free radicals on the nylon chains and the subsequent formation of hydroxyl, carbonyl and carboxyl groups. It is also important to mention that the dyeing process mainly occurs through the amorphous regions. The etching away of the amorphous regions during the plasma treatment (particularly for longer treatment time) can lead to lowering of the dye uptake. Therefore the optimum treatment time needs to be found. Yoon et al. and Thomas et al., have found that longer plasma treatment decreases dye uptake (Thomas et al., 1998; Yoon et al., 1996). It may be noted that the oxygen is more reactive than nitrogen and hence the dye uptake is slightly more for oxygen treated samples. The etching caused due to oxygen plasma is also more as shown in Fig. 2 (e and f).

Plasma polymerization of acrylic acid (PPAA) onto the nylon fabric incorporates good amount of hydroxyl, carbonyl and carboxylic acid groups onto the surface as evident from FTIR studies. These functional groups are responsible for wettability and hence dye uptake. The dyebath exhaustion is slightly more in case of PPAA deposited nylon fabric as compared to that of gaseous plasma treated samples, because of the functional groups which are incorporated during the deposition of PPAA. Deposition causes reduction in the capillary action therefore; we have observed slightly more wetting time for PPAA samples as shown in Table 2. However, when dyeing is carried out for 15 minutes, which is sufficient time for the penetration of dye into the fabric, a major role of functional groups is observed on the dyeing behavior rather than wetting time. The deposition is evident from SEM micrographs as shown in Fig. 2 (g and h).

The increase in the dye uptake due to plasma treatment is also evident from the measurement of K/S values shown in the Fig. 6. The bar-graph shows K/S values for control and plasma treated samples for four minutes in different gases. The highest gain is seen to be for PPAA deposited nylon fabrics followed by oxygen treated sample. This trend is similar to that observed for the data of dye bath exhaustion.

4.5 Few results of case studies

4.5.1 Dyeing behavior of nylon fabric treated in APGD

Similarly, nylon fabric was treated in atmospheric pressure glow discharge, for various durations of time, it was found that there is increase in the dye uptake with time as shown in Fig. 7. The dye used in these studies was acid dye-red. It may be seen that when the dyeing time was 15 minutes, the differences in the K/S values of the control and the atmospheric pressure plasma (He +air) treated is quite noticeable. The increase in dye is significant. However, as the dyeing time is increased to 60 minutes the equilibrium dye uptake is reached for control as well as plasma treated samples and the difference reduces. This proves that the plasma pretreatment can reduce the time of dyeing and as a result power can be saved.

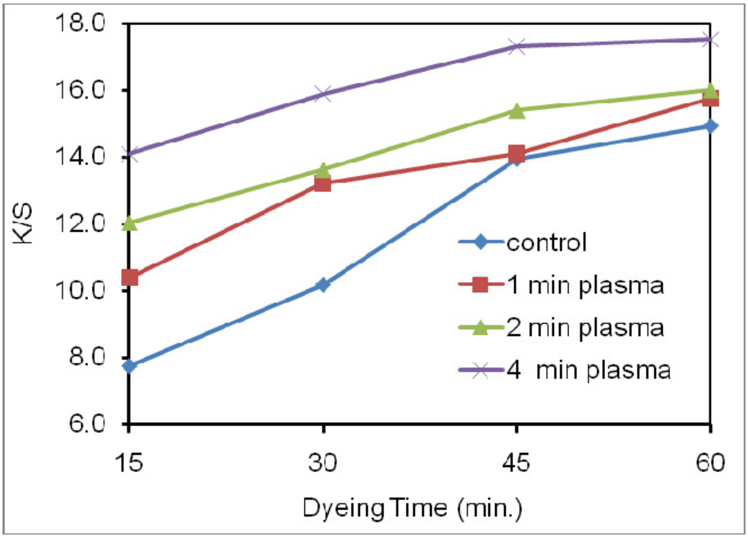


Fig. 7. K/S values of Nylon fabrics dyed with reactive dye after subjecting the fabrics to atmospheric pressure plasma for different duration of time.

4.5.2 Dyeing behavior of cotton fabric treated in air plasma

In another recent study (just results are summarized), cotton fabrics (desized, scoured and bleached) were treated with air plasma (RF), for 4 minutes. In order to understand the effect of such treatment on dyeing behavior, it was decided to use three different dyes namely, direct dye, reactive dye and natural dye. The direct dye used was Congo red, the reactive dye used was Red-M and natural dye was Thar. When dyeing was carried out and measurements were done for the dyed samples, it was noticed that, in the case of direct dye, the colour strength after plasma treatment were found to have decreased by 2.1 %. However, in the case of reactive dye, there was an increase in colour strength by 3.2%. The natural dye Thar showed a marginal decrease by 1%. It was surprising that, when the plasma treatment, enhances the wettability of cotton fabrics to a great extent, the increase in the dye uptake was not similar. This makes us believe that, the interaction of dye with the polymer (fibre) is important for improved dye uptake. The tremendous work carried out for wool fibres has revealed that while the plasma treatment, invariably leads to increase in the dye uptake, it is not so for other types of fibres (polyester, cotton, nylon etc.). There are several conflicting results of increase at times and decrease for other cases. Our analysis shows that, in addition to the type of gaseous plasma, the structure and morphology of the fibre is important. If a proper group of dye is used, the interaction of the dye with the fibre becomes compatible leading to increase in the dye uptake. Our conflicting results in case of cotton fabric just described above may be explained as follows:

In case of direct dye, the dyeing phenomena is supposed to be due to diffusion of the dye molecule into the fibre, whereas reactive dye reacts with the OH group of the cellulose chain. The natural dye Thar has a very long chain with many CH groups and possibly cannot diffuse into the fibre. The very short (few seconds) plasma treatment of cotton fabrics leads to removal of wax and other impurities from the surface of the fibre. Further treatment with plasma (up to 5 min) leads to removal of the amorphous portions of the material, thereby decreasing the possibility of interaction with the OH groups of the cellulose chain. There also occurs cross linking on the surface, which would hinder the diffusion of the dye molecules. The plasma interaction etches the surface and the effective area is enhanced and also oxygen moieties are incorporated and will contribute to synergistic effect leading to enhanced dye uptake. However, there is a competitive process of cross-linking and as a result the net dyeing may not always show increase.

4.5.3 DC plasma effect on polyester fabric

Similarly in another experiment, we thought interesting to see the effect of DC plasma on polyester fabric. Oxygen was used as precursor gas. Plasma treatment of polyester fabrics was carried for different durations of time. The morphological changes in the fiber structure were assessed by SEM which revealed the formation of rough surface together with voids and cracks. The loss of weight increased with the treatment time while the tenacity was affected to a small extent. Moisture regain and wettability was found to be improved with increasing treatment time. The fabrics developed yellowness after the plasma treatment that increased with time. Such plasma treated fabrics were dyed with disperse dye in HTHP machine. The dye uptake was found to have increased initially up to 10 minutes and slightly decreases at higher time of treatment. The increase in the dye uptake was due to combined effect of the production of polar group on the surface, etching of the surface creating higher effective area and the creation of voids and cracks, which can facilitate entry of dye molecules into the interior of the fibre. The maximum increase was found to be 2% . Such minor rise in the dye uptake is probably due to other competitive process of cross linking reaction on the surface which do not allow penetration of the dye into the interior. Therefore when the time of treatment was increased beyond 10 min there appears to be slight reduction in the dye uptake. This behavior is shown in Fig. 8 below.

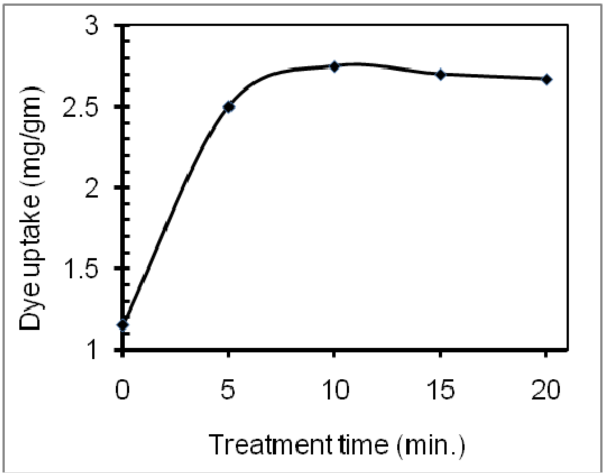


Fig. 8. Dye uptake of DC plasma treated polyester fabric

5. Conclusions

The present paper has described the results of dyeing behaviour for plasma treated nylon, polyester and cotton fabrics. Mainly air, nitrogen and oxygen gases were used together with vapours of acrylic acid in a low pressure atmosphere. There is substantial enhancement in the dye uptake of nylon fabrics. This result is similar to the observation when plasma processing is done in APGD. In case of polyester and cotton, however, the enhancement in the dye is not substantial. Rather the type of dye (acid, disperse or natural) played an important role.

The survey of literature as well our own work regarding the effect of plasma on dyeing behaviour shows that whereas there is always enhancement in the dye uptake of wool fibers, it is not necessarily so for polyester, cotton and other fibers. Although etching of surface, creation of voids and formation of C=O, COOH, OH groups occurs to facilitate higher dye uptake, there exist competing processes of increased crystallinity and cross-linking on the surface which may not allow the diffusion of the dye molecules. Therefore the selection of the fibre, nature of gas, process time and the type of dye all play a major role. Thus clear understanding of plasma process is of utmost importance to utilize the technology on the industrial scale. Further the type of plasma i.e plasma produced by different power sources like A.C., D.C., low pressure, atmospheric pressure gives more or less similar results as far as dyeing property is concerned, although morphology and structural differences are observed.

6. Scope for future work

It is necessary to standardize experiments with reference to several process parameters such as pressure, flow rates, power etc for each type of fabrics. Further the type and structure of dye molecule should also be considered. Surface analysis in terms of morphology, radical formation, bond formation and its lifetime need to be understood. This understanding may help in deciding about the importance of plasma process if enhanced dye uptake is the aim.

Even if the increase is small, if the process can lead to sufficient dye uptake at a reduced temperature or time, it would serve a good purpose. Advantages of the process in terms of eco-friendliness, water saving and energy saving be explored and emphasized so that the technology is acceptable to all.

Further work needs to be carried out by using pulsed plasma as it may avoid the degradation of fabrics when subjected to longer durations of treatments. In-situ cooling of the samples is also desirable to maintain the temperature of substrate constant. It is also necessary to find the electron and ion densities or rather the number of ions hitting the sample to calculate the energy deposited during processing.

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4

From Murex Purpura to Sensory Photochromic Textiles

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1. Introduction

Throughout history the function and the original role of the textile changed very little. One could only think of only few generations of textiles that would bear significant differences when compared one to another. Textiles were to provide the necessary shielding against climatic conditions and only later on in history the shear design of it became more importance. Nowadays, textile engineers and technologists like to think there is a new generation of textiles emerging. This thinking is supported by new functionalities being added onto textiles in the last few several decades. For this to happen, it was necessary to combine state of the art electronics and newly synthesized organic molecules which would bring the functionality of the textile to another level. Scientists of various research branches working together, looking at issues and solving problems applying multisciplinary approaches was the right angle of looking at things. Results of this can be seen daily, as textiles are emerging into a new era in which "know how" and "state of the art" have to be combined to give products of highly added values. Producing "highly added value" products can give the leverage to companies of the western world in an ongoing "battle" against massively produced, low quality textiles of mainly eastern origin.

Although, the way to commercialization of many of the ideas of how to upgrade the functionalities of the textile is long, the results may be far greater than the challenges encountered. Often, the answer on how to do it lies in using technologies and knowledge that have been around for centuries. Therefore, this paper will deal with the phenomenon of photochromics, which has first been noticed in 19th century and so far not exploited nearly enough within the realm of textiles (Hepworth et al., 1999). It will cover the historical overview, division of photochromic systems and their synthesis, principals and triggering mechanisms, various fastness property issues and applicability to fibres of different origin (Shuiping et al., 2010). Application methods and state of the art shall be described thoroughly, providing scientific and technological achievements from the relevant literature references (Durr & Bouas-Laurent, 1990).

Group of authors addresses the combination of photochromism phenomenon and textile in general as newly derived system, bearing all the qualities of a sensory material. Within it, molecule of photochromic dye may be observed as "smart", as it is triggered by a specific and quantifiable physical value. Properly applied, this "smart dye" and adequate textile fibre form a textile sensor capable of sensing and reacting to a particular impulse in a predictable manner (Czarnik, 1995; Van Langehove, 2007).

Described as such, the system bears all the necessary qualities of a smart textile. It is capable of alerting and protecting the wearer from the very specific threat as it has been specifically designed, calibrated and optimized.

From the textile engineer's, namely dyer's point of viewing things, not much has changed. Only the concept of "colour all the time" has changed to "colour at the right time" principle, which may be observed as one of the options of giving leverage to textile companies in search of means and ends of once again reclaiming the leader status on the worldwide market.

2. Chromism

In this text photochromism shall be addressed in a context of products of high added values. These high added values result from functionalities being added, thus moving away from the classical concept of a textile product. The differences between a classical and a high added value product are numerous; production process may be far technologically more demanding, number of functionalities may be increased significantly, technical applicability may be greater and finally the greatest difference may be between the price of production and that of an final product.

When discussing the term photochromic, one should first clear out the term „chromic". Chromism is a process that induces a reversible colour change of components consisting of a chemical compound. This includes changes on the molecular level like cleavage of the chemical bonds or changes on the level of molecular conformations. In most of the cases, chromism is based on changes ocurring inside of the molecule, among electrons. This especially implies „pi" and „d" electron positions so that the phenomenon is induced by various outside stimulus bearing the ability of altering electronic density of the compound or a substance (Lee, S. J. et al. 2006; Nakazumi, 1997).

It is well known that many of the natural compounds possess chromic property, while a number of artificial compounds of specifically characterized chromic properties have been synthesized so far (Shibahashi, 2004). Chromism refers to the phenomenon in which colour is the result of a broad spectral interactions among incident light and material (Bamfield, 2001). These interactions may be categorized into following five groups:

- Reversible change in colour
- Absorption and reflection of light
- Absorption of energy followed by the emission of light
- Absorption of light and energy transfer or transformation of energy
- Use (manipulation) of light

These chromic effects are caused by:

- Perycyclic reactions (cyclization, cycloaddition)
- Cis-trans isomerization
- Intermolecular group transfers
- Intermolecular hydrogen transfers
- Dissociation (cleavage of the bonds)
- Electron transfer

Phenomenon including a change in colour of a chemical compound is named according to external stimulus causing the reaction, either physically or chemically (Viková, 2004). Many, but not all of these reactions are reversible. The classification is as follows:

- Photochromism – change in colour of a compound is light induced, based on izomerization among two different molecular structures

- Thermochromism – change in colour of a compound is heat induced, most frequent form of chromism
- Electrochromism – change in colour of a compound is caused by an electrical current. Induced by the acceptance or donation of electrons. The phenomenon is characteristic for compounds of redox active localities, such as metal ions and metal radicals
- Solavtochromism – change in colour of a compound is caused by solvent polarity. Most of the solvatochromic compounds are metallic complexes
- Ionochromism – change in colour of a compound is ion induced
- Halochromism – change in colour of a compound is caused by change in pH
- Tribochromism – change in colour of a compound is mechanically induced (friction)
- Piezochromism – change in colour of a compound is mechanically induced (pressure)
- Mechanochromism – change in colour of a compound is induced by deformation
- Hygrochromism – change in colour of a compound is induced by presence of moisture
- Chemochromism – change in colour of a compound is induced by specific chemical agents i.e. toxic gasses, detergents etc.

Over the past ten years, investigations on thermochromic pigments have gained popularity. These are aimed at obtaining new effects on dyed textile materials. Using a conventional technique of textile printing in combination with thermochromic pigment an intelligent textile is obtained. Intelligence is defined by the ability of the printed textile to change colour in accordance to the presence of an outside stimulus. In this case temperature changes ocurring within the close environment of the textile (Karlessi, et al. 2009; Kulčar et al., 2010; Maeda, S. 1999).

As far as quality of the chromic materials goes, it will depend on several parameters:

- Intensity of change in colouring of a compound
- Change in colouring
- Conditions of transition, change
- Dynamics of colour change
- Interval of change
- Simplicity of use
- Reversibility
- Number of colour change cycles it is capable of withstanding
- Fatigue resistance
- Fastness to heat, light, moisture (atmospheric conditions)
- Allergic reactions

3. Photochromism

The phenomenon of photochromism is an analogue to all chromic processes. The change in colour is influenced by light in a reversible way (Fig. 1) (Cheng, 2007). Uncoloured material doesn't absorb light and may only be activated by energetically rich photons of the near UV electromagnetic spectra. Many of the inorganic materials such as copper, mercury, various metal oxides and some minerals exhibit the photochromic phenomenon (Van Gemert, 1999a, b). However, their use is considered inappropriate for textile materials and substrates. Organic molecules such as spiropyrans, spirooxazines and fulgides are suitable for use on textiles (Bouas-Laurent & Dürr 2001).

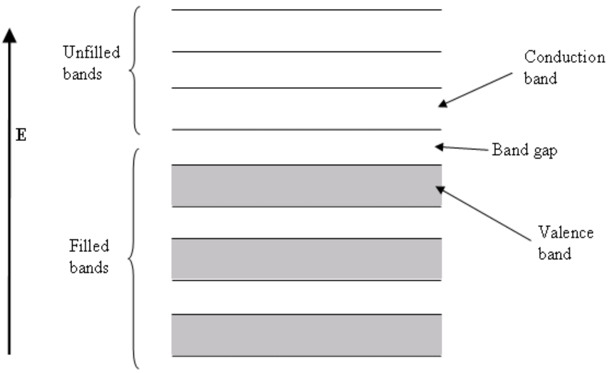

Fig. 1. Mechanism of photochromism

The very principle, the triggering mechanism of photochromism is as follows: chemical compound transitions from form A into a form B, each of them of a specific absorption spectra implying specific colouring of the form, as well. The triggering mechanism is UV light induced (process of activation). As a result of incident UV light, compound changes its colour (Bouas-Laurent & Dürr 2001).

$$\text{A (colourless)} + h\nu_1 \rightarrow \text{B (coloured)} \tag{1}$$

Upon removal of the light source the colouring disappears as the molecule return to their inactivated state i.e. rest state. Deactivation is usually a slower process than activation and hysteretic behavior is noted. In terms of the dynamics of deactivation, visible light spectra and heat increase it, while polar solvents decrease it. Colouring is usually of lower intensity at higher temperatures i.e. reversing proportionate.

$$\text{A (coloured)} + h\nu_2 \rightarrow \text{B (colourless)} \tag{2}$$

By definition, discolouring of the chemical compound caused by UV part of the electromagnetic spectra is called negative photochromism.

There are three different groups of chemical processes on which the transformation of form A into form B is based:
- Trans-cis isomerization
- Variation of conditions under which a metal is oxidized
- Homolytic or heterolytic cleavage of the chemical bond

These reactions have to be reversible in order to be characterized as photochromic. Otherwise, the reaction may be observed as usual metameric reaction (Bouas-Laurent & Dürr 2001).

3.1 Historical overview

The phenomenon of colour changing compound has been noticed and used for millennia. The first known, written documentation is that on Tyrian purple, dating 350 years B.C. i.e. back to the times of Alexander the Great. Dye was obtained from sea snails (Murex Brandaris and Murex Purpura). Applied onto textile material, the dye is in its uncoloured form and reveals true colouring only after being exposed to sunlight.

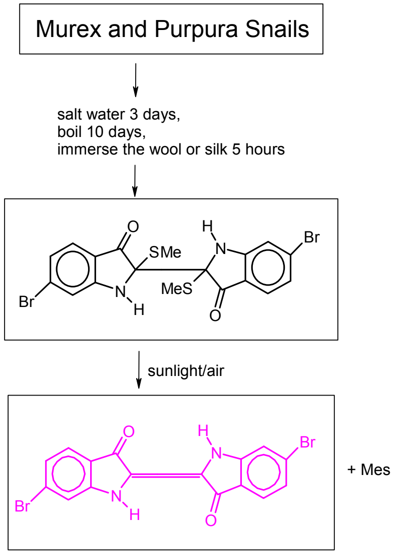

Fig. 2. Preparation of the dye obtained from Murex

Brief description on preparation of the dye and chemical change occurring on molecular level is given in figure 2 (Durr & Bouas-Laurent, 1990).

As far as natural photochromic dyes go, rhodopsin is considered a photosensitive compound of reversible colour capacity. It is present in retina of the eye. Activating mechanism of rhodopsin is of photochromic triggering mechanism. Activated by light, it produces a nerve stimulus, transmitted to the cortex to provide visual perception. Rhodopsin has been discovered inside primitive bacterium, Halobacterium halobium. In it, it is responsible of transforming sunlight into energy, which classifies metabolism. Technical applications of rhodopsin, considered as photoswitchable biomaterial include optical data storage and security applications (Hampp, 2005a, b).

Investigations on photochromics on scientific level date back to 19th century. It was J. Fritzsche who first noticed photochromic property of a solution of tetracene, while later on E. Ter Meer noticed it on solid potassium salt of dinitromethane (Bouas-Laurent & Dürr 2001).

3.2 Demands on photochromic system

Ideally, any organic photochromic system should be of following qualities:

1. Development of colour in photochromic systems – in order of being classified a sensor, the dynamics of colour development must be a rapid reaction to source of UV light
2. Return to the rest state (colourless) – the rate of fading of the system has to be controllable and all possible influences, such as influence of heat or sunlight, investigated
3. Wide palette of colours – range of the colours being exhibited as a result of irradiation by UV light should be across the visible range of light
4. Rest state in which colour is not exhibited – the state in which there is no excitement of the electrons, caused by an external stimuli should be as colurless as possible

Photochromic dye appropriately applied onto textile material forms a photochromic system, which in case of fulfilling the abovementioned demand is in fact a sensor (Billah, 2008).

Sensor capable of reacting to UV light of exactly defined spectra and intensity in a pre-programmed, controllable manner. Described as such, system alerts and protects the wearer against negative influence of UV irradiation and classifies the very definition of a “smart textile”. Having fulfilled all of these demands, investigations should be made to find out whether any derived qualities have arisen as a result of applying photochromic molecules onto textile fibres. These qualities may be an increment in UPF (Ultraviolet Protection Factor), a very interesting value for light fabrics in which bear constructional characteristics, such as the type and density of weave cannot provide satisfying UV-R protection. Another interesting quality could be certain antibacterial or antifungal properties added onto textile materials (Bamfield, 2001).

3.3 Classes of photochromic compounds

Photochromic compounds can be divided into five main classes fitting the requirements of an ideal photochromic compounds. These are, as follows:

1. Spiropyrans (Spiroindolinobenzopyrans)
2. Spironaphtoxazines
3. Naphtopyrans (Chromenes)
4. Fulgides
5. Diarylethenes

In terms of applicability to textile fibres, spiropyrans, spironaphtoxazines and chromenes have been found as most suitable considering fatigue, life time and fastness properties. Therefore, this paper will cover physic-chemical properties of these classes of dyes, suitability of use on natural and man-made fibres and several technological techniques of application.

3.4 Spirobenzopyrans

This is a widely studied class of photochromic compounds. They are consisted of a pyran ring, in most cases 2H-1-bezopyran and heterocyclic ring (Fig. 3). Link between the rings is a common spiro group (1.1). The mechanism by which the photochromism occurs is actually cleavage of the carbon-oxygen bond, caused exclusively by irradiation with UV light. The result is a ring-opened coloured species, called “merocyanine” form or MC, which can be cis-(1.2), trans–(1.3) or ortho-quinoidal form 1.4 (Bamfield, 2001, Oda, 2008).

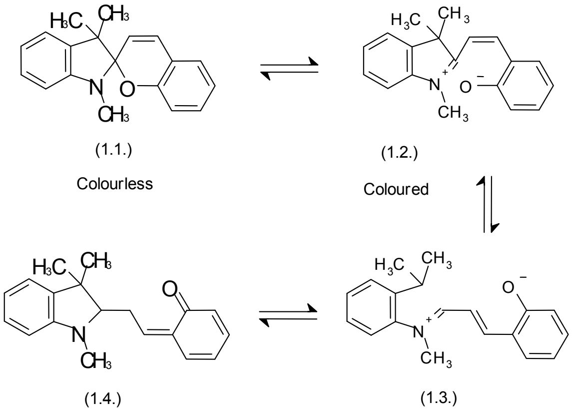

Fig. 3. Spiroindolinobenzopyran and ring opened merocyanine quinonoid form

A large number of substituents are possible for spiropyran ring. Pyran ring is most often substituted benzo or naphtopyran. Heterocylic component can be varied, as a long list of ring systems is available: indole, benzthiazole, benzoxazole, benzselenozole, quinoline, acridine, phenathridine, benzopyran, naphtopyran, xanthenes, pyrolidine and thiazolidine.

3.4.1 Synthesis of spiroindolinobenzopyrans

Synthetic pathway to spiroindolinobenzopyrans (Figure 4.) begins with synthesis of Fischer's Base (1.5 - 1.6). Spiroindloino compound is an obtained by condensation of Fisher's base (1.6; R=alkyl) with salicyaldehyde (1.7.). Another route of synthesis may be with indolinium compound bearing different N-alkyl groups (1.6; R=alkyl) and different ring substituents; chemical reaction of synthesis is shown in Figure 4 by alkylation of a 2-methylindole to obtain (1.8.; R=alkyl) (Keum et al., 2007).

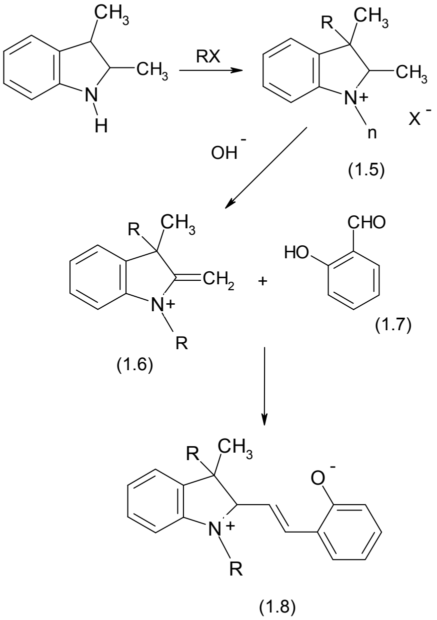

Fig. 4. Synthetic pathway to BIPS and derivatives

6-nitro-1′,3′,3′-trimethylspiro [2H-1-benzopyran-2,2′-indoline] (6-nitro-BIPS) may be considered to be most studied of all spiro-organic photochromics. Therefore, its synthesis shall b e described thoroughly. Description refers to a slightly modified literature method (Inoue et al., 10968; Sivadjian 1968). Fischer's base, 1,3,3-methyleneindoline (3,5 g; 0,02 mol) is dissolved 40 ml of absolute methanol. To this solution, 3,35 g of 2-hydroxy-4-nitrobenzaldehyde (0,02 mol) in small proportions is added over the period of 10-15 minutes. The obtained pink-brown solution is refluxed for 2 h. The reaction mixture evaporated to a small volume in an air draft. Fine powder is collected by filtration and washed with absolute ethanol and than air-dried. This was recrystallized from boiling n-hexane with a small amount of activated charcoal. Pale yellow microcrystalline powder is obtained (Clarke, 1995).

The route to 1,3,3-trimethyl-spiro[indoline-2,3′-[3H]napht[2,1-b][1,4]oxazine (NISO) is quite similar. Stechiometric compaunds of Fischer's base and 1-nitroso-2-naphtol are refluxed in alcohol or toluene for 2-4 hours (Ono and Asada, 1970). Product is collected by filtration, washed with alcohol and air-dried. It is recrystallized from boiling n-hexane with a small amount of activated charcoal. A pale greenish powder was obtained. Both Qiso and BISO can be prepared by similar methods (Hurditch & Kwak, 1987).

3.4.2 Spectral properties of spiroindolinobenzopyrans

MC form of the spiropyran dyes shows great absorbance in the visible region of the spectrum, typical of merocyanine dyes. This open chain form of the molecule is thermally instable; therefore a rapid scanning absorption spectrophotometer must be used to measure absorption within visible spectrum. Polarity of the solvent plays a key role in preparation of the spiroindolinobenzopyrans as it shifts λ_{max} of the solutions. Use of non-polar organic solvent is preferable as the compounds aren't water soluble. These classes of compounds are of strongly positive solvatochromic effect, which can be seen from the changing shape of the absorption curve and its position moving hypsochromically as the solvent polarity increases (Suppan & Ghonheim, 1997). In table 1. the changes of λ_{max} in closed (SP) and open (MC) form of the NISO, as a result of solvent polarity are shown (Keum et al., 2007).

λ_{max} of the closed SP form of NISO [nm]				λ_{max} of the open form MC of NISO [nm]	
Ethanol	Methanol	Methylene Chloride	Hexane	Solvent	λ_{max} [nm]
345	345	346	347	Ethanol	610
317	317	317	319	Acetone	600
297	303	302	303	Toluene	590
				Hexan	560

Table 1. The changes of λ_{max} in closed (SP) and open (MC) form of the NISO depending on solvent polarity

Also, parent substituents play a key role in λ_{max} changes of spiroindloinobenzopyran; especially in the 3,6,8-positions. From the table 2. it can be seen that they have the biggest influence on spectral properties of the coloured form of the spiroindolinobenzopyran.

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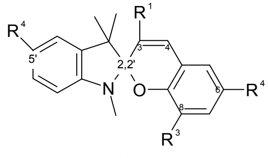
<tr><td colspan="5">

(1.9)</td></tr>
<tr><td>R¹</td><td>R²</td><td>R³</td><td>R⁴</td><td>λ_{max} [nm]</td></tr>
<tr><td>Ph</td><td>NO_2</td><td>OCH_3</td><td>H</td><td>625</td></tr>
<tr><td>H</td><td>NO_2</td><td>OCH_3</td><td>Ph</td><td>568</td></tr>
<tr><td>H</td><td>OCH_3</td><td>NO_2</td><td>Ph</td><td>625</td></tr>
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<tr><td>H</td><td>H</td><td>NO_2</td><td>H</td><td>544</td></tr>
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Table 2. Absorption maximum of the coloured form of substituted BIPS (in ethanol)

3.5 Spironaphtoxazines

Spironaphtoxazines are a very interesting group of compounds that can be used on textile fibres (Billah, 2008; Lee, E. et al. 2008). This is because of their increased fatigue and resistance towards photodegradation. Structurally, they are nitrogen containing analogues of the spiropyrans. Photochromic reaction of opening spironaphtoxazine ring (Son et al. 2007a, b) derivative to its MC form is shown in Figure 5 (Bamfield, 2001).

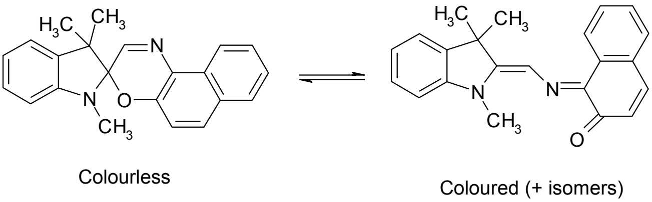


Fig. 5. Spironaphthoxazine photochromic forms

3.5.1 Synthesis of spiroindolinonaphtoxazines

The synthetic pathway to spironaphtoxazines is based on reaction between 1-hydroxy-2-nitroso bearing aromatic ring and 2-alkylidene heterocycle, such as Fischer's base (1.6; R=H). Naphtoxazines may be chosen from a list of substituents as the stability of nitrosonaphtols starting materials are much more stable than the nitrosophenols required for the parent benzo analogue (Coimbra, 2005). Synthetic pathway of obtaining alkyl substituted naphtoxazines, benzo- and heterobenzo-annulated derivatives is shown in Figure 6. Aqueous solution of corresponding phenolate and sodium nitrate is acidified. Heating the mixture in methanol under reflux gives condensation of nitrosonaphthols with indolines.

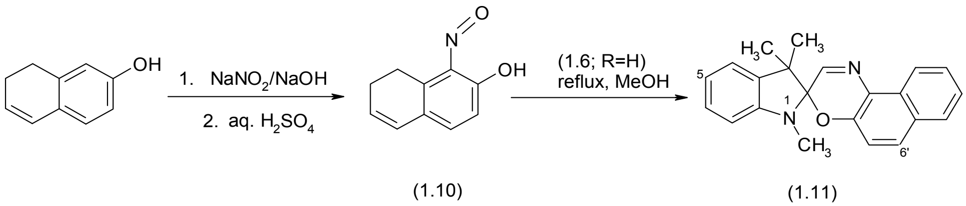
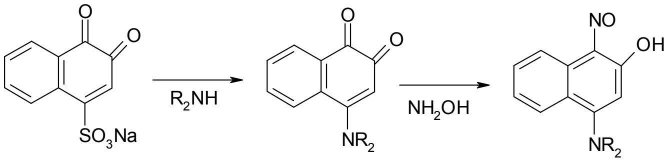


Fig. 6. Synthetic route to spiroindolinoaphthoxazine

Most important positions for substitution, affecting colour and fatigue are the 5-position and 6′-position, responsible for both colour properties (expressed as OD-optical density) and molar coefficient coefficient. The substituent on the 1-position has a kinetic effect on the rate of loss of colour back to the rest state. Important thing achieved by described syntheses are overcome colour range issues (550 – 620 nm). Important bearing amino substituents on 6′-position are synthesized from 4-substituted-1-nitroso-2–naphtols (1.14), prepared from (1.12) via (1.13) (Fig. 7).

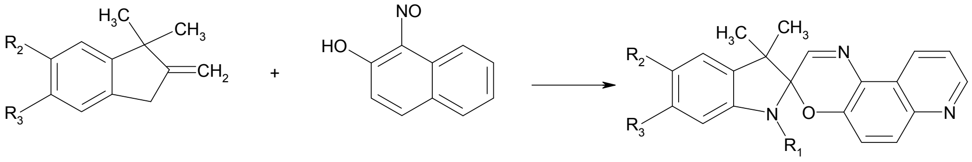


(1.12) (1.13) (1.14)

Fig. 7. Analysis of position 5 and 6′ in synthetic route to spiroindolinoaphthoxazine

3.5.2 Spectral properties of spiroindolinonaphtoxazines

The λ_{max} of the ring opened spiroindolinonaphtoxazine is at 590 nm. Also, they show a negative solavtochromic shift. Absorption moves hypsochromically (20-60 nm) in less polar solvents (Kim, 2007), Figure 8.



(1.15) (1.16) (1.17)

Fig. 8. Synthetic pathway to spiroindolinopyridobenzoxazines

Commercially important group of spiroxazines are those in which the naphthalene ring is replaced by quinoline to give spiroindolinopyridinobenzoxazines (1.17) (Suh et al. 2007). Synthesis is a reaction between 5-nitroso-6 hydroxyquinoline (1.16) with alkyl substituted 2-methlenindolines (1.15). The data on absorption effects caused by substitution on 5- and 6′-position are given in table 3.

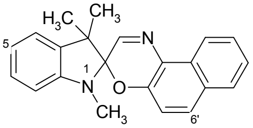
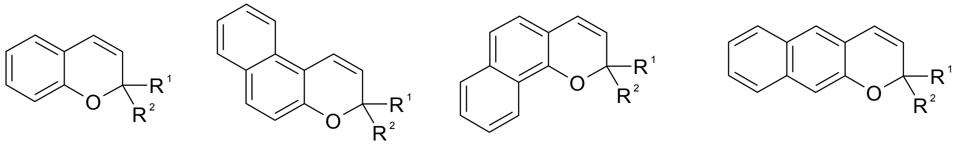
		
6' - substituent	5 - substituent	λ_{max} [nm]
H	H	605
Indolino	H	592
Indolino	OCH_3	623
Indolino	Peperidino	637
Piperidino	H	578
Piperidino	Cl	568
Piperidino	CF_3	560
Morphilino	H	580
Diethylamino	H	574

Table 3. Substituent effects on the absorption maximum of the coloured state of spiroindolinonaphthoxazines

3.6 Benzo and naphtopyrans (chromenes)

Both benzo and naphotpyrans are based on 2H-chromene ring system (Figure 9). These systems can be divided: 2H-benzopyrans (1.18) and three isomers of napohtopyrans (1.19-1.21). Due to the little or no photochromic behavior, isomer in 1.21 will not be discussed. Although substituents on R1 and R2 position may be a part of carbocyclic spiro ring, they are usually unconnected substituents such as gem dialkyl or aryl groups (Pardo, 2010).



(1.18) (1.19) (1.20) (1.21)

Fig. 9. Chemical structure of 2H-benzopyrans and three isomers of napohtopyrans

In terms of photochromic mechanism, it is quite similar to that of spiropyrans shown in Figure 10. Presence of UV irradiation induces cleavage of C-O ring, thus breaking the pyran ring and giving zwitterionic form or more likely cis- and trans-quinoidal forms (1.16). Studies on the dynamics of the reaction have shown that formation of cis-quinoidal form occurs in picoseconds, followed by trans-form in nanosecond. Isomers (1.19) and (1.20) show quite different photochromic behavior. Isomer (1.20; R1,R2=Ph) produces a more bathochromic coloured activated state than (1.19; R1, R2=Ph) (λ_{max} = 481 nm vs 432 nm), a large increment in colouration, but a very slow fade rate back to the inactivated state.

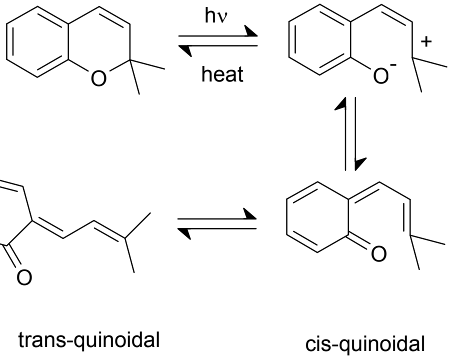


Fig. 10. Photochromic behavior of chromenes

3.6.1 Synthesis of benzopyrans and naphtopyrans

The synthetic method for more important 2,2-diaryl derivatives (1.25) involves the reaction of 1,1-diarylprop-2-yn-1-ol (1.24) with a substituted phenol or naphtol in the presence of acid catalyst. The alkynols are prepared by reaction of benzophenone (1.22) with Na or Li derivative of an alkynide, such as the trimethylsilyil acetylide (1.23), Figure 11.

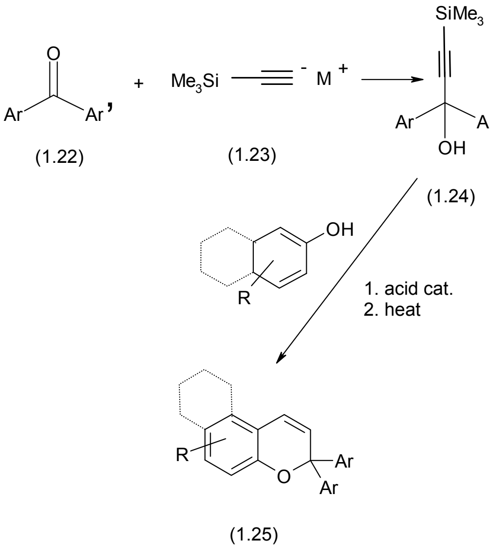


Fig. 11. Synthesis of diaryl benzo- and naphtopyrans

3.6.2 spectral and physical properties of diarylnaphtopyrans

Like the classes of spirobenzopyrans and spironaphtoxazines, diarylnaphtopyrans show significant solvatochromic behaviour. Influence of the substituents in the 3-phenyl rings on the properties of 3,3-diaryl-3H-naphto[2,1-pyrans] (tab. 4 and 5).

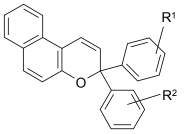
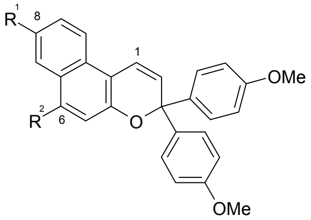
					
R^1	R^2	λ_{max}	ΔOD	$T_{1/2}$[s]	Solvent
H	H	430	-	11	A
H	4-MeO	458	-	8	A
H	4-CF_3	422	-	28	A
4-MeO	4-MeO	475	-	3	A
4-MeO	4-CF_3	440	-	4	A
4-MeO	4-NMe_2	512	-	1	A
4-NMe_2	4-NMe_2	544	-	0,5	A
H	H		0,36	45	B
2-F	4-MeO	456	1,0	170	B
2-F	3,4-diMeO	472	1,05	203	B
2-Me	4-MeO	469	2,40	600	B
2,6-diF2	4-MeO	450	2,23	1800	B

Table 4. Influence of substituents in the 3-phenyl rings on the properties of 3,3-diaryl-3H-naphto[2,1-b]pyrans (A = toluene solution; B = imbibed into diethyleneglycol bis(allyl carbonate) polymer)



R^1	R^2	λ_{max}	IOD	$IODF_{10}$%	Solvent
H	H	475	0,20	50	A
MeO	H	456	1,89	7	A
H	MeO	502	0,55	41	A
H	H	475	0,12	45	B
MeO	H	456	1,42	10	B
Piperidino	H	452	1,95	11	B
Piperidino	H	452	1,95	13	B

Table 5. Influence of substituents in 6- and 8-positions on the properties of 3,3-diaryl-3H-naphtho[2,1-b]pyrans (A = polyurethane; B = Spectralite)

Whereas:
$IODF_{10}$ - percentage loss in initial optical density 10s after removing UV irradiation source
λ_{max} – refers to the absorption maximum of the coloured state
ΔOD – the change in optical density (absorbance) on exposure to the xenon light source
$t_{1/2}$ – fade rate, time expressed in seconds for the ΔOD to return to half of its equilibrium value.

4. Textile applications

Photochromic compounds as the ones represented in this chapter are commercially available from a number of suppliers, such as: Sigma Aldrich, PPG Industries and James Robinson. So far, virtually all application techniques have been investigated in efforts of functionalizing the textile fiber with photochromic systems. Some application methods have been proven advantageous over the other, such as embedding into the polymer matrix in the spinning phase of the "man-made" fibers (polypropylene). Other processes may include dyeing and screen printing, which are considered more appropriate since the demand on photochromic textiles is limited to piece garments, rather than to batch production (Billah, 2008; Canal, 2008; Nelson, 2002).

4.1 Exhaust dyeing with photochromic compounds

The group of authors of this chapter has made significant efforts in functionalizing textile fibres with photochromic dyes. Therefore, this chapter will give a review of several papers covering this issue, namely application of photochromic compounds using the means of exhaust dyeing. In the context of dyeing technology, photochromic compounds may be observed as disperse dyes appropriate for dyeing "man-made" fibres. The dyeing process has to be set accordingly.

Most of the investigation were done using Sigma Aldrich dyes of 97% purity and alterations on the level of the dye molecule were made. Selected dyes are shown in the Table 6.

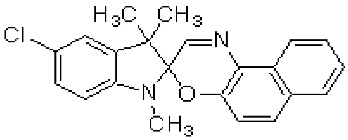
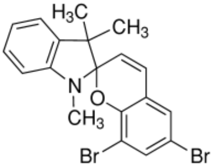
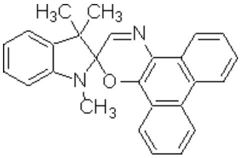
 5-Chloro-1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3′-(3H)naphth[2,1-b](1,4)oxazine] D1	 1',3'-Dihydro-8-the methoxy-1',3',3'-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-(2H)-indole] D2	 1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3′-(3H)naphth[2,1-b](1,4)oxazine] D3

Table 6. Selected photochromic dyes

Photochromic dyes were prepared by dissolving in small quantities of acetone AC, as dissolving in acetone results in clear solutions, exhibiting photochromic reaction under UV-A (λ_{max} = 354nm). Fibres chosen for the investigations were PA6 and PES, while the process of dyeing was set to satisfy the demands of disperse dyes. Exhaustion of dyes from the dyebath and onto the fibre was done according to the schematic of the process in the Figure 12. Textile substrates were dyed under laboratory conditions in Polycolor Mathis dyeing apparatus. Dyeing was commenced at 25 °C and was raised gradually to 100 °C and continued at that temperature for another 60 minutes. Textile samples were than rinsed at 40 °C, followed by hot rinsing at 80 °C.

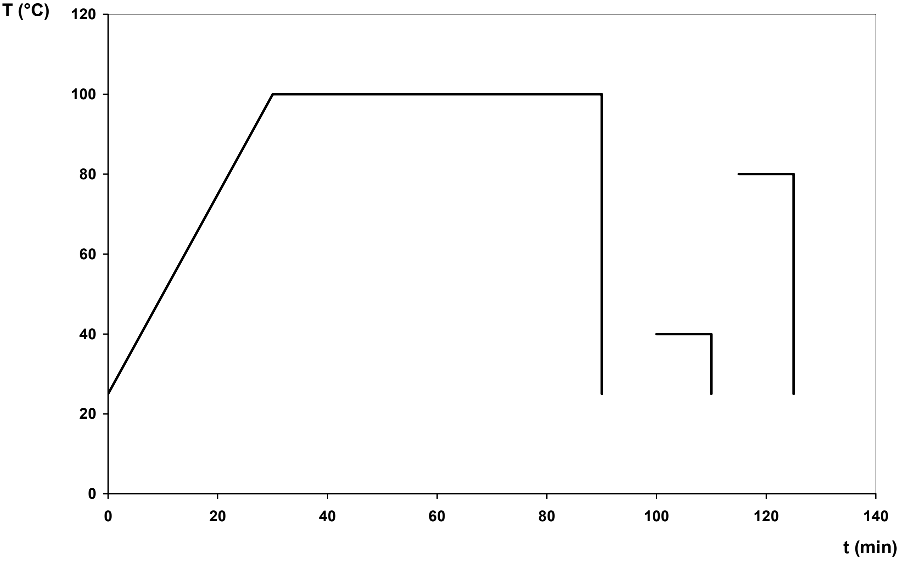
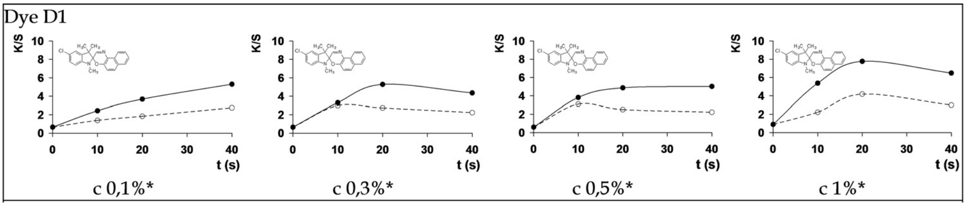


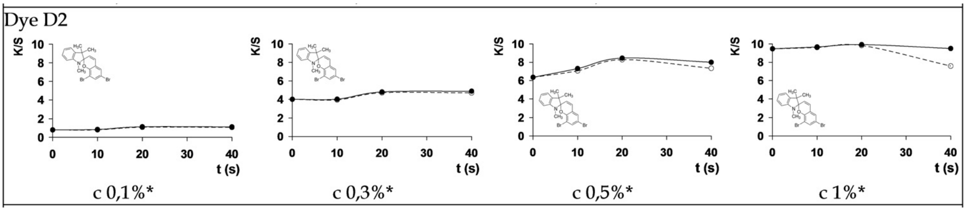
Fig. 12. Schematic of the dyeing process

Textile samples were dyed in concentrations of 0,1%, 0,3%, 0,5% and 1% calculated according to weight of fibres. Liquor to goods ratio was set to 1:20 and pH set to 4,5. Materials were dyed according to the process scheme shown in Figure 11. Kemonecer WET (non-ionic tenside) was used as an auxiliary chemical acting as an surfactant.

To investigate photochromic property of obtained photochromic textiles, samples were submitted to source of UV light in Solarscreen Test Camber to determine photochromic effect. Samples were irradiated in periods of 10, 20, 40 seconds and spectrophotometrically measured accordingly to determine the ability to respond to UV light. Fade was done by exhibiting in dark in the very same intervals in which the samples were irradiated. Spectrophotometric measurement was done on Datacolor, Spectraflash SF-600 CT-PLUS® Photochromic property was expressed through K/S values (eq. 3) (Fig. 13 and 14) and a*/b* coordinates (Fig. 14) calculated from value of remission.

$$K/S=(1-R^2)/2R \tag{3}$$





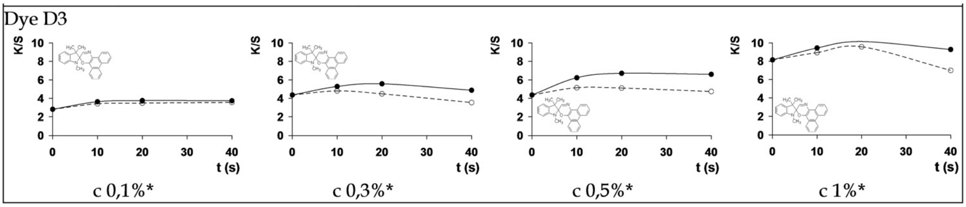


Fig. 13. K/S value of PA fibre vs. concentration of the dye (* on weight of the fibre (owof)) (— UV irradiated samples, --- after removal from UV source)

As seen in K/S graphs, PA is considered more suitable substrate for applications of photochromic dyes, while low obtained K/S values of PES substrate indicate this fibre unsuitable for dyeing by photochromics. Significant influence of dye concentration on obtained K/S values was obtained with maximum value (K/S≈8) reached after 20 seconds UV irradiation time for PA sample dyed by 1% of Dye 1. Dyeing by Dye 3 resulted in colored substrates (PA and PES) of distinct photochromic property expressed through increased K/S values measured at same wavelength (λ_{maxPA} = 600 nm).

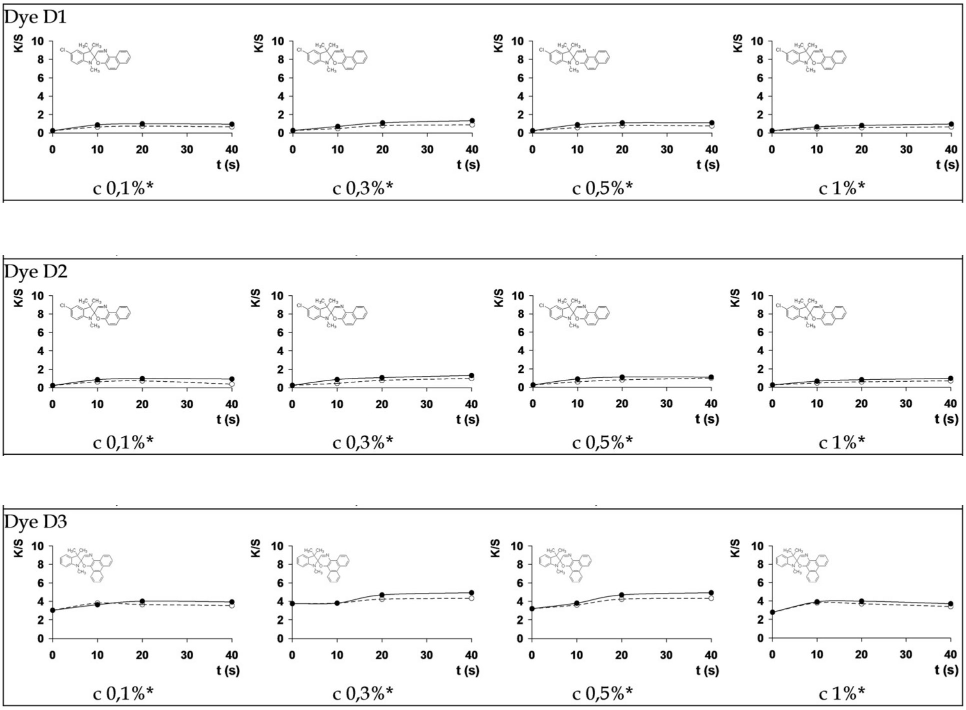


Fig. 14. K/S value of PES fibre vs. concentration of the dye (* on weight of the fibre (owof))
(— UV irradiated samples, --- after removal from UV source)

Low K/S value obtained for PES fibres confirm the influence of fibres structure on effectiveness of the dyeing process which was found to be appropriate for PA fibres, while in the case of PES carrier should have been added or process carried out at higher temperature then 100 °C. Ideally, this would increase the volume of amorphous area in PES by decreasing crystallinity. Because of low obtained values for PES fibres only a*/b* coordinates for PA fibres are shown (Fig. 15).

Shown a*/b* graphs refer only to PA samples dyed by the greatest investigated amount of dye (1% owof) (Fig. 15).

Lowest color depth was obtained in PA samples dyed by D1. After exposition to UV, lightness of the samples (D1-PA) increases, while chromacity is less than in samples dyed by D2 and D3, although difference in chromacity of UV irradiated and unirradiated sample is greatest in PA samples dyed by D1. Aforesaid, suggests the advantage of subjective reasoning over reading instrumental data only.

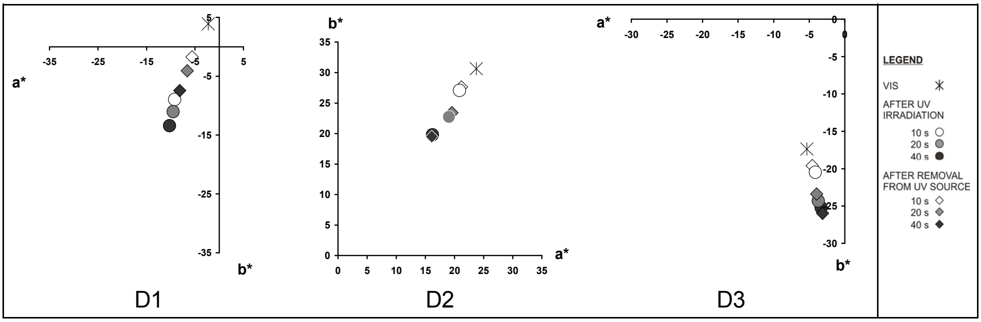


Fig. 15. a*/b* coordinates of PA samples dyed by 1% (owof) of photochromic dye

5. Conclusion

During the last ten years the traditional textile industry, that during the decades has favored quality, has changed its strategy to support the innovation and the creation of new products and functionalities. Accordingly, a rapidly growing trend is noticeable in the field of smart fabrics and intelligent textiles that can sense and react to environmental conditions or stimuli from mechanical, thermal, chemical, electrical or magnetic sources. Research by this group of authors supports and represents a contribution to the field of testing and optimization applications of photochromic dyes in textiles. In the future, research of the authors will be aimed at analyzing photochromic textile materials using state of the art instrumental analyses, such as FTIR and HPLC, supported by different spectrophotometric methods. Potentials of these materials will be researched in terms of sensory properties, with emphasis on their accuracy to react in preprogrammed manner to a very specific level of ultraviolet irradiation. Relationship among colour strength and UV irradiation levels will be researched using statistically designed experiments. In terms of application methods, screen printing will be given most attention, this statement being supported by the fact that presence of photochromic dyes or pigments is needed only on the surface of the textile material. This would well broaden the number of substrates, whereas in dyeing, only a small number is really suitable. In regards to the price of the final product, printed substrates should be favoured due to their obvious economical viability and feasibility. In terms of ecology, exemption of wastewater should be advantageous over dyeing.

In terms of "high added value" photochromic textiles should be considered as such, while the number of functions is increased significantly when compared to conventional textiles. Colour phenomenon is used to sense and detect harmful UV rays, while it is only exhibited under irradiation of UV light. Therefore, one can speak of colour at the right time, rather than of colour all the time. Dyes described in this paper may also provide necessary protection from UV spectra, while the energy is used for rearrangements on molecular level of the dye, thus increasing the number of conjugated double bonds, which is experienced as colour.

From this paper one could conclude great potentials of such dyes as described in this paper. Research and results shown imply to broadened use of photochromic dyes and expansion possibilities from ophthalmics to virtually any polymer if applied properly.

6. Acknowledgment

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5

Dyeing of Environmentaly Friendly Pretreated Cotton Fabric

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1. Introduction

Raw cotton fibres have to go through several chemical processes to obtain properties suitable for further dyeing and use. With scouring, non-cellulose substances (wax, pectin, proteins, hemicelluloses…) that surround the fibre cellulose core are removed, and as a result, fibres become hydrophilic. Conventional scouring processes of cotton are conducted at temperatures up to 130 °C in a very alkaline medium (pH 10–12) with sodium hydroxide. Since a non-specific reagent is used in the treatment, it attacks impurities but it also causes damages to the cellulose portion of the fibres. Several auxiliary agents, such as wetting agents, emulsifiers and sequestering agents, which improve the efficiency of scouring and reduce the damage of fibres, are also added to the scouring bath.

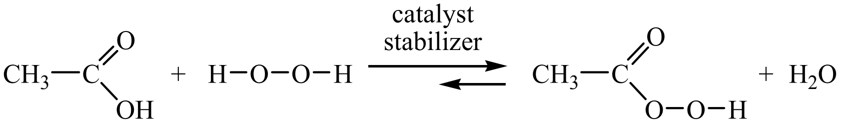
Scouring is regularly followed by a bleaching process, which removes the natural pigments of cotton fibres. Cellulose fibres are most frequently bleached with hydrogen peroxide resulting in high and uniform degrees of whiteness. The water absorbency also increases, however, during the decomposition of hydrogen peroxide, radicals that can damage the fibres are formed. For this reason, organic and inorganic stabilizers and sequestering agents are added to the treatment bath.

Hydrogen peroxide is not ecologically disputable. The large amount of water used to rinse and neutralize the alkaline scoured and peroxide bleached textiles is ecologically disputable. Namely, the bleaching process is conducted in an alkaline bath at pH 10 to 12 and at temperatures up to 120 °C. Due to high working temperature, a large amount of energy is consumed. Auxiliary chemicals added into the bath increase the TOC and COD values of effluents. Upon neutralization of highly alkaline waste baths, large amounts of salts are produced. Consequently, the textile industry is considered one of the biggest water, energy and chemical consumers (Alaton et al., 2006; Warke & Chandrate, 2003).

To comply with more and more rigorous environmental regulations and to save water and energy, biotechnology and several types of enzymes have entered the textile sector. Many review (Jayani et al., 2005; Galante et al. 2003) and scientific (Gummandi & Panda, 2003; Buchert et al., 2000) papers describe the use of different enzymes for textile finishing. Pectinases are an efficient alternative to sodium hydroxide in the removal of non-cellulose substances from the cotton fibre surface (Preša & Tavčer, 2008a; 2008b). This process occurs at moderate temperatures in a slightly acidic (Calafell & Garriga, 2004; Li & Hardin, 1998;

Sawada et al., 1998, Buschle-Diller et al., 1998) or alkaline (Etters, 1999; Durden et al., 2001; Lenting & Warmoeskerken, 2004) medium and is dependent on the type of pectinase. Pectin acts as a sort of cement or matrix that stabilizes the primary cell wall of cotton fibres. Pectinases decompose insoluble pectin into smaller particles thereby destabilizing the structure in the outer layers. The weakened outer layers can be removed in a subsequent wash process to such extent that following finishing processes and dyeing can be easily preformed (Etters, 1999; Losconzi et al., 2004; Cavaco-Paulo & Gubitz, 2003). It has been established that agitation of the treatment bath is very important for pectinase to function efficiently (Anis & Eren, 2002; Li & Hardin, 1998) and that selected sequestering agents can improve their effectiveness (Losonczi, 2005). Since enzymes act selectively, no damage to fibres occur during treatment. Also, it has been observed that after enzymatic treatment, baths are less polluted than baths after scouring with sodium hydroxide (Losonczi et al., 2005; Choe et al., 2004).

Bleaching with peracetic acid (PAA) is an alternative to bleaching with hydrogen peroxide (Tavčer, 2010). It is a powerful oxidizing agent (redox potential: 1.81 eV) (Preša & Tavčer, 2009) with excellent antimicrobial and bleaching properties. It is efficient at low concentrations, temperatures and in neutral to slightly alkaline medium. Its products of decomposition are biologically degradable. In the past, it was prepared in situ from acetic acid anhydride and hydrogen peroxide (Rucker, 1989; Wurster, 1992). However, the risk of explosion during the synthesis reaction prevented affirmation of peracetic acid as a bleaching agent in industry. In recent years, peracetic acid has become interesting (Hickman, 2002; Križman et al., 2005; Križman Lavrič et al., 2007). Several commercial products are available as balanced mixtures of peracetic acid, acetic acid and hydrogen peroxide (Equation 1). They are stabilized with a minimum amount of sequestering agent. Today, peracetic acid products available in the market are safe, simple to use, and price-effective. Equation 2 shows the reaction that occurs when peracetic acid is used for bleaching.



$$CH_3-C(=O)OH + H-O-O-H \xrightleftharpoons{\text{catalyst stabilizer}} CH_3-C(=O)-O-O-H + H_2O \quad (1)$$

$$CH_3COOOH + \text{impurities} \longrightarrow CH_3COOH + \text{oxidised impurities} \quad (2)$$

Both processes, scouring with pectinases and bleaching with peracetic acid, are conducted at temperatures of 50–60 °C for 40–60 minutes and pH 5–8. If both processes could be combined into one process, huge amounts of water, energy, time, and auxiliary agents can be saved. In a recent study (Preša & Tavčer, 2008b), it was confirmed using a viscosimetric method that pectinases retain their activity in the presence of peracetic acid and that combined processes are feasible.

The objective of our work was to compare the properties of enzymatically-scoured and peracetic acid-bleached cotton fabrics treated by two-bath and one-bath scouring/bleaching methods, with respect to conventionally-treated fabrics (alkaline scoured and bleached with hydrogen peroxide) with emphasis on their degree of whiteness and dyeability.

Dyeability of differently pretreated fabrics is very important for industry and was studied from many aspects before. The dyeing behaviour of cotton fabrics treated with different enzymes by using reactive, cationic and acid dyes showed that cationic and acid dyes were more sensitive to the enzymatic treatment used as reactive dyes (Canal et al., 2004). When dyed with bireactive dyes the dyeing showed excellent evenness and their capacity to cover differences in whiteness arising from different pretreatment processes was significant. On the contrary, the dyeings with acid and cationic dyes revealed, with large differences in dye exhaustions, that each enzymatic system produces different ionisable residues on the primary wall of the cotton fibre (Canal et al., 2004). The importance of charges and functional availability on the fibre surface after different bioscouring treatments for their dyeing behaviour was also exposed by Calafell and co-workers (Calafell et al., 2005).

The ability of reactive dyes to cover the differences in whiteness from different bioscouring and bleaching processes when dyed in dark shades was confirmed by several researchers (Fakin et al., 2008, Loszonci et al., 2004).

Our research will upgrade the above results with reactive dyeing of differently scoured and differently bleached cotton fibres in medium and light shades and estimate the processes from the ecological point of view.

2 Experimental

2.1 Materials

Desized cotton fabric, 100 g/m^2, was obtained from Tekstina, Slovenia. Acid pectinase Forylase KL (AP) was supplied from Cognis, Germany, and alkaline pectinase Bioprep 3000L (BP) from Novozymes, Denmark. Cotoblanc HTD-N (anionic wetting and dispersing agent, alkansulphonate with chelator) was supplied from CHT, Germany. H_2O_2 35% (HP) and peracetic acid (PAA) as a 15% equilibrium solution in the commercial bleaching agent Persan S15 were obtained from Belinka, Slovenia. Foryl JA (nonionic wetting agent) and Locanit S (ionic-nonionic dispersing agent) were obtained from Cognis, Germany and Lawotan RWS (nonionic wetting agent) was obtained from CHT, Germany. Sodium hydroxide was supplied from Šampionka, Slovenia, and acetic acid and sodium carbonate were supplied from Riedel-de Haen, Germany.

2.2 Treatment methods

The cotton fabric was scoured according to three different procedures using sodium hydroxide, acid pectinase or alkaline pectinase. The scoured fabrics were bleached with two bleaching agents: hydrogen peroxide and Persan S15. The abbreviation of processes and treatment conditions are displayed in Table 1. Enzymatic scouring and one-step treatments were performed 60 minutes at 55 °C, than the temperature of the bath was increased to 80 °C for 10 minutes to deactivate the enzymes. To activate peracetic acid in AP/PAA treatment, the pH was adjusted to 8 after 30 minutes. Demineralised water was used in all processes. The treatments were performed on the Jet JFL apparatus manufactured by Werner Mathis AG loaded with 50 g of fabric at a liquor ratio of 1:20. After all treatments, the bath was discharged and the jet was filled sequentially with fresh water heated to 80 °C, 60 °C and 25 °C to rinse the fabric. After alkaline scouring and peroxide bleaching, the fabrics were additionally neutralized with a neutralizing bath containing acetic acid and rinsed with cold water.

Process	Conditions
AS - Alkaline scouring	3 g/l NaOH, 2 g/l Cotoblanc HTD-N, 95 °C, 40 minutes
AP - Scouring with acid pectinases	5 ml/l Forylase KL, 0.75 ml/l Foryl JA, 2 ml/l Locanit S and CH_3COOH to pH 5.5, 55 °C, 40 min.
BP - Scouring with alkaline pectinases	0.05 % Bioprep, 0.5 g/l Lawotan RWS, Na_2CO_3 to pH 8, 55 °C, 40 min.
HP - bleaching with hydrogen peroxide	7 g/l H_2O_2 35%, 1 g/l Cottoblanc HTD-N, 4 g/l NaOH 100%, 95 °C, 40 min
PAA - bleaching with peracetic acid	15 ml/l Persan S15, 55 ml/l Na_2CO_3 0.5 M, 0.1g/l Lawotan RWS, pH 8, 55 °C, 40 min
AP+PAA - one step scouring with acid pectinase and bleaching with peracetic acid	5 ml /l Forylase KL, 0.75 ml/l Foryl JA, 2 ml/l LocanitS, 15 ml/l Persan S15
BP+PAA - one step scouring with alkaline pectinase and bleaching with peracetic acid.	0.05 % Bioprep 3000L, 0.1 mL/L Lawotan RWS, 15 mL/L Persan S15, pH 8 with NaOH, 55 °C, 40 min.

Table 1. The abbreviation of processes and treatment conditions

2.3 Dyeing procedure

Dyeing the pre-treated fabrics was performed at 60 °C for 90 minutes with 0.5% and 2% Cibacron rot F-B. 30 g/L Na_2SO_4 and 8 g/L Na_2CO_3 was used for pale shade and 50 g/L Na_2SO_4 and 11 g/L Na_2CO_3 for medium shade. The weight of the dyed samples was 5 g. Finally, the cotton was soaped, washed and air dried. Dyeing was performed in closed beakers on an Launder-Ometer (Atlas).

2.4 Analytical methods

Prior to the measurements, fabrics were conditioned 24 hours at 20 °C and 65% relative humidity. The degree of whiteness and the colour values were measured on the Spectraflash SF600 Plus using the CIE method according to EN ISO 105-J02:1997(E) standard and EN ISO 105-J01:1997(E), respectively. Weight loss due to the pretreatments was determined by weighing the fabric samples before and after pretreatment and was expressed in percent. Water absorbency was measured according to DIN 53 924 (velocity of soaking water of textile fabrics, method for determining the rising height). Measurements of tenacity at maximum load were performed on Instron Tensile Tester Model 5567. The mean degree of polymerization (DP) was determined with the viscosimetric method in cuoxam.

Samples of remaining bleaching and scouring baths were collected after all treatments. Their ecological parameters (pH, total organic carbon (TOC), chemical oxygen demand (COD), biological oxygen demand (BOD_5)) were measured, the consumption of water and energy was estimated (Preša, 2007).

3. Results and discussion

3.1 Whiteness

The achieved degrees of whiteness (W) and tint values (TV) are presented in Table 2. The desized (untreated) sample (D) had a degree of whiteness of 11.1. After alkaline scouring, the fibres swelled, became smoother and clean of non-cellulose impurities and the degree of whiteness increased to 19.5. However, after scouring with acidic and alkaline pectinases, both samples had lower degrees of whiteness relative to the desized sample, i.e. the sample treated with acidic pectinases (AP) had a whiteness degree of 8.2, and the sample treated with alkaline pectinases (BP) had a whiteness degree of 8.4. Negative TV values demonstrated that all scoured and desized samples had a red shade. After alkaline scouring, the red shade decreased, whereas after both bioscourings, the red shade increased.

The degree of whiteness of all scoured samples increased significantly after hydrogen peroxide bleaching. The differences in whiteness from previous scouring disappeared. Alkaline and bioscoured samples have a whiteness values above 84 and the red shade almost disappeared.

With peracetic acid bleaching, a high degree of whiteness was not achieved and the differences in whiteness from the previous scouring remained visible. The sample, which was alkaline scoured prior to bleaching (AS+PAA), had the highest degree of whiteness (72.7), whereas both bioscoured samples had lower degrees of whiteness (57.7 AP+PAA and 57.3 AP+PAA). The red shade was visible on all peracetic acid bleached samples and was more on bioscoured than on alkaline scoured fabrics, which suggests that bleaching with peracetic acid is not as effective as bleaching with hydrogen peroxide. This occurs because bleaching with peracetic acid proceeds at a low temperature and pH, where the impurities remaining after scouring could not be fully oxidised. Bioscoured fibres contained also more waxes and other impurities that hindered the successful oxidation with peracetic acid at mild conditions. Bleaching the alkaline scoured fabrics with peracetic acid is more effective since the impurities were removed from cotton fibres to a higher extent in the previous process and the pigments within fibres were more exposed to the oxidant's influence. This is confirmed by comparing data of the mass loss during treatments (Table 3).

The degrees of whiteness after a one-bath treatment (68.7 AP/PAA and 69.6 BP/PAA) were higher than those after two-bath bioscouring and bleaching with peracetic acid and close to the whiteness achieved after alkaline scouring and bleaching with peracetic acid. This can be explained by the fact that at the bleaching conditions of peracetic acid (55 °C, pH 8), hydrogen peroxide, which was present in the balanced mixture with peracetic acid, was not consumed, whereas at temperature 80 °C, which was the finite temperature of the one-bath process, hydrogen peroxide was activated, which further increased the degree of whiteness.

	Scouring		HP		PAA		Scouring/PAA	
	W	TV	W	TV	W	TV	W	TV
D	11.1	-9.1	-	-	-	-	-	-
AS	19.5	-7.6	84.12	-0.45	72.7	-0.95	-	-
AP	8.2	-9.73	85.59	-0.37	57.7	-2.05	68.7	-1.3
BP	8.4	-9.6	85.07	-0.36	57.3	-1.9	69.6	-1.2

Table 2. Whiteness (W) and tint values (TV).

3.2 Fabric properties

Table 3 represents the loss of weight, rising height in warp direction, tenacity at maximum load and degree of polymerization (DP) of differently pretreated cotton fabric samples.

The **loss of weight** demonstrates that scouring with NaOH is more intensive and removes more incrusts than enzymatic scouring. The loss of mass after alkaline scouring was ca. 1.3% and after enzymatic scouring, was less than 1%. During hydrogen peroxide bleaching, the loss of mass was greater in those samples, where the loss of mass was lower during scouring; alkaline scoured only 0.25%, acid pectinases scoured 1.2% and alkaline pectinases scoured 0.73%. This suggests that hydrogen peroxide bleaching removed a large portion of compounds, which remained on fibres after scouring. The total mass loss after scouring and hydrogen peroxide bleaching was similar for all samples.

Peracetic acid bleaching also removed a certain part of the noncellulosic substances, which remained on fibres after scouring, but the quantity was lower relative to hydrogen peroxide bleaching. Bleaching with peracetic acid did not equalize the differences in the loss of mass, which is in agreement with the whiteness results. We can conclude that high temperature and high pH are conditions that contribute decisively to the removal of non-cellulosic impurities. Specifically, waxes cannot be removed completely when all processes are conducted at low temperatures and neutral pH, as is the case for bioscouring and peracetic acid bleaching.

	Weight loss (%)	Rising height (cm)	Tenacity (cN/tex)	DP
D		0	18.47	2482
AS	1.27	2.9	18.45	2432
AP	0.30	2.7	16.96	2451
BP	0.89	2.5	17.95	2385
AS+HP	1.52	3.0	16.65	1774
AP+HP	1.51	3.0	17.12	1947
BP+HP	1.62	2.8	16.83	2004
AS+PAA	1.30	2.8	16.94	2278
AP+PAA	0.65	2.9	18.12	2318
BP+PAA	0.95	2.9	13.75	2399
AP/PAA	0.40	2.7	16.94	2438
BP/PAA	0.60	2.8	18.84	2300

Table 3. The loss of mass, rising height in warp direction, tenacity at maximum load, degree of polymerization (DP)

The remained substances influence on the water absorbency and consequently alkaline scoured samples had the highest absorbency. Bleaching improved the absorbency of the scoured fabrics, particularly of enzymatically scoured ones. However, the difference in rising height was so small, that all the samples could be considered absorbent.

There were no higher differences in **tenacity at maximum load** between the de-sized and differently treated samples. On the other hand, the results of **DP** demonstrate that bleaching with hydrogen peroxide decreased the degree of polymerization significantly, while other processes preserved the DP values close to the starting value. The bioscouring and bleaching with peracetic acid in a one bath or two bath processes causes no damage to fibers and this is one of the benefits of such processes.

3.3 Dyeing

Colour strengths (expressed as K/S value) and colour differences, ΔE*, of the fabric samples dyed with 0.5% and 2% of Cibacron red F-B are presented in Tables 4 and 6, respectively. The lightness values, L*, croma, C*, and hue, h, are presented in Tables 5 and 7. A standard for colour difference calculation was in each set of processes the alkaline scoured sample.

	Scouring		HP		PAA		Scouring/PAA	
	K/S	ΔE*	K/S	ΔE*	K/S	ΔE*	K/S	ΔE*
D	4.02	-	-	-	-	-	-	-
AS	4.04	-[a]	2.61	-[b]	3.89	-[c]	-	-
AP	4.04	3.74	2.73	0.26	3.89	1.26	3.78	0.58
BP	4.23	3.04	2.72	0.22	4.10	0.85	3.97	0.30

a-standard for scoured fabrics, b-standard for HP bleached samples, c-standard for PAA bleached and one-bath treated fabrics

Table 4. Colour strengths (K/S) and colour differences (ΔE*) of the fabric samples dyed with 0.5 % of Cibacron red F-B.

K/S values of all samples dyed with one concentration of dye after only scouring are similar. No significant differences were observed between the colour depths of alkaline and enzymatic pretreatments. On the contrary, colour differences between alkaline scoured and enzymatic scoured samples dyed in light shades are significant (ΔE* is above 3). This is explained by differences in whiteness after scouring, which was not covered in light shade dyeing, whereas they were covered in dark shade dyeing to a greater extent (ΔE*≈1).

The colour strengths of the samples dyed after scouring and bleaching are very similar within a set of samples, but they differ between differently bleached samples. K/S values on all hydrogen peroxide bleached samples were lower than those obtained for all peracetic acid bleached samples, and this relationship exists on pale and medium-dyed samples. We can conclude that the differences in whiteness, which were visible on samples after scouring and bleaching, remained to a certain extent after dyeing. The lighter fabrics achieved lower K/S values relative to darker fabrics when dyed under same conditions.

ΔE* values reveal that bleaching with hydrogen peroxide enabled the achievement of equal pale and medium colours on alkaline and bioscoured samples (ΔE*<0.3), while the colour differences between alkaline and bioscoured samples were higher when the samples were bleached with peracetic acid and dyed (ΔE*≈1). The colour of one-bath pretreated and dyed fabrics was close to the colour of alkaline scoured, peracetic acid bleached and dyed sample (ΔE*<0.6), which confirms that hydrogen peroxide bleaching covered the differences in colour arising from different scouring methods, while peracetic acid bleaching preserved those differences.

The colour evenness was excellent for all samples. The standard deviation of ten colour difference values ΔE^* was below 0.06 for all dyed samples. We can conclude that all presented types of pretreatment are appropriate for further dyeing with reactive dyes, but the initial colour of the material should be considered when the dyeing recipes are prepared.

	Scouring			HP			PAA			Scouring/PAA		
	L*	C*	h [°]	L*	C*	h [°]	L*	C*	h [°]	L*	C*	h [°]
D	57.4	44.4	351.8	-	-	-	-	-	-	-	-	-
AS	58.4	46.1	351.0	59.5	48.8	350.8	59.3	47.4	350.5	-	-	-
AP	57.4	43.6	351.6	59.0	49.4	350.7	58.9	46.2	350.6	59.3	46.9	350.2
BP	57.7	43.9	351.8	59.1	49.3	350.9	59.1	46.6	350.4	59.4	47.2	350.3

Table 5. Lightness values (L*), croma (C*) and hue (h) of the fabric samples dyed with 0.5 % of Cibacron red F-B.

	Scouring		HP		PAA		Scouring/PAA	
	K/S	ΔE*	K/S	ΔE*	K/S	ΔE*	K/S	ΔE*
D	13.24	-	-	-	-	-	-	-
AS	13.42	-[a]	9.72	-[b]	13.38	-[c]	-	-
AP	14.17	0.84	9.57	0.03	13.10	1.15	13.19	0.81
BP	13.33	1.27	9.55	0.03	13.26	1.00	14.25	0.65

a-standard for scoured fabrics, b-standard for HP bleached samples, c-standard for PAA bleached and one-bath treated fabrics

Table 6. Colour strengths (K/S) and colour differences (ΔE*) of the fabric samples dyed with 2 % of Cibacron red F-B and standard deviation in brackets.

	Scouring			HP			PAA			Scouring/PAA		
	L*	C*	h [°]	L*	C*	h [°]	L*	C*	h [°]	L*	C*	h [°]
D	44.7	54.6	356.0	-	-	-	-	-	-	-	-	-
AS	45.3	56.0	356.2	46.0	58.5	357.0	46.2	57.0	356.1	-	-	-
AP	44.6	54.9	356.3	46.2	58.5	356.9	45.7	56.0	355.8	45.7	56.4	355.9
BP	44.1	55.0	356.4	46.2	58.4	356.9	45.4	56.4	356.0	45.7	56.6	356.0

Table 7. Lightness values (L*) croma (C*) and hue (h) of the fabric samples dyed with 2% of Cibacron red F-B and standard deviation in brackets.

3.4 Ecological parameters

Conventional treatment of cotton fibres was conducted in an alkaline environment: final pH at alkaline scouring and at bleaching with hydrogen peroxide was around 12.5. Such alkaline baths should be neutralized prior to drainage into the sewage system. At neutralization, salts that additionally load wastewaters are produced.

While bleaching with peracetic acid and at both combined processes, the final pH value of the bath was near 6. Since neither of these processes requires neutralization of fibres, the treatment process can be shorter and less expensive.

While scouring with pectinases and bleaching with peracetic acid, the consumption of energy required to heat the bath was also lower. Conventional processes of scouring and bleaching were performed at temperatures near the boiling point, whereas bioscouring and bleaching with peracetic acid were conducted at a temperature of 55°C. Due to the lower temperature, less energy was required.

The consumption of water and energy is the lowest at combined scouring/bleaching treatments. Consequently, at these processes arises the lowest amount of effluents and the produced wastewater is biodegradable (Preša & Tavčer, 2009).

4. Conclusions

Enzymatically and alkaline scoured cotton fabrics have similar water absorbency, tenacity at maximum load and degree of polymerization. Because of lower loss of mass and lower whiteness of enzymatically scoured fabrics noticeable differences in colour occur between differently scoured samples dyed to light hues. The colour differences are overcame at medium and pale shades.

During bleaching with hydrogen peroxide the differences in whiteness arising from previous scouring processes disappeared. All samples obtained high whiteness values. At bleaching with peracetic acid the obtained whiteness values are lower and the differences from previous scouring processes remained visible. This causes that the colour differences between differently scoured samples, which were bleached with hydrogen peroxide prior to dyeing, are not visually perceivable, while they remained visible on samples bleached with peracetic acid at light and medium shade dyeing.

At one-bath processes of scouring/bleaching with pectinases and peracetic acid the degree of whiteness of fabrics is higher than at two-step scouring and bleaching with peracetic acid, but lower than at bleaching with hydrogen peroxide. The colour of dyed fabrics is equal to alkaline scoured and peracetic acid bleached fabric.

The different shades obtained on differently pretreated fabrics are the consequence of their different initial whiteness values. All other parameters are very similar, the exhaustion rate, the fixation rate and the fastness properties (Preša, 2007). The bioscouring and bleaching with peracetic acid, especially the one-bath processes, are suitable treatments before dyeing with reactive dyes. Lower amount of water and energy is consumed than at conventionally pretreatment and the fibres are not damaged at all. For reproducible dyeing the initial colour of the fabric should be considered when preparing the dyeing recipes.

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6

Improvement in Acrylic Fibres Dyeing

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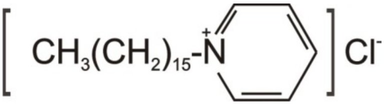
1. Introduction

At the interface of an electrically charged textile fabric and an aqueous solution containing an electrolyte, a surface-active agent, or a dye, an electrical double layer is set up. An electrokinetic potential or zeta potential, ζ, is developed when one of these two charged surfaces moves with respect to the other. This potential plays an important role in the electrical characterization of textile materials and in dyeing and, more generally, in many important wet processes to which textile fibers are subjected (Dai, 1994; Jacobash, 1985; Lokhande, 1970; Teli, 1993). In our opinion, the most appropriate electrokinetic technique to study the zeta potential of fibrous systems is the streaming potential method (Espinosa &Gonzalez, 1991, Gonzalez &Espinosa, 1988).Studies of the sorption of ionic and reactive dyestuff on textile fabrics shows that the electrokinetic potential and surface charge density of fibers can be influenced to a great extent by surfactant and dyes (Anders, 1965). Analysis of the solid surface free energy, together with electrokinetic measurements of the system and an investigation of the adsorption of surfactants and dyes on textiles, provides extensive information about dyeing and finishing mechanisms of fabrics (Peters, 1975). The determination of the surface free energy of a solid surface is important in a wide range of problems in pure and applied science. The surface free energy concept can be used for investigating physicochemical surface properties of textile fabrics and the results of these investigations can be correlated with important technical properties of textile applications (Grundke et al., 1991, Chibowski & Gonzalez, 1993; Holys &Chibowski, 1992; Espinosa et al., 1997; Chibowski et al. 1998). Because of the importance of acrylic fibers in textile industry, investigations in improving their dyeing properties are very interesting. In the present study, we have used as acrylic fibres samples of 100% pure Leacril fibers, of 1.3 dtex, from Montefibre S.A., Barcelona (Spain). Leacril fibers practically do not swell in water (Shukla et al., 1991). The retention of water vapor on the fibers is of the order of ca. 0.8% (Frushour & Knorr, 1985). These fibers are hydrophobic in nature, and they are not easily penetrated by the dyes ((Lokhande, 1970). The use of the surfactants to assist wetting of textile fabrics and, more particularly, for the level of dyeing has become widespread (Cegarra et al. 1984). In the present study, we have used various cationic and reactive dyes in the dyeing process of Leacril fibers. For improvement in Leacril fibers dyeing, we have used various surfactants in the pretreatment of the fibers, in order to obtain the conditions that increase the amount of dye uptaken by the mentioned acrylic fibers. On the other hand, also our purpose is to know the different physico-chemical mechanisms that govern the adsorption of different dyes onto the textile materials when these materials have been pretreated with different ionic surfactants.

2. Effect of n-cetylpyridinium chloride on the zeta potential and surface free energy of the leacril fibers

Acrylic fibers consist of ca. 90% acrylonitrile and ca. 9% vinyl acetate,(Frushour & Knorr, 1985). Sulfur dioxide and potassium persulfate were used as initiating agents for the copolymerization reaction. These compounds produce a large number of both sulphonate and sulfate end-groups on the fiber (Adamson, 1982). These end-groups are ionized in aqueous medium and hence these groups produce negative charge on the fiber surface. The fibrous samples were rinsed repeatedly with deionized water until the conductivity of the washing water remained constant. Finally, they were dried in an oven at 313 °K.

In this work we have used N-Cetylpyridinium chloride (N-CPCl) surfactant, as the agent which we have tested for the pretreatment of Leacril to improve the posterior adsorption of different dyes onto Leacril fibers. This surfactant is A.R. grade from Merck, and was used without further purification. Chemical structure is shown in scheme 1.



Scheme 1.

Water with a conductivity of ca. 10^{-6} S cm^{-1} was used to prepare the different solutions. For the determination of the zeta potential of Leacril fibers, we have used porous plugs with constant Leacril content (1 g) and densities of packing in the plug of 75.7, 86.6, 101, 121.2, 151.5 and 202 kg m^{-3}, in the streaming potential experiments. An Anton Paar EKA, Electrokinetic Analyzer, from Graz (Austria) was used for the determination of the zeta potential of the Leacril samples in the pretreatment of the fibers with the surfactant and also in the posterior dyeing, with different dyes, of the above pretreated samples. The samples of untreated Leacril fibers were conditioned before the electrokinetic and sorption experiments with solutions of N-Cetylpyridinium chloride at temperatures of 283°K., 293°K., 303°K. and 313°K. for 72 h, this time being sufficient to attain equilibrium.

For the determination of the zeta potential of the system, the models of bundle of capillaries, Goring and Mason, Biefer and Mason, and Chang and Robertson (Goring & Mason, 1950; Biefer & Mason, 1050; Chang & Robertson, 1967) were applied to evaluate the zeta potentials of the Leacril plugs. However we have verified that the Goring and Mason model is, in our case, the model which presents a superior correlation coefficient both over the whole tested range of concentration of N-Cetylpyridinium chloride in solution and for all the investigated packing densities of Leacril in the plug (Espinosa &Giménez, 1996).

In the Figure 1, are shown the zeta potentials obtained for Leacril, as a function of the molar concentration of N-CPCl at 293°K. It can be observed that the values of zeta potential are not high. The zeta potential of the system is negative at low concentrations of the surfactant in solution. Zeta potential sign changes at concentrations higher than ca. 2×10^{-5} M of surfactant in solution, its value being zero at this concentration. It increases for values up to 10^{-4} M of N-CPCl, where ζ is maximum, and then decreases as the concentration of the surfactant in solution increases. Further, zeta potential is very low at concentrations between 5×10^{-3} M and 10^{-2} M of surfactant.

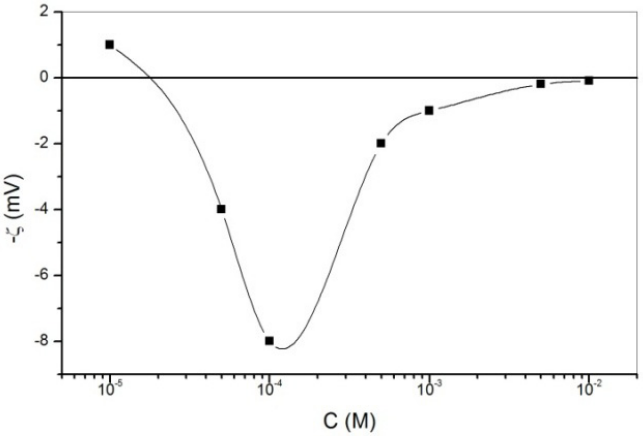


Fig. 1. Zeta potential of Leacril, as a function of NCPCl concentration 293°K..

Sorption experiments at different temperatures have been done to explain the electrokinetic behavior. Figure 2 shows the amount of N-CPCl in the Leacril, Meq, at different temperatures, as a function of the final (equilibrium) concentration of the surfactant in solution.

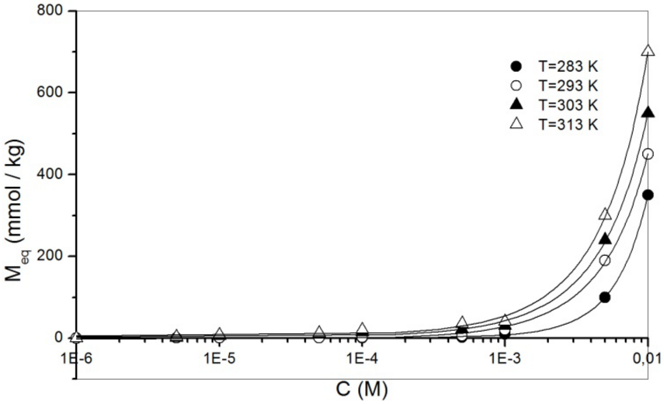


Fig. 2. Amount of NCPCl adsorbed, M_{eq} , at different temperatures.

It can be seen that M_{eq} increases with both increasing concentration of N-CPCl in solution and increasing temperature of sorption. The amount of surfactant taken up by the fiber is low when the equilibrium concentration is lower than 10^{-4} M, and increases abruptly above this value, attaining a value of 730mmol/kg at 10^{-2} M of surfactant in solution and 313°K. The results shown in Figures 1 and 2, suggest a mode of binding that can be interpreted, probably, on the basis of electrostatic attraction between both the sulphonate and sulfate end-groups of the Leacril fibers and the cation of the surfactant. The increase of the amount of surfactant taken up by the fiber at increasing temperature of the sorption is due, probably, to the increasing ionization of the sulphonate and sulfate end-group of the Leacril at pH=5.8, and the electrostatic attraction between the mentioned end-groups of the fiber and the cation of the surfactant is favored by the increasing temperature of sorption of the system under these conditions. The fact that the positive value of the zeta potential decreases in the concentration range where the highest amount of the surfactant in the fiber, M_{eq}, appears (Figures 1 and 2), shows that the electrostatic interactions cannot be the only interaction responsible for the uptake of the surfactant by the fibers, some sort of specific interactions between Leacril and N-CPCl must exist. Given the hydrophobic character of the Leacril and the amphiphilic nature of the surfactant molecules, hydrophobic attractions between the fiber and the hydrophobic part of the surfactant might account for the interaction, explaining the sorption of N-CPCl on the Leacril even when it is hindered by electrostatic repulsion. The low zeta potential values for $5\text{x}10^{-3}$M and 10^{-2}M surfactant concentration must be consequence of double layer compression.

On the other hand, analysis of the solid surface free energy together with investigation of both, the adsorption and electrokinetic behavior of the system, in the process of adsorption of surfactants and dyes onto textile fabrics, provide extensive information concerning the dyeing, wetting, and finishing mechanisms of the textile materials (Mittal, 1993). Such an investigation has not been reported previously for Leacril fabric, and studies of the surface free energy of Leacril in the processes of dyeing are very scarce.

According to the van Oss et al. approach (Van Oss, 1987,1988a, 1988b, 1989, 1992a,1992b1994), the interaction between a liquid and a solid surface can be determined from the relationship between the work of adhesion of the liquid to the solid surface, W_a,and the work of cohesion between the liquid molecules, W_c, which is called work of spreading W_s and it is defined by the equation:

$$W_a - W_c = W_s = 2\sqrt{\gamma_S^{LW} \cdot \gamma_L^{LW}} + 2\sqrt{\gamma_S^{+} \cdot \gamma_L^{-}} + 2\sqrt{\gamma_S^{-} \cdot \gamma_L^{+}} - 2\gamma_L \qquad (1)$$

Where $\gamma_S^{LW}, \gamma_S^{+}$, $\gamma_S^{-}$and $\gamma_L^{LW}, \gamma_L^{+}, \gamma_L^{-}$ were the components, Lifshitz-van der Waals, and acid-base, electron-acceptor and electron-donor, of solid surface and liquid, respectively. The thermodynamic characterization of the fabric surface was determined, using the thin-layer wicking method (Chibowski, 1992; Chibowski &Gonzalez, 1993; Chibowski & Holysz, 1992; Duran et al., 1994). According to the Washburn equation, eq.[2], a linear relationship must be obtained between the time (t) that a liquid takes to penetrate a distance (x) through a thin porous layer of a solid, in our experiments, through a piece of Leacril fabric of $25\text{x}4$ cm^2 :

$$x^2 = \frac{Rt}{2\eta} \triangle G \qquad (2)$$

where $\triangle G$ is the surface free energy change that takes place when the initial solid-air interface is substituted by the solid-liquid interface in the wicking process. R is the average pore radius of the solid, and η the viscosity of the liquid. In order to determine four unknown parameters of the solid surface, R effective radius porous, and the surface free energy components, γ_S^{LW}, Lifshitz-van der Waals component, γ_S^{-}, electron-donor and γ_S^{+}, electron-acceptor components, four wicking systems can be considered in which different values of ΔG in eq. [2] appear. This systems result from the combination of two kind of liquid, non-polar and polar liquid, and two different situations of the solid sample, precontacted strip, if the sample has been previously exposed to saturated vapor of the liquid, and bare strip, when the sample is clean and dry. The situations studied were:

1. When the liquid used wets the solid completely, we used a non-polar liquid such us n-decane, and the solid has been previously saturated with its vapor in such a way that a

duplex film is formed onto the solid surface (precontacted plate), then ΔG_P in the wicking process is: $\Delta G_P = \gamma_L$, (the surface tension of the liquid) and then R can be estimated.

2. The same liquid (n-decane) is used as above, but the strip has not been exposed to the saturated vapor (bare strip) the specific free energy changes, ΔG_b, in the penetration process, is determined from the difference between work of adhesion, W_a and work of cohesion W_c. This allows determination of γ_S^{LW} and eq. [2] is given by:

$$\Delta G_b = W_a - W_c = 2\sqrt{\gamma_S^{LW} \cdot \gamma_L^{LW}} - 2\gamma_L \tag{3}$$

3. The solid surface is precontacted with a polar liquid vapor but the penetrating liquid (water or formamide) does not completely spread onto the solid surface. A dynamic contact angle, θ, appears and ΔG_P is now:

$$\Delta G_P = \gamma_L cos\theta \tag{4}$$

4. The same liquid as in case (iii) is used. The solid surface is bare and the liquid forms a dynamic contact angle, θ. In this situation free energy changes involved are:

$$\Delta G_b = \gamma_L cos\theta + W_a - W_c = \gamma_L cos\theta + 2\sqrt{\gamma_S^{LW} \cdot \gamma_L^{LW}} + 2\sqrt{\gamma_S^{+} \cdot \gamma_L^{-}} + 2\sqrt{\gamma_S^{-} \cdot \gamma_L^{+}} - 2\gamma_L \tag{5}$$

From the combination between eq.[4] and eq. [5], and using two different polar liquids as water and formamide, we can obtained the values of the acid-base components, γ_S^{+}, γ_S^{-} of the solid surface (Chibowski et al., 1998).

Our experiments were performed with water, n-decane, and formamide (Table 1). Straight lines are obtained in the plots of the penetrated distance, x, vs. the time of penetration, t. From the slope of the straight lines, ΔG is obtained, and from this data, the surface free energy components of the fabric are estimated.

Liquid	γ^{TOT} (mJ/m^2)	γ^{LW} (mJ/m^2)	γ^{+} (mJ/m^2)	γ^{-} (mJ/m^2)
n-Decane	23.9	23.9	0	0
Diiodomethane	50.8	50.8	0.0	0.0
Water	72.8	21.8	25.5	25.5
Formamide	58	39.0	2.28	39.6

Table 1. Surface tension parameters of liquids used for thin-layer wicking and contact angle measurements.

The results are shown in Table 2.

N-CPCl C(M)	γ_S^{LW} (mJ/m^2)	γ_S^{+} (mJ/m^2)	γ_S^{-} (mJ/m^2)
0	43.35	0	60.50
10^{-4}	44.4	0.14	57.81
$5 \cdot 10^{-4}$	45.7	0.16	55.71
10^{-3}	46.96	0.19	53.59
10^{-2}	47.9	1.40	35.80

Table 2. Lifshitz-van der Waals, and acid-base components of surface free energy of Leacril as function of the concentration N-CPCl of the treatment.

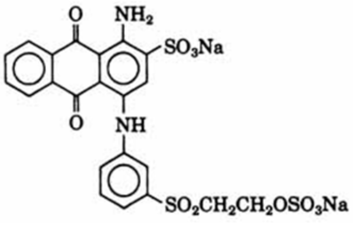
In Table 2, we observe that there are no appreciable differences between the obtained values of γ_s^{LW} in the different processes investigated. The high value for γ_s^- 60.5 mJ/m², obtained in the case of untreated Leacril, is probably due to the presence of sulphonate and sulfate end-groups in the Leacril fabrics (Espinosa et al. 1997a, 1997b; 1998). These groups are donors of electrons and produce a high value in the component γ_s^- for untreated Leacril. This above value is similar to that obtained by van Oss et al. with water-soluble polyethyleneoxide (PEO) (van Oss, 1994). A value of $\gamma_s^- = 60.5$ mJ/m² consistent with these authors, findings suggests that the Leacril surface is a stronger electron donor and hence hydrophilic in nature. Also consistent with van Oss et al., values of γ_s^- higher than28.3 mJ/m² indicate that the solid surfaces that present this behavior have a hydrophilic character. In our case, for Leacril fabrics, the hydrophilicity of the surface could be attributed to the presence of the sulphonate and sulfate end-groups on the surface of the fabric due to their strong electron-donor character (Espinosa et al., 1998).

In previous studies (Espinosa & Giménez, 1996; Espinosa et al.,1997), it was discussed that the adsorption of N-CPCl on Leacril fabrics probably occurs by electrostatic attraction between the cation of the surfactant and the sulphonate and sulfate end-groups of the Leacril. These processes produce a decrease in the negative charge of the Leacril, and, the γ_s^- decreases with the increasing treatment of Leacril. This may be observed in Table 2. In contrast, γ_s^+ is almost constant for both untreated Leacril and treated Leacril with increasing concentrations of NCPCl in solution. The small variation of the values of γ_s^+ shown in Table 2 is not sufficiently significant to allow conclusions to be reached about this question.

The value of γ_s^- 35.8 mJ/m², at 10^{-2} M of N-CPCl in the treatment of the fabric (Table 2) is probably due to the presence of N^+ - pyridinium groups in the N-CPCl adsorbed on the fabrics, which is very evident at the highest concentrations of the surfactant on the fabric (see Fig. 1 and Table 1). In this process, there is probably a notable acid-base neutralization due to the interaction between the cation of the surfactant and the sulphonate and sulfate end-groups on the surface of the Leacril.

3. Effect of n-cetylpyridinium chloride on the adsorption of a reactive dye onto leacril fabrics

In this study, we have used the samples of Leacril fibers above mentioned in the paragraph no. 1 of this work. Also we have used the above surfactant N-Cetylpyridinium chloride in the pretreatment of Leacril, before of posterior dyeing of Leacril with the reactive dye. The reactive dye used has been Remazol Brilliant Blue R (RBB-R), C.I. 61200, reactive blue 19, and this dye is an amineantraquinone vinilsulphonated. This dye is referred by Hagen et al. (Hagen et al.,1966). On the other hand, this dye is of AR grade from Sigma Chemical Co. (USA) and was used without further purification. The chemical structure of the RBB-R dye is shown in scheme 2:



Scheme 2.

Experiments were done as we have described in part 1. In Figure 3 are shown the zeta potential of the system untreated Leacril/RBB-R, as a function of the concentration of RBB-R in the liquid phase. We have used the Goring and Mason model for the determination of the zeta potential of the above system. All the values of the zeta potential of the system (Fig. 3) are negative. The increase in the zeta potential for concentrations of dye between 10^{-6} M up to 10^{-5} M of dye in solution can be attributed at the hydrophobic interactions between the fiber and the hydrophobic part of the dye molecule. In this process, the electric charge of the interface increase due to the presence of sulphonate groups in the dye onto the surface of fibers, in the adsorption process of the dye onto the Leacril in these conditions. On the other hand, by concentrations of dye higher than 10^{-5} M the chemical reactions between the $-NH_2$ and $-NH$ groups of the reactive dye and the sulphonate and sulfate end-groups of Leacril could be the responsible of the decrease in the zeta potential of the system shown in Figure 3 in this range of dye concentration. In this process the negative charge of the fiber and hence the zeta potential of the system, decrease in this range of concentration of reactive dye.

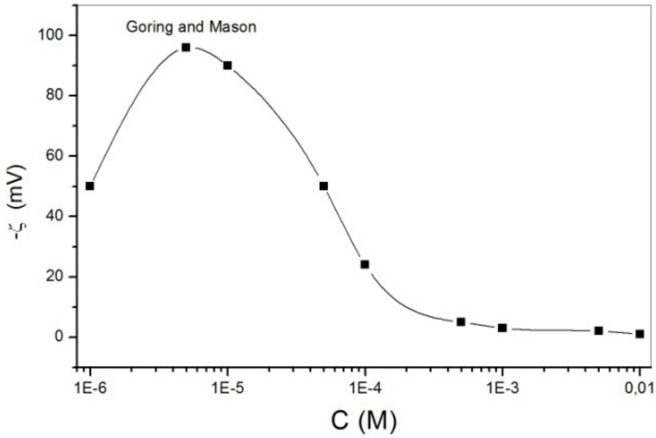


Fig. 3. Zeta potential of the system untreated Leacril/RBB-R, as a function of RBB-R concentration.

In Fig. 4 are shown the amount of RBB-R uptaken by untreated Leacril at equilibrium, M_{eq} as function of the equilibrium concentration of dye in solution, at different temperatures of adsorption. This adsorption is scarce at concentrations of dye lower than 10^{-4} M and increases abruptly for the highest concentrations of dye in the liquid phase. Also it can be observed that this adsorption is favored by an increase in the temperature of adsorption process of the RBB-R onto the fiber. This behavior can be explained for the above chemical reactions between the above mentioned groups of the fiber and the reactive dye. This fact confirms the behavior of the zeta potential of the system shown in Figure 3.

With the aim of to improve the dyeing conditions of the Leacril fibers with RBB-R, we have used 10^{-3}M of N-CPCl in the pretreatment of the Leacril. Subsequently, the treated Leacril with 10^{-3}M of the surfactant, have been dyed with different concentrations of RBB-R at the same temperatures used in the Figure 4. Also we have determined the zeta potential of the system in these conditions. In Figure 5 can be observed the behavior of the zeta potential of the system as a function of the equilibrium concentration of the reactive dye in the liquid phase for untreated Leacril and for Leacril treated previously with 10^{-3}M of the above surfactant. Also we have used the Goring and Mason model for the determination of the zeta potential in these conditions.

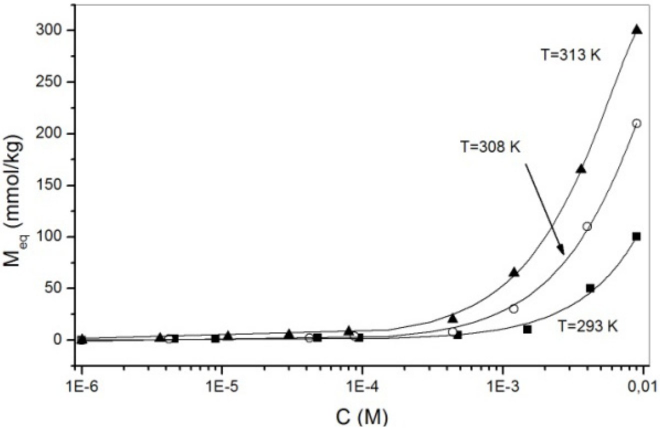


Fig. 4. RBB-R uptaken by untreated Leacril at equilibrium, M_{eq}, at different temperatures, as function of the equilibrium concentration of dye in solution.

In Figure 5, it can be observed a similar behavior of the zeta potential of the system in both cases. However, in this Figure can be observed that the zeta potential values of the system are higher for Leacril treated with 10^{-3} M of N-CPCl that in the case of untreated Leacril, in all range of concentration of RBB-R in the liquid phase. In Figure 5 the increase in the zeta potential for treated fiber in the range of 10^{-6}M up to 10^{-5}M of RBB-R in solution could be explained by the increase of the hydrophobic interactions between the hydrophobic part of the reactive dye and the hydrophobic parts of the Leacril/N-CPCl in the pretreatment of the Leacril.

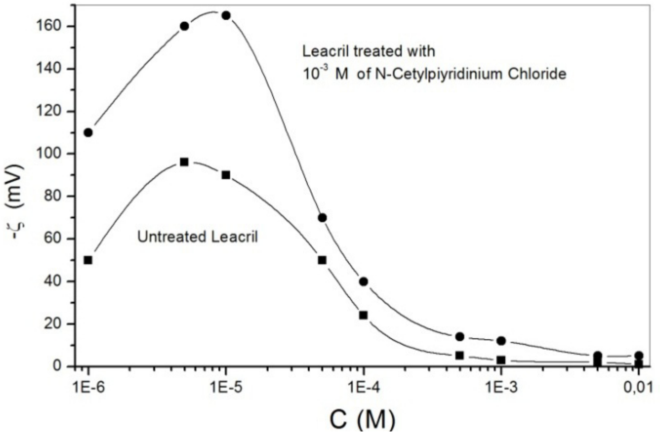


Fig. 5. Zeta potential of untreated Leacril and for Leacril treated previously with 10^{-3} M of N-CPCl as a function of RBB-R concentration.

In these processes the negative charge of the Leacril increases due to the presence of sulphonate groups in the molecules of the reactive dye adsorbed onto the pretreated fiber. When the concentration of the reactive dye in solution is between 10^{-5}M up to 10^{-2}M, the electrostatic interactions between both the cationic group of the pyridinium ring of the surfactant previously adsorbed and the sulphonate groups of the RBB-R could be responsible of the strong decreased in the negative value of zeta potential of the system in the concentration range mentioned. On the other hand, the chemical reactions between the groups $-NH_2$ and $-NH$ of the RBB-R and the sulphonate and sulfate end-groups of the Leacril also contributes in a great measure at the strong decrease in the zeta potential of the system treated Leacril/RBB-R at the highest concentrations range of the reactive dye in the liquid phase. Hence, due to the above adsorption mechanisms the negative zeta potentials of the system treated Leacril/RBB-R attain higher values in the case of pretreated Leacril with 10^{-3}M of N-CPCl that in the case of untreated Leacril, in all concentration range of RBB-R in the liquid phase. It is evident in Figure 5 that the reactive dye is adsorbed in a superior amount for treated Leacril with the surfactant than in the case of untreated Leacril.

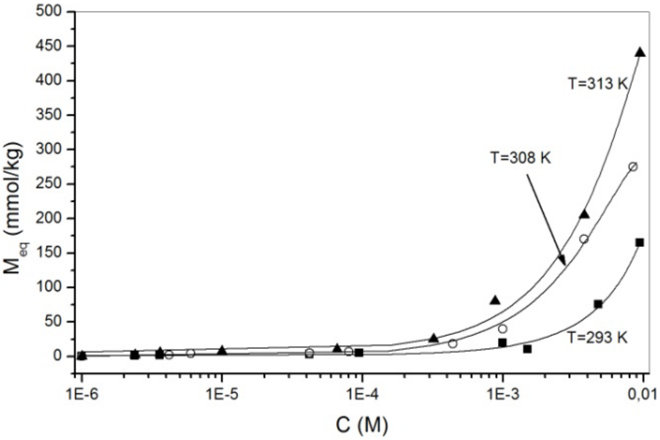
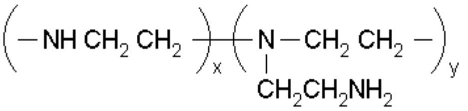


Fig. 6. Amount of RBB-R uptaken by Leacril pretreated with 10^{-3} M N-CPCl at equilibrium, M_{eq}, as function of the equilibrium concentration of dye in solution, at different temperatures.

In Figure 6 are shown the amount of the RBB-R adsorbed at equilibrium, $M_{eq,}$ onto pretreated Leacril with 10^{-3} M of the surfactant as a function of the equilibrium concentration of the reactive dye in solution. These experiments have been done at the same temperatures shown in the above Figure 4. It can be seen in Figure 6, that all the values of $M_{eq,}$ of pretreated Leacril with the surfactant are higher than they are in the case of untreated Leacril shown in Figure 4. Also it can be seen, that an increase in the temperature of adsorption favors the adsorption of RBB-R onto pretreated Leacril. These facts show that, probably, the above mentioned chemical reactions between the treated fibers and the RBB-R dye are responsible for the strong adsorption of the reactive dye onto the treated Leacril (Gonzalez et al., 1987; Espinosa et al., 1997c). It is evident that the pretreatment of the Leacril with the surfactant improve the adsorption of the RBB-R onto Leacril.

4. Influence of polyethyleneimine ion on the adsorption of rbb-r onto leacril fibers

In other works, we have also observed the positive effect of the pretreatment of Leacril with a polycationic surfactant, polyethyleneimine ion PEI, in the posterior adsorption of this reactive dye (Giménez et al., 2007; Ramos et al., 2006). Chemical structure of this compound is shown in scheme 3.



$$\left(-NH\,CH_2\,CH_2 - \right)_x \left(-\underset{\displaystyle CH_2CH_2NH_2}{N} - CH_2\,CH_2 - \right)_y$$

Scheme 3.

In Fig. 7 it is shown the amount of RBB-R adsorbed onto Leacril fiber previously treated with different concentrations of PEI as function of the equilibrium concentration of dye in solution, in the range between 10^{-6}M to 10^{-3}M, and at 293°K. As mentioned before, the amount of reactive dye adsorbed onto Leacril untreated at room temperature is scarce; we think that the attractive interactions are very weak and do not overcome the mutual electrostatic repulsion anionic functional groups. However, when the fibers are pretreated with increasing concentrations of the polyelectrolyte in solution, the amount of reactive dye adsorbed increases, reaching values of 90 mmol/kg of dried fiber, at 10^{-3}M RBB-R in liquid phase, for a concentration of 5 g/l of PEI in the pretreatment, and at room temperature. These data could be very interesting for textile industry because the process takes place at low temperature.

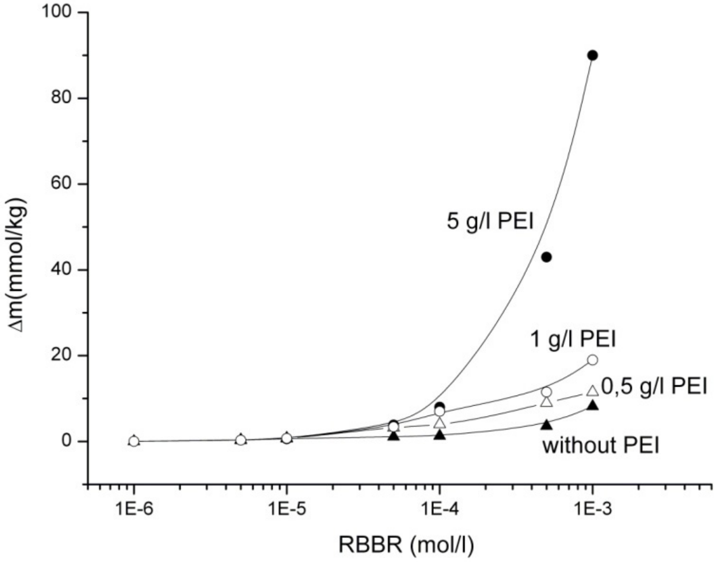


Fig. 7. Amount of RBB-R uptaken by Leacril pretreated with different concentration of PEI in solution as function of RBBR concentration at 293°K .

The evolution of zeta potential of the Leacril pretreated with different concentration of PEI as function of dye aqueous solution of RBB-R concentration is represented in Fig. 8. It can be observed that the zeta potential of the system increases to reach positive values when Leacril has been pretreated with PEI, in the range of low concentrations of dye in solution. This fact could be due to the presence of amine groups from the PEI molecules adsorbed onto Leacril, possibly ionized, providing the cationic charge density to the fiber as we have observed in previous works (Ramos et al. 2006). This effect becomes more significant as the PEI concentration of the pretreatment gets higher. On the other hand, we have found that at the highest RBB-R concentrations in the liquid phase, zeta potential decreases. In our opinion, probably this is caused by the presence of the RBB-R molecules in the fiber surface, which could be taken up by chemical reaction between the amine groups of PEI previously adsorbed and the reactive β-sulfato-ethylsulfanyl group of dye molecule. Finally, the negative charge of sulfonate groups of dye molecules adsorbed onto Leacril surface would justify the decrease in zeta potential values at the highest concentration tested.

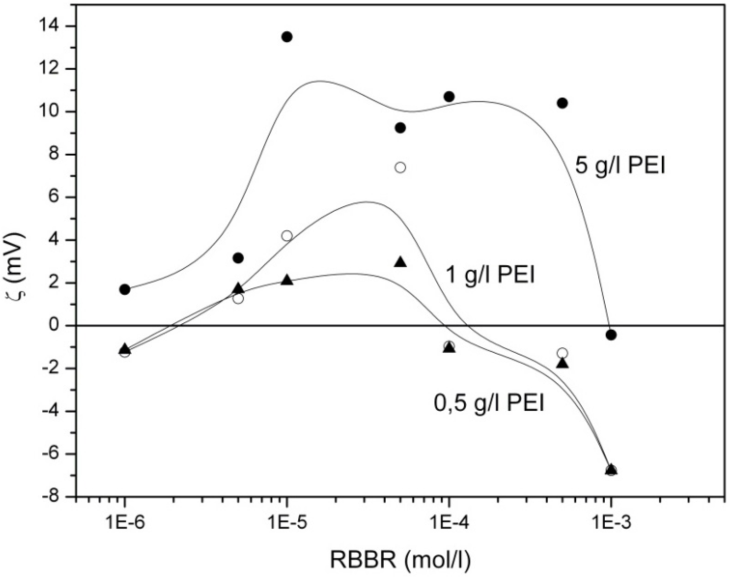


Fig. 8. Zeta potential of Leacril pretreated with different concentration of PEI as function of RBB-R concentration at 293°K .

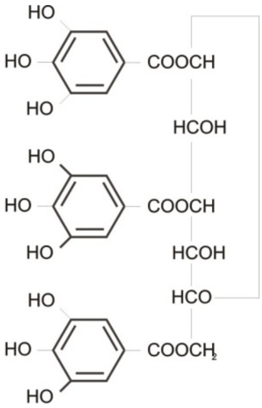
In table 3 are shown the evolution of the Surface free Energy components of Leacril pretreated with 5g/l PEI as function of two concentrations of RBB-R, and also it is presented the components of dye molecule, determined with contact angle measurements and using van Oss method. The most significant result exposed in this table could be the decreases of the electron-donor component value, γ_S^-, of the fiber-PEI with the concentration of RBB-R. In our opinion, the chemical interactions between the reactive acid groups of RBB-R molecule in water solution and the basic amino groups of PEI molecules previously adsorbed over Leacril surface could explain why electron-donor character of the surface falls from an initial value of 58 mJ/m^2 to 20 mJ/m^2 for the higher concentration of dye tested.

RBB-R C(M)	γ_S^{LW} (mJ/m^2)	γ_S^+ (mJ/m^2)	γ_S^- (mJ/m^2)	γ_S^{TOT} (mJ/m^2)
0	36±2	2.5±0.4	58±6	74±5
10^{-5}	60±3	0.01±0.1	54±1	61±4
10^{-3}	58±1	0.5±0.1	20±1	64±2
Pure RBB-R in solid phase	43.8±0.4	1.0±0.2	35.7±0.8	56±1

Table 3. Surface free energy components of Leacril pretreated with 5 g/l PEI and later dyed with RBB-R.

5. Effect of the tannic acid onto the zeta potential and surface free energy components of leacril fibers

In this part of the work we have used tannic acid as a surface active agent in the treatment of the Leacril fibers. This compound could be interesting to improve the conditions of dyeing the above acrylic fibers with a cationic dye (Chibowski et al., 1998). Chemical structure is shown is scheme 4.



Scheme 4.

Tannic acid, $C_{76}H_{52}O46$, was A.R. grade from Merck, and it was used without further purification. It is a derivative of glucose in which five hydroxyl groups are substituted for digalic acid. The result is a large number of phenolic hydroxyl groups in the tannic acid molecule.

The adsorption measurements of tannic acid onto Leacril were conducted using 1 g of the fibers that was contacted with 100 mL of the solution in the concentration range from 10^{-6} to 10^{-2} M in conical Pyrex flasks fitted with ground glass stoppers. The flasks were kept in a water bath at a desired temperature. Both the adsorption kinetic (from $5x10^{-5}$ M solution) and adsorption isotherms were determined at 275, 283, 293, and 303°K. The maximum absorbance was at $\lambda = 271$ nm. The adsorption equilibrium has been attained within 2-3 h. However, the adsorption measurements were conducted up to 24 h. To determine kinetics of the adsorption, first it was measured every second minute, up to the 30nd minute of the process duration, then every 4-5 min, and later for longer periods of time. Zeta potentials of

Leacril fibers versus tannic acid concentration were determined by the streaming potential method, and we have used the three different models of the capillary, although the significant levels were always higher than 95%, the best fit was obtained with the linear model of Goring and Mason. For determination of the surface free energy components by the thin-layer wicking method (42-4 strips of the fabric, 25 cm long and 2.5 cm wide, where first equilibrated in tannic acid solutions (10^{-5} – 10^{-2} M) for 24 h at 293°K, then dried in an oven at 313°K, and kept in a desiccators. Finally, to determine critical micelle concentration (c.m.c) in tannic acid solutions, the surface tension of the solutions was measured with a Rame-Hart goniometer.

First the adsorption kinetic of tannic acid on Leacril surface from 5x10^{-5} M solution was studied at four temperatures, 275, 283, 293, and 303°K. The results of the measurements are presented in Figure 9.

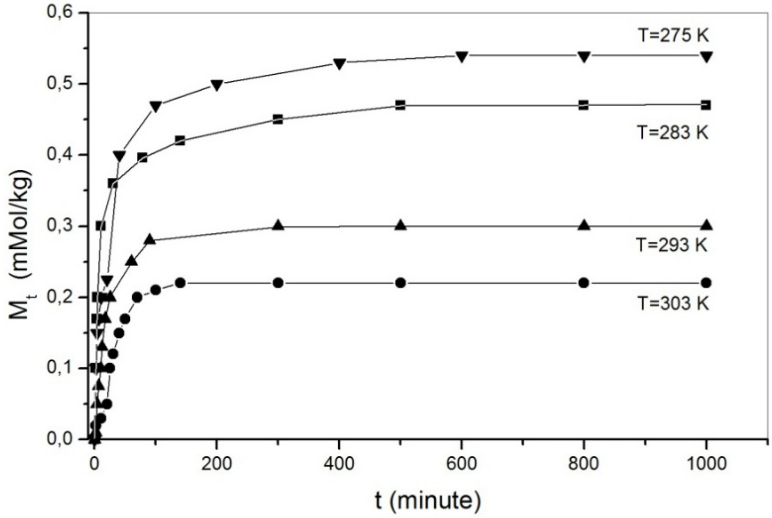


Fig. 9. Adsorption kinetic of tannic acid on Leacril surface at different temperature.

It is seen that even at the highest temperature,303°K, the adsorption process lasts no more than 100 min and is very fast. The adsorbed amounts of tannic acid decrease with increasing temperature, which points out that the adsorption is physical in nature. To better visualize the adsorption kinetics, the parameters describing the process are listed in Table 4. Because the shape of the curves of adsorption kinetic suggests a first-order process, the rate constant can be determined from the following equation (Anders&Sonesa, 1965; Peters, 1975, Lyklema 1995)

$$M_t = M_{eq}(1 - e^{-kt}) \tag{6}$$

Where M_t is the adsorbed amount of tannic acid on the Leacril surface at time t, M_{eq} is equilibrium adsorbed amount, and k is the empirical rate constant. This equation has been solved numerically and thus obtained values of the rate constant are listed in Table 4 together with equilibrium amounts adsorbed, M_{eq}. Then, the half-adsorption times were calculated for particular temperatures, which for first-order processes are expressed as follows

$$t_{1/2} = \frac{ln2}{k} \tag{7}$$

which is independent of initial concentration of the adsorbate. These values are also placed in Table 4. Having determined the rate constant k, it is possible to calculate the activation energy of the adsorption process from an Arrhenius type equation

$$k = A \cdot e^{-(E/RT)} \tag{8}$$

whose logarithmic form should be a linear dependence against 1/T, and this appeared to be the case in the studied system. As can be seen from Table 3, the rate constant k decreases with the adsorption process temperature increase. From the slope, the activation energy can be estimated. It was found to be 13.63kJ/mol. Finally, Fick's equation may be applied to calculate the diffusion coefficient D at the cylindrical walls of the fibers, (Crank 1956)

$$\frac{M_t}{M_{eq}} = \frac{4}{\pi^{1/2}}\left(\frac{D \cdot t}{a^2}\right)^{1/2} \tag{9}$$

For short periods of time, t, a, is the fiber radius, which for this Leacril was 1.5 x 10^{-3} cm. This equation is only exact for a constant concentration of the surfactant on the surface, whose condition is actually never fulfilled exactly. Nevertheless, the calculated values may be informative for the total insight into the adsorption process. We observe that the apparent diffusion coefficient decreases from 5.39 x 10^{-10} to 1.14x10^{-10} cm^2/s, if the temperature of adsorption increases from 275 to 303°K. This is obviously a consequence of the decreasing adsorption with the temperature increase and may be a result of higher thermal energy of tannic acid molecules in the solution. It is also possible to calculate the activation energy of diffusion, E*, using again an equation of Arrhenius type

$$D = D_0 \cdot e^{-(E^*/RT)} \tag{10}$$

Here D is the diffusion coefficient and D_o is a factor that may be interpreted as the diffusion coefficient for the activation energy being zero. The slope of logarithmic form of this equation (which is linear against 1/T) allows calculation of the energy. For the system studied, the calculated value is 38.13 kJ/mol. This value is about twice that estimated for the activation energy of the diffusion for NCPCl on Leacril (48) and is much higher than that given above for the activation energy of this adsorption process (13.63 mJ/mol).

T (K)	k (min^{-1})	$\tau_{1/2}$ ·10^{-3} (min)	M_{eq} (mmol/kg)	D ·10^{-10} (cm^2/s)
275	50.39	13.75	0.54	5.39
283	44.92	15.43	0.47	4.34
293	31.73	21.84	0.30	2.64
303	30.60	22.65	0.22	1.14

Table 4. Equilibrium adsorbed Amounts of Tannic Acid, M_{eq}, Adsorption rate constant, k, half time of adsorption,τ, and diffusion coefficient, D.

On the other hand, the adsorption isotherms of tannic acid at 275, 283, and 303°K versus its equilibrium concentration in the range of 10^{-6}–10^{-2}M are presented in Figure 10. Similarly as in the kinetic experiments, the adsorption decreases with increasing temperature. The isotherms are concave and the adsorbed amount increases with the increase of equilibrium concentration. The behavior of both the adsorption kinetics and the adsorption isotherms

(Figures 9 and 10) of tannic acid with different temperatures, is similar, adsorption decreases with increasing temperature. This results, can be explained, probably, because of the hydrogen bonding generated between the reactive groups of Leacril and the phenolic hydroxyl groups in the tannic acid molecules adsorbed onto the surface of Leacril (Jacobash et al., 1985, 1988).

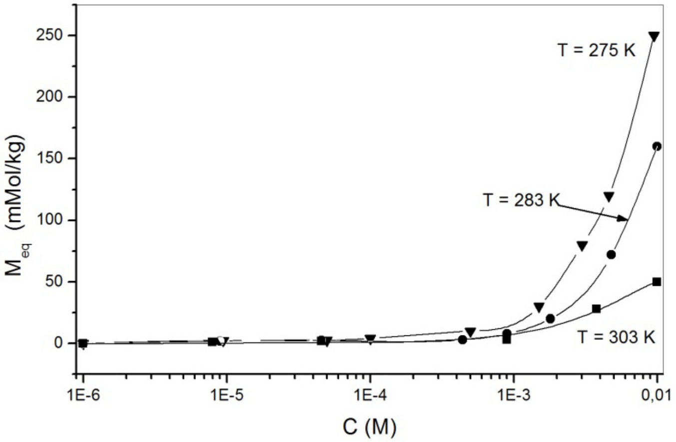


Fig. 10. Adsorption isotherms of tannic acid at 275, 283, and 303°K versus its equilibrium concentration in the range of 10^{-6}–10^{-2}M.

The surface free energy components of Leacril bare and treated with tannic acid are shown in Table 5.

tannic acid C (M)	γ_S^{LW} (mJ/m^2)	γ_S^+ (mJ/m^2)	γ_S^- (mJ/m^2)	W_S (mJ/m^2)
0	43.3	0.00	60.5	-5.6
10^{-5}	51.2	0.66	62.2	9.2
10^{-4}	51.2	0.00	48.5	-5.4
10^{-3}	51.2	0.00	12.0	-41.4
10^{-2}	66.9	28.5	10.8	15.9

Table 5. Surface free energy components of Leacril surface and work of spreading of water of untreated and treated with different concentration of tannic acid.

It can be seen that the apolar Lifshitz-van der Waals interaction, γ_S^{LW}, increases slightly after the surface treatment with 10^{-5}-10^{-3} M solutions, from 43.4 mJ/m^2 (untreated surface) to 51.2 mJ/m^2, but the component does not change after treatment in this concentration range. When the surface was equilibrated with 10^{-2}M solution, the component increases up to 66.9 mJ/m^2. The analysis of the electron acceptor component, γ_S^+ (Table 3), show how its values is practically zero for bare surface and with adsorbed tannic acid solutions from 10^{-5} to 10^{-3} M. However, it becomes significant (28.5 mJ/m^2) if the surface was contacted with 10^{-2} M solution. The changes of the electron donor component, γ_{S^-} , are more complicated. At the lowest concentration of tannic acid (10^{-5}M) the component is practically the same as for the untreated surface, but the surface treated with higher tannic acid concentrations becomes less electron-donating. To learn about hydrophobicity of the surface, the work of spreading for water was calculated. Some interesting conclusions can be draw from these values. The work for the bare surface of Leacril is a small negative. This means, that a water droplet will not fully spread on its surface. Thus, the surface is slightly hydrophobic. After equilibration with 10^{-5}M tannic acid, it becomes low hydrophilic because positive work of spreading. With increasing concentration of tannic acid (10^{-4} and 10^{-3}M) it becomes increasingly hydrophobic, and finally when equilibrated with 10^{-2}M tannic acid, the surface converts to hydrophilic. To explain such behavior, determination of c.m.c for tannic acid could be helpful. The c.m.c was determined from surface tension measurements of its solutions. The results are shown in Figure 11, from which results show that c.m.c of tannic acid lies at ca. $3x10^{-4}$M solution.

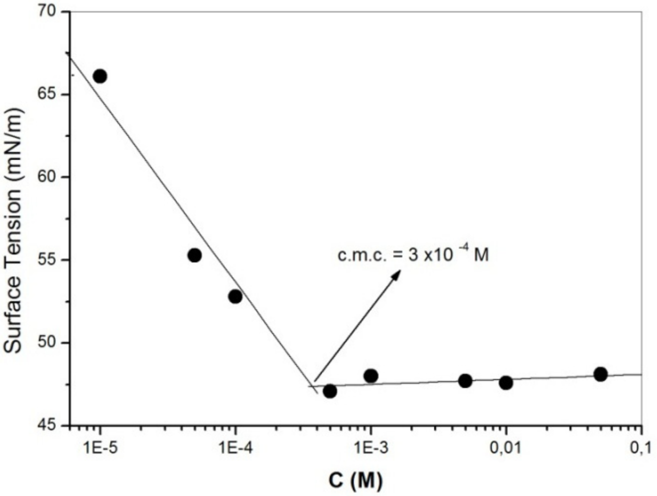


Fig. 11. c.m.c of tannic acid obtained from surface tension of tannic acid solutions against its concentration.

Taking this into account, the changes in the hydrophobicity of tannic acid treated Leacril can be explained as follows. At low concentration (10^{-5} M) only a few molecules of tannic acid are adsorbed on the Leacril surface (see Figure 10), probably by hydrogen bonding between phenolic hydroxyl groups of the acid and sulphonate and sulfate end groups of the Leacril., as well electrostatic interaction. The molecules may lie flat. With this, more polar hydrogen bonding interactions appear on the surface, and the surface becomes slightly hydrophilic. When the concentration of tannic acid increases, there is less and less room for the adsorbed molecules and they have to pack, probably, with polar groups directed toward the Leacril surface. This leads to increasing hydrophobization of the surface (10^{-4} and 10^{-3}M). However, at concentrations above $3x10^{-4}$M micellarization takes place, and on the surface premicelles and then micelles adsorb. It is possible to imagine that in the case of, say two-molecule premicelles, they have mutually saturated polar interactions thus giving rise to hydrophobicity of the Leacril surface.However, when micelles are already formed and adsorbed on the surface, their polar –OH groups will interact with the Leacril surface, as well as directed toward liquid phase (water), thus causing hydrophilization of the surface, which results from Table 5.Thus, it seems that the changes of surface free energy components of Leacril caused by the adsorbed tannic acid molecules can be explained with a help of c.m.c of tannic acid solutions.

To evaluate possible electrostatic interaction, determinations of the zeta potential were conducted by means of the streaming potential method. As was discussed in above paragraph, three models of the capillary bundles were considered, and it seems to us that the most appropriate one is that Goring and Mason. Zeta potential values as a function of tannic acid concentration applying three models of capillary bundles are plotted in Figure 12.

It is seen that the zeta potentials are small negative, but the absolute values drop practically to zero when the concentration is higher than 10^{-4} M. In our previous paper (Chibowski et al., 1998),) we have found that the hydrogen and hydroxyl ions are potential determining for the Leacril surface and the isoelectric point occurred at pH= 2.2. The decrease in zeta potentials in tannic acid solutions with its increasing concentration may be explained by adsorption of tannic acid molecules whose polar groups are partially dissociated, thus possessing positive charge. Anyway, from the results presented in Figure 12 it can be concluded that the electrostatic interaction plays a minor role in the adsorption process of tannic acid and total interfacial interactions, because the zeta potentials are low. It may be postulated that apolar Lifshitz-van der Waals and polar Lewis acid-base interactions are the dominant ones.

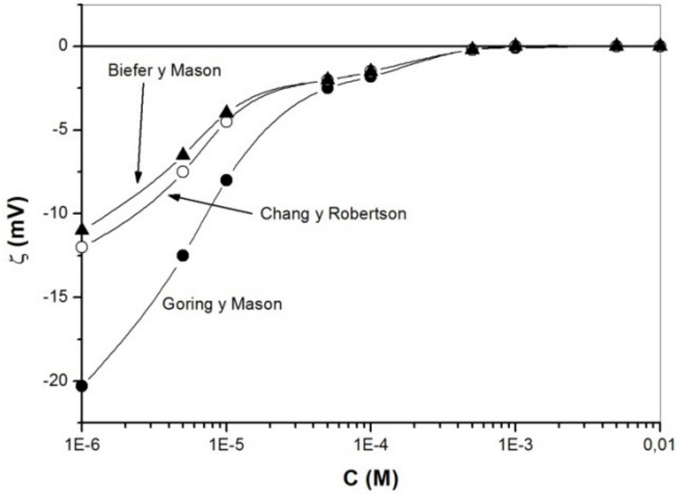
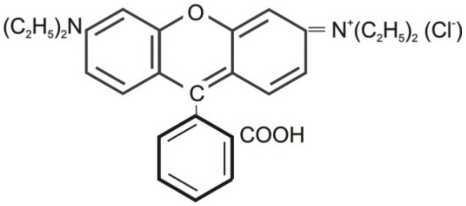


Fig. 12. Zeta potential of Leacril fibers as function of tannic acid concentration.

6. Effect of tannic acid on the sorption of a cationic dye onto leacril fibers

Our purpose in this study is to investigate both the electrokinetic behavior of Leacril fabrics in the process of adsorption of a cationic dye where the Leacril fibers were previously treated with tannic acid and the behavior of the surface free energy components in the above treatment of fibers and also in the adsorption process of the cationic dye on Leacril pretreated with tannic acid. These studies are very interesting with the aim of improving the dyeing properties of Leacril, as has been observed before with cellulosic fibers.(Espinosa Jimenez et al., 1986). To explain the interactions between Leacril pretreated with tannic acid and later died with the cationic dye, the electrostatic contribution will be analyzed from data of the ζ potential of the system Leacril pretreated with tannic acid/cationic dye at different concentrations of dye in the liquid phase.

The cationic dye used is Rhodamine B (C.I. 45170). The molecular structure of this dye is shown scheme 5.



Scheme 5.

Temperatures tested in our experiments of adsorption were 283, 293, 303, and 313°K. The adsorbed amount was determined after conditioning the fibers with the solution under study for 96 h, this time being sufficient to attain the equilibrium. We have measured the optical absorbance of the dye solutions at a wavelength of 554 nm.

Figure 13 shows the behavior of the zeta potential of the system untreated Leacril/Rhodamine B at different concentrations of the cationic dye in solution for the different models of capillary bundles above described, but, the model that presents the highest correlation coefficient to obtain the data of the zeta potential of the system is the linear model of Goring and Mason that is the model to be employed to obtain zeta potential of the different pretreatments of the Leacril with tannic acid.

We can observe that the zeta potential increases in absolute value for concentrations of dye from 10^{-6} to $5x10^{-6}$ M of dye solution. The negative value of the zeta potential of the fiber at the lowest concentrations of dye in solution can be attributed to the existence on the surface of Leacril of the sulphonate and sulfate end groups ionized at pH 4, which is the pH condition. On the other hand, the increase in absolute value of the zeta potential of the system shown in Figure 13 for concentrations of the cationic dye from 10^{-6} to $5x10^{-6}$M in solution can be explained by the increase of the ionization of the carboxyl group of the Rhodamine B in the molecule of dye at the mentioned value of pH 4. Also this behavior can be explained by the increase in the hydrophobic attractions between the hydrophobic chains of the dye and the Leacril fiber in aqueous media. This fact favors the approximation of the carboxyl groups of the cationic dye to the surface of the fiber. For concentrations above $5x10^{-6}$M Rhodamine B in solution one can observe a strong decrease in the absolute value of ζ potential of the system. For the highest range of concentration of dye in solution the zeta potential of the system changes its sign. This change of sign is shown between ca. 10^{-4} and 10^{-2} M of cationic dye in solution. The mentioned decrease of the zeta potential and the change of the sign observed in this parameter can be attributed to the electrostatic attraction between the sulphonate and sulfate end groups of the Leacril and the amine groups of the Rhodamine B. The low values observed in the zeta potential of the system for 10^{-4} to 10^{-2}M of dye in solution also can be attributed to the compression of the electric double layer.

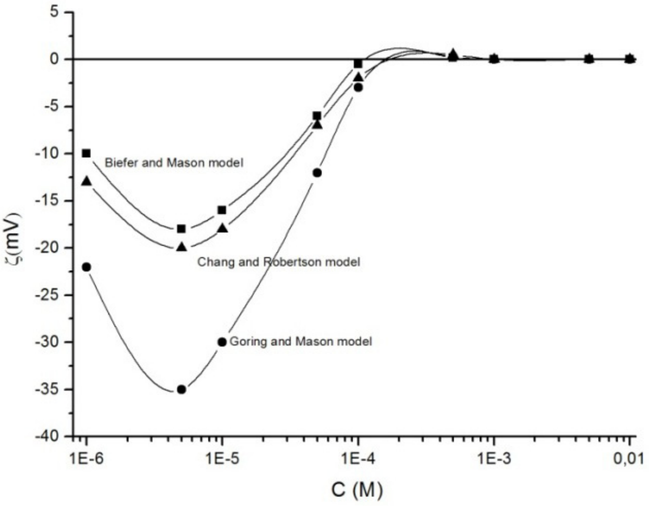


Fig. 13. Zeta potential of the system untreated Leacril/Rhodamine B at different concentrations of the cationic dye in solution for the different models of capillary bundles.

On the other hand, we have carried out adsorption experiments of Rhodamine B on Leacril at different temperatures. Figure 14 shows the amount of Rhodamine B adsorbed on Leacril, M_{eq}, at different temperatures as a function of the final (equilibrium) concentration of the dye in solution.

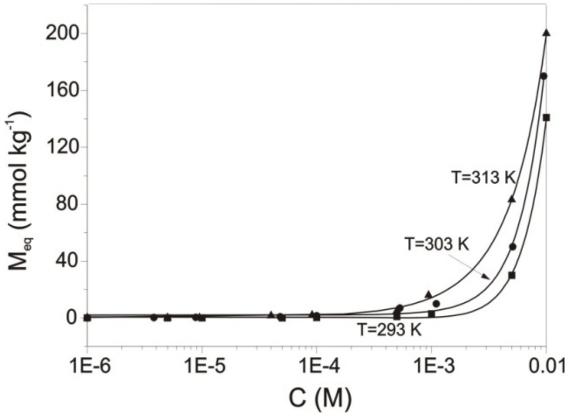


Fig. 14. Amount of Rhodamine B adsorbed on Leacril, M_{eq}, at different temperatures as a function of the equilibrium concentration of the dye in solution.

It can be seen that M_{eq} increases in all cases with both increasing concentration of dye in solution and increasing temperature of adsorption. The amount of dye taken up by Leacril is low when the equilibrium concentration is lower than 10^{-4}M of dye and increases abruptly above this value, attaining a value of ca. 200 mmol/kg at 10^{-2}M of dye in solution and 313°K. The observed increase in M_{eq} with the increase in temperature of adsorption can be attributed to the increasing ionization of the sulphonate and sulfate end groups of the Leacril with increasing temperature of the system. The fact that the values of zeta potential of the system are very low in the range of concentration higher than 10^{-4}M of dye in solution and, on the other hand, the values of adsorption, M_{eq}, obtained in the same range of concentration increase with the concentration of dye and with temperature of adsorption shows that the electrostatic interaction cannot be the only interaction responsible for the uptake of dye by Leacril: some sort of specific interactions between Leacril and the dye must exist. Given the hydrophobic character of Leacril and the amphiphilic nature of the dye molecules, hydrophobic attractions between the fiber and the hydrophobic part of the dye might account for the interaction, explaining the sorption of Rhodamine B on the Leacril even when it is hindered by electrostatic repulsion. However, the behavior of the zeta potential, practically constant, at the highest range of concentration of dye in the liquid phase also must be a consequence of electrical double layer compression.

With the aim of improving the dyeing process of Leacril with a cationic dye, we have treated the Leacril fibers with different concentrations of tannic acid and later the treated fibers have been dyed with increasing concentrations of Rhodamine B from 10^{-6} to 10^{-2}M of dye in solution. Figure 15 shows the behavior of the zeta potential of untreated Leacril and Leacril pretreated with two concentrations of tannic acid versus the molar concentration of the dye in solution. The obtained values of the zeta potential of the system shown in this figure have been obtained from the linear model of Goring and Mason, which has the highest correlation coefficient.

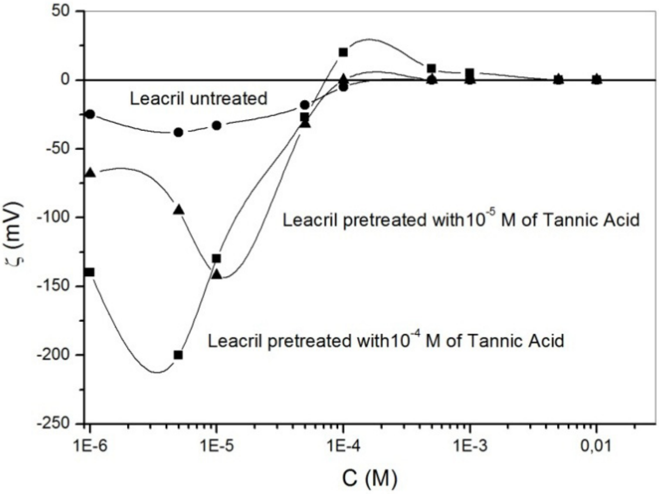


Fig. 15. Zeta potential of Leacril untreated and pretreated with two concentrations of tannic acid versus the molar concentration of the Rhodamine B in solution.

It can be observed that the effect of the tannic acid on the zeta potential of the system pretreated Leacril/Rhodamine B is a general increase in the absolute value of the zeta potential of the system for the all the range of concentration of dye in solution tested. The effect of the tannic acid is more marked at the higher concentrations of this compound in the pretreatment of Leacril. For the concentration range lower than 10^{-4} M of dye in solution and pretreatment with 10^{-5}M tannic acid, it can be observed an increase of the zeta potential of the system from 10^{-6} to 10^{-5}M of dye, where a maximum value of the zeta potential exists. At still higher concentrations of dye in solution (from 10^{-5} to 10^{-4}M), an abrupt decrease in the zeta potential of the system can be observed. The increase in the zeta potential of the system from 10^{-6} to 10^{-5}M can be explained by the formation of hydrogen bonding between the phenolic hydroxyl groups of the tannic acid and the sulphonate and sulfate end groups of Leacril. In this process the negative charge is increased and hence the zeta potential of the system is also increased. Also, this behavior can be explained by the increase in the hydrophobic attractions between the hydrophobic groups of the dye and the pretreated Leacril fiber in aqueous media. This fact favors the approximation of the carboxyl group of the cationic dye to the surface of the fiber being this group ionized at the acid medium (pH = 4). Figure 15 shows that increasing the concentration of tannic acid in the pretreatment of Leacril results in an rise up of zeta potential of the system due to increasing formation of hydrogen bonding between the phenolic hydroxyl groups of tannic acid and the sulphonate and sulfate end groups of Leacril, even, the observed maximum of zeta potential of the system is displaced to the lowest concentration of cationic dye in solution. This fact is in according with the hypothesis proposed before.

The strong decrease observed in the zeta potential of the system for concentrations higher than 10^{-5}M of dye in solution in the two pretreatments of Leacril with tannic acid can be explained by the electrostatic attractions between the amine groups of the Rhodamine B and the sulphonate and sulfate end groups of Leacril. This fact is particularly marked for increasing pretreatment of Leacril with the tannic acid. It can also be observed that in the range of concentration from ca. 4×10^{-5} to 10^{-4}M of dye in solution, the zeta potential of the system changes its sign. The change of sign is displaced to the lowest range of concentration of dye in the liquid phase when the Leacril fibers are pretreated with increasing concentrations of tannic acid. This fact shows that the tannic acid increases its effect on the dyeing of Leacril with the cationic dye at increasing concentration of tannic acid in the treatment of the fibers. The low values observed in zeta potential of the system from 10^{-4} to 10^{-2}M of dye in solution also can be attributed to the compression of the electric double layer.

On the other hand, we have carried out adsorption experiments of Rhodamine B on pretreated Leacril (with 10^{-5} and 10^{-4}M tannic acid) at different temperatures of adsorption. Figures 16 and 17 show the amounts of Rhodamine B adsorbed on Leacril, M_{eq}, at different temperatures as a function of the final (equilibrium) concentration of the dye in solution. It can be seen that M_{eq} increases in all cases with increasing concentration of dye in solution. Also, it can be observed that at the highest temperature the amount adsorbed decreases. This behavior can be explained by the formation of hydrogen bonding between the carboxyl group of Rhodamine B and the phenolic hydroxyl groups of the tannic acid preadsorbed onto the fiber. (Hiemenz, 1986). Also, this fact can be explained by the electrostatic attraction between the cation of the dye and the negative charge of the fiber generated by the existence of phenolic hydroxyl groups on the fiber and the existence of sulphonate and sulfate end groups of Leacril. When comparing the values of adsorption, M_{eq}, in Figures 16 and 17 for the two treatments of Leacril with tannic acid, one can see that the adsorption of Rhodamine B on Leacril is favored by the increasing tannic acid concentration in the pretreatment. This shows the effect of tannic acid on the sorption of a cationic dye onto Leacril. On the other hand, the behavior of the zeta potential in Figure 15 at the highest range of concentration of dye in solution, where the values of the zeta potential are very low, suggests the existence of other interactions in the systems mentioned above. Hence it is necessary to carry out other studies with the aim of understanding this behavior, such as determinations of evolution of surface free energy components of Leacril with the treatment.

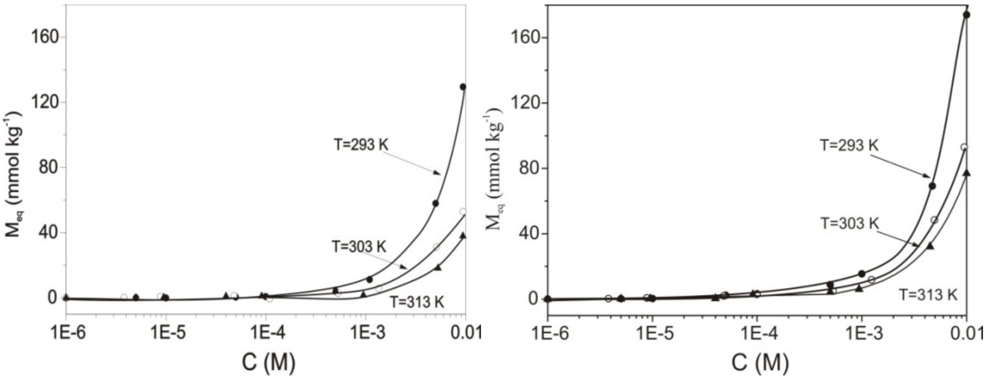


Fig. 16. and 17. Amount of Rhodamine B adsorbed on Leacril pretreated 10^{-5} M and 10^{-4} M of tannic acid, M_{eq}, at different temperatures as a function of the equilibrium concentration of the dye in solution, respectively.

Surface free energy components of treated Leacril dyed with Rhodamine B are shown in Table 6. To explain the behavior shown in Table 6, Table 7 shows the values of surface free energy of untreated Leacril of tannic acid and Rhodamine B in solid phase, from contact angle measurements.

Rodamine B C(M)	γ^{LW}(mJ/m^2)	γ^{+} (mJ/m^2)	γ^{-} (mJ/m^2)
10^{-5}	60.8±0.02	0.7±0.4	61.7±0.4
10^{-4}	47.5±0.5	0.5±0.5	53.6±0.5
10^{-3}	38.1±0.3	1.3±0.4	52.3±0.1
10^{-2}	37.4±0.4	1.4±0.5	51.6±0.1

Table 6. Surface free energy components of Leacril treated with different concentration of RhodamineB.

Material	γ^{LW} (mJ/m^2)	γ^{+} (mJ/m^2)	γ^{-} (mJ/m^2)
Untreated Leacril[a]	43.3±0.4	0±0.5	60.5±0.1
Tannic acid	38.2±0.3	0.4±0.4	58.7±0.1
Rhodamine B[b]	38.6±0.2	1.4±0.4	51.7±0.4
Leacril treted with 10^{-4} tannic acid	51.2±0.2	0±0.1	48.5±0.3

Table 7. Surface free energy components f or untreated Leacril, tannic acid and RhodamineB pure in solid phase , and Leacril treated with 10^{-4}M of tannic acid.

In table 6 we can observe that the Lifshitz-van der Waals component, γ_S^{LW}, decreases with the increase in the amount of Rhodamine B taken up by the fabric, up to the value of 37.4 mJ/ m ^{2}. This value is very close to the value of 38.6 mJ/m^2 obtained for pure Rhodamine B with contact angle measurements. These results can be explained by the greater fixation of the dipoles of the molecules involved in these processes of adsorption. On the other hand (Table 7), the electron-acceptor component γ_S+, increases slightly from 0.7 to 1.4 mJ/m ^{2}, which corresponds to the value of this component obtained for Rhodamine B from contact angle measurements. The electron-donor component, γ_S- , decreases from 61.7 to 51.6 mJ/m^2. These values correspond practically to the obtained values of this component for untreated Leacril and Rhodamine B, respectively. This observed behavior of the components, $\gamma_S{}^{LW}$, γ_S+, and $\gamma_S{}^-$, for the dyeing of Leacril with the cationic dye can be explained for the total covering of the Leacril fabric with the cationic dye due to the adsorption of this chemical component onto the Leacril surface. The high values of the electron-donor component, γ_S- , observed in Table 6 can be attributed to the presence of both amine and carboxyl groups in the molecule of Rhodamine B, these groups being strong donors of electrons. Also, the value of 61.7 mJ/m^2 for the dyeing of Leacril with 10^{-5}M Rhodamine B can be attributed to the presence of the above groups on the surface of the Leacril and mainly the presence of sulphonate and sulfate end groups on the Leacril fabric that at lowest concentration range of dye in solution are not totally blockaded for the molecules of the cationic dye.

On the other hand, Table 7 shows the values of the components of the surface free energy, $\gamma_S{}^{LW}$, γ_S+, and γ_S- , for the dyeing of Leacril with increasing concentrations of Rhodamine B, this fabric being pretreated with 10^{-4} M tannic acid. It can be seen in this table, that the Lifshitz-van der Waals component, $\gamma_S{}^{LW}$, of the system notably decreases with increasing concentration of Rhodamine B used in this treatment. This fact can be due to the increasing of the adsorption of the dye onto Leacril at increasing concentration of this cationic dye, which is favored by the presence of the mordant, tannic acid, in the pretreatment. These results can be explained by the greater fixation of the dipoles of the molecules involved in these processes by the presence of the tannic acid in the surface of the fabric which produces a greater adsorption of the cationic dye according to the results shown in Figures 16 and 17 of this work. The obtained value of $\gamma_S{}^{LW}$ for pretreated Leacril and dyeing with 10^{-3} M Rhodamine B, 37.6 mJ/m^2 is close to the value of 38.6 mJ/m^2 obtained for pure Rhodamine B (Table 7) and the general behavior of this component is to decrease their value in the presence of tannic acid preadsorbed onto the fabric. These facts show that the effect of tannic acid is to favor the adsorption of the cationic dye onto the Leacril fabric.

Rodamine B C(M)	γ^{LW}(mJ/m^2)	γ^+(mJ/m^2)	γ^-(mJ/m^2)
10^{-5}	55.7±0.6	1.6±0.5	40.8±0.2
10^{-4}	38.9±0.2	2.37±1	60±5
10^{-3}	37.6±0.2	4.6±0.4	65.9±0.2

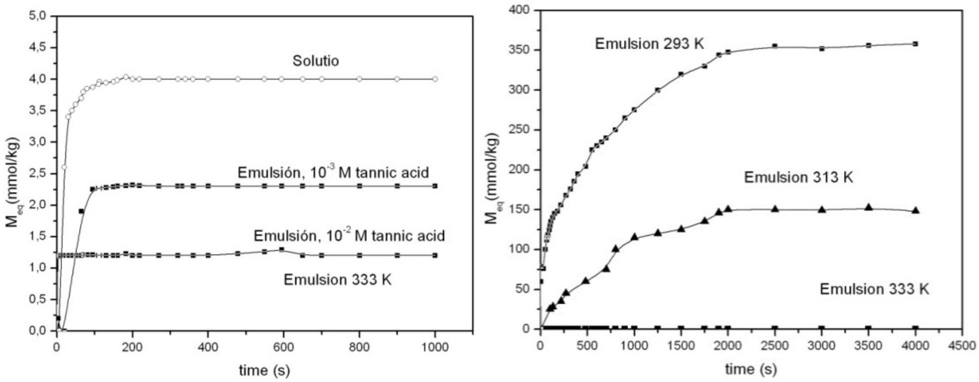
Table 8. Surface free energy components for Leacril pretreated with 10^{-4}M of tannic acid and died with different concentration of Rhodamine B.

In Table 8 it can be seen that the electron-donor component, $\gamma_S{}^-$, of the surface free energy increases from 40.8 to 65.9 mJ/m^2 for Leacril pretreated with 10^{-4} M tannic acid and subsequently dyed with increasing concentrations of the cationic dye Rhodamine B. This behavior can be explained by the increasing presence on the surface of Leacril of the hydroxyl end groups of the tannic acid taken up by Leacril in its treatment and also by the presence on the surface of the fabric of both the carboxyl groups and amine groups of the chromophore of the Rhodamine B taken up by Leacril in its dyeing. These groups have a strong electron-donor character and their effects on the behavior of the surface free energy are additive. Hence the high value of $\gamma_S{}^-$ obtained for 10^{-3}M Rhodamine B by the pretreatment of the fabric with the tannic acid, this value being 65.9 mJ/m, is higher than the value obtained for this component by Rhodamine B (Table7). This fact shows the additive effects of the groups mentioned above on the behavior of γ_S^- in these processes of dyeing Leacril with the assistance of the mordant, tannic acid. The behavior of the electron-acceptor component, γ_S^+, observed in Table 5, where an increase of this component is observed, having the value of 4.6 mJ/m^2 for 10^{-3}M Rhodamine B can be due to the formation of micelles of the cationic dye since the c.m.c of Rhodamine B is close to 10^{-3} M (this data was obtained from conductivity measurements). In these conditions the micelles are adsorbed, but now with polar heads directed also towards the solution phase. Hence this fact leads to an increase in the electron-acceptor component, γ_S^+, for the higher concentration range of Rhodamine B in solution.

7. Study of the leacril dyeing process by a cationic dye from an emulsion system

In this part of the work a dye-in-emulsion dyeing process onto Leacril was investigated using a cationic dye, Rhodamine B. The process was analyzed through the changes in surface free energy of the Leacril. To our knowledge, no work has been reported in the literature dealing with the application of the dye-in-emulsion system to improve the adsorption onto Leacril. The Leacril used is the same of the above studies. The emulsion of Rhodamine B was prepared in the following way: 0.15 ml of n-hexadecane was dissolved in 7.7 ml of 2-propanol (p.a.) placed in a 100-ml flask, and then 10 ml of 0.01 M tannic acid was added (as a surfactant) in which 48 mg of Rhodamine B (as a cationic dye) was dissolved. The content was mixed and doubly distilled water (Milli-Q System) was added up to a volume of ca. 50 ml. Next, the flask was placed in an ultrasonic bath for 15 min and again water was added to reach the final volume of 100 ml. Finally, the obtained emulsion was shaken vigorously by hand.

Studies of the kinetics of Rhodamine B adsorption onto Leacril fibers were carried out, both from its solution alone or from the emulsion (Chibowski et al., 2001). In both systems the dye concentration was 10^{-5}M, and in the case of the emulsion tannic acid was present as a mordant agent and/ or stabilized the emulsion. For the experiments of adsorption kinetics, in Pyrex conical flasks fitted with ground glass stoppers, 1 g Leacril fiber samples were conditioned with 250 cm^3 of a 10^{-3} M aqueous solution of Rhodamine B or the emulsion. The flasks were immersed in a water bath and the temperature was kept constant within ± 0.1°K. The adsorption was carried out at 293, 313 and 333 K. The amount of adsorbed dye on the Leacril fibers was determined from absorbency as measured with a Hitachi U-2000 spectrophotometer at a 554-nm wavelength, at which the maximum absorbency occurred. Moreover, desorption experiments were also carried out for Rhodamine B from the Leacril surface. These experiments were conducted by washing with deionized water 1g samples of Leacril fibers dyed under the described above conditions. Desorption experiments were carried out in a thermostated bath at constant agitation and a temperature of 293°K. The zeta potentials of the Leacril suspensions in water (Milli-Q system) and in tannic acid solutions were determined electrophoretically. The water pH was regulated with the help of HCl or NaOH concentrated solutions. Zetameter ZetaPlus/Pals (Brookhaven Co) was applied for this purpose. To obtain Leacril powder the fibers were ground in a coffee mill after being cooled in liquid nitrogen. To determine the Leacril surface free energy components the thin-layer wicking technique was applied.



(a) (b)

Fig. 18. (a) Amount of Rhodamine B adsorbed onto Leacril from its 10^{-3}M emulsion phase containing- 10^{-3}M tannic acid at 293, 313, and 333°K, as function of time. (b) Amount of Rhodamine B from its 10^{-3}M solution onto Leacril, as function of time.

Isothermal rates of adsorption are shown in Figures 18A and 18B. The curves in Figure 18A relate amounts of cationic dye Rhodamine B adsorbed onto Leacril from its 10^{-3}M solution in the emulsion phase containing 10^{-3} M tannic acid at 293, 313, and 333°K, respectively. In Figure 18B are shown the adsorbed amounts of Rhodamine B from its 10^{-3}M solution alone. Because the adsorption from the emulsion at 333°K is small, therefore in Figure 18B is also shown adsorption of Rhodamine B from the emulsion at this temperature. From Figures 18A and18 B it is evident that at 293 and 313°K the adsorption of dye on the Leacril is much higher in the case of the emulsion. However, at 333°K the adsorption of dye is much lower from the emulsion than from the solution of Rhodamine B. Moreover, with increasing temperature the adsorbed amount decreases from emulsion, while it increases from solution. A decreasing adsorption with increasing temperature of the process is typical for physical adsorption. The shape of the adsorption isotherms is evidence of the first-order process and therefore the adsorption rate constant can be estimated from an equation relating adsorption vs time [6]. We have determined the values of the rate constant and half-adsorption time eq. [7] presented in Table 9.

Temp. (°K)	$kx10^3$ (min^{-1})	$t_{1/2}$ (min)	M_{eq} (mmol/kg)	D x 10^{10} Cm^2/s)
Emulsion of the Dye				
293	125.7	5.51	325.2	9.75
313	124.4	5.57	140.6	1.30
333	107.6	6.44	3.15	1.10
Solution of the Dye				
293	65.5	10.3	21.85	0.44
313	77.3	8.96	32.2	1.12
333	120.8	5.73	55.51	1.52

Table 9. Equilibrium adsorbed Amounts of Rhodamine B, M_{eq}, Adsorption rate constant, k, half time of adsorption,t, and diffusion coefficient, D for the systems 10^{-3}M Rhodamine B in emulsion/Leacril and systems 10^{-3}M Rhodamine B in solution/Leacril.

As it can be seen from this table, when Rhodamine B was adsorbed from the emulsion system the rate constant k decreased a little with increasing temperature, and for adsorption from the solution k increased markedly. The adsorption rate constants from emulsion are practically the same at 293°K and 313°K, and they are much higher than those determined for adsorption from the solution at the same temperatures.

Looking for an explanation for such relationships the activation energies and diffusion coefficients for the adsorption process were determined next. Applying the equation [8] of this work, the activation energies E of the adsorption process of the dye in the case of both emulsion and solution were then estimated. The results obtained are E= 3.2 kJ/mol, for the emulsion system, and E=11.7 kJ/mol, for the adsorption from solution. These values show that the activation energies are low and hence it can be concluded that both processes are governed by interactions of a physical nature. On the other hand, applying equations [9], we have obtained the values of the apparent diffusion coefficient, D, for the adsorption process from both the emulsion and solution, respectively. These values are also presented in Table 9. Moreover, it is also possible to determine the activation energy of diffusion process, E*, applying the equation [10] of this work. The calculated results for E* in the diffusion process of the dye from emulsion and solution are following E* = 45.0 kJ/mol for the emulsion and E*= 25.4 kJ/mol for the solution. It appears that the activation energy for the diffusion process is much higher in the emulsion system than in the solution. From the data given in Table 9 and the determined activation energies of adsorption and diffusion one may conclude that the adsorption process in both systems is diffusion controlled. It is much faster in the case of the emulsion than the solution system although it needs higher activation energy. If one assumes that the hydrocarbon forms a film on the Leacril surface, then the diffusion activation energies would indicate that a higher energy is needed to diffuse through the film into the surface. Another reason might be that the Rhodamine B molecules interact (hydrogen bonding) with tannic acid which stabilizes the emulsion droplets. Therefore, a higher energy is needed to adsorb such "complexes" on the Leacril surface, possibly together with the hexadecane droplets. At higher temperatures (313 and 333°K) the diffusion coefficients are practically the same for both systems (Table 9), and both processes occur at similar rates. It is worth mentioning that no visible extraction take place from the aquous solution of Rhodamine B to the hexadecane phase after vigorous shaking of the system. The same was true if the dye was dissolved in 1 M isopropyl alcohol. This concentration corresponds to that used in the emulsion. We have also found that tannic acid caused formation of a very stable emulsion of water droplets in hexadecane. This means that tannic acid because of its molecule structure is a very good stabilizing agent for both oil-in-water and water-in-oil emulsions. These observations support the above discussion.

The adsorption strengths were also tested by desorption experiments. It was realized by means of a washing process with deionized water. The dyed fibers were placed in a bath with a mechanical stirrer at the temperature of 293°K. These results are presented in Figure 19. The desorbed amounts of the dye are much higher for the sample dyed from 10^{-3}M solution of Rhodamine B (ca. 4 mmol/kg) than for the sample dyed from the emulsion phase and the same concentration of tannic acid (ca. 2.5 mmol/kg). Moreover, the desorption of the dye decreases essentially when the dyeing process have been conducted from the emulsion system and at an increased amount of tannic acid present (10^{-2}M). The results in Figure 19 clearly show that at room temperature the dyeing process of Leacril with Rhodamine B from the emulsion is of a superior efficiency, especially when 10^{-2} M tannic acid is present as a stabilizing agent, whose role seems to be crucial.

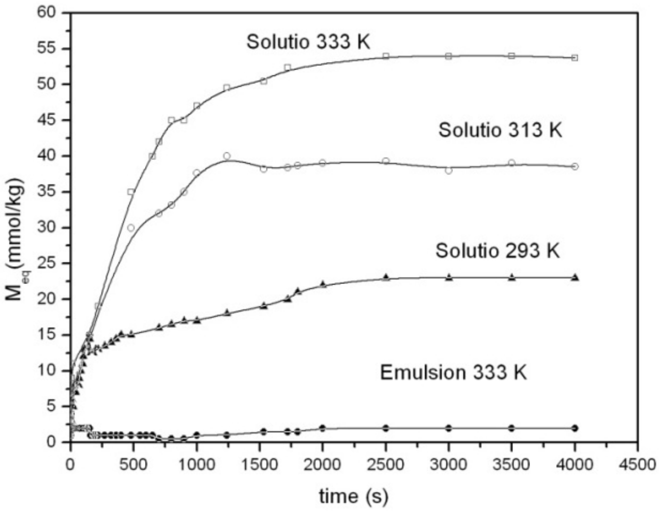


Fig. 19. Kinetic of Rhodamine B desorption from Leacril surface at 293°K adsorbed from 10^{-3}M solution or emulsion.

To obtain more information about the dyeing processes of Leacril from both the emulsion and solution of the cationic dye used, the surface free energy components of the Leacril samples dyed at various temperatures and different conditions were determined. The components are collected in Tables 10 and 11, together with calculated values of the work of spreading for water, W_S.

Temp of dyeing (K)	γ_s^{LW} (mJ/m^2)	γ_s^{+} (mJ/m^2)	γ_s^{-}(mJ/m^2)	W_s (mJ/m^2)
293	53.7	0.0	58.4	0.01
313	52.5	0.2	54.6	1.1
333	53.8	0.1	24.5	-23.9

Table 10. Surface free energy components and work of spreading of Leacril dyed with 10^{-3}M Rhodamine B from emulsion containing 10^{-3}M of tannic acid at different temperatures.

Sample of Leacril	Temp (K)	γ^{LW} (mJ/m^2)	γ^{+} (mJ/m^2)	γ^{-}(mJ/m^2)	W_s (mJ/m^2)
0	293	51.9	0.02	53.9	-2.8
10^{-3} M Tannic acid treated	293	59.3	0	56.6	2.3
10^{-3} M Tannic acid treated	333	54.0	0.41	52.1	2.4
10^{-2} M Tannic acid treated	293	63.6	0	66.9	11.5
10^{-3} M Rodamine dyed	293	31.8	1.3	52.3	-3.4
10^{-3} M Rodamine dyed	333	53.7	0.4	55.1	4.2

Table 11. Surface free energy components and work of spreading of Leacril dyed with 10^{-3}M Rhodamine B from solution and treated with different concentration of tannic acid at different temperatures

In Table 10 are shown the components of Leacril samples dyed (10^{-3}M Rhodamine B) at various temperatures from the emulsion system and with 10^{-3} M tannic acid. The Lifshitz-van der Waals component, γ_S^{LW}, is practically the same, but the electron-donor component, γ_S- , decreases markedly with increasing temperature. It may be due to a partial change in the surface structure, from a crystalline at 293 K to an amorphous one above 353°K. However, the results presented in Table 11 deals with the Leacril dyed surface in the system where hexadecane was present. The low value of the electron-donor component (24.5 mJ/m^2) for the surface dyed from the emulsion at 333°K indicates that the surface became less polar after the adsorption process had taken place. Indeed, the work of spreading is highly negative, being their value of W_S = - 23.9 mJ/m^2, so the surface is hydrophobic and although the adsorbed amount of the Rhodamine was low (Table 8 and Figures 18A and 18B) the surface hydrophobicity protects against its dewashing from the surface (Figure 19). Because for the same system at lower temperatures (293 and 313 °K) the polar component is much higher, one would conclude that the decrease in polarity is mainly due to the surface structure transition. However, it seems this is not the only reason, if one compares the results presented in Table 10. It should be mentioned that the apolar and electron acceptor components for untreated Leacril surface shown in this table are somewhat different than those obtained previously (38.1 and 1.3 mJ/m^2, respectively), while the electron donor component is practically the same (previously 52.3 mJ/m^2). This is probably due to a different lot of the Leacril sample used in these experiments.

From Table 10 it can be seen that treatment of the surface with tannic acid (10^{-3} M or 10^{-2}M) at 293°K causes an increase in nonpolar, γ_S^{LW} , and electron-donor , γ_S^-, components, while at 333 °K the changes are minor relative to the untreated sample of Leacril. But, the treatment of the surface with Rhodamine Bsolution (10^{-3}M) alone at both temperatures does not change much the polar component. It shows that the role of hexadecane in lowering the electron-donor interaction of the Leacril surface at 333°K is probably also important. Obviously, the studied systems are very complicated and an unambiguous mechanism of the observed changes cannot be given yet. The changes in polar components are surely due to changes in kind and density of the polar groups present on the Leacril surface originating from tannic acid, Rhodamine B molecules, and the Leacril surface itself. Thus the decrease in γ_S^- must be due to a decrease in the surface density of the electron-donor groups and/or shielding of these groups by the hexadecane film. In Fig.18 B it was observed an increase in adsorption from its solution with the temperature, in this situation electrostatic mechanism of the adsorption can be considered.

In Figure 20 are shown zeta potentials of Leacril surface as a function of pH. As can be seen from this figure the Leacril surface is negatively charged above pH 3, because of the presence of some amounts of sulfate and sulfonate end-groups. On the other hand, Rhodamine B molecules possess positively charged amine groups. With increasing temperature the number of the dissociated groups may increase, which is reflected in the increased adsorption (Figures 18A and B). On the other hand in tannic acid solutions (10^{-5}-10^{-2} M) the zeta potential of Leacril is practically constant and amounts to -12.5 ± 1 mV, as determined by electrophoresis and using the Smoluchowski equation. This means that tannic acid is not potential determining for the Leacril surface and the zeta potentials are about the same as those in water in this pH range.

To summarize briefly, dyeing of the Leacril surface with a cationic dye, Rhodamine B, from the emulsion phase at 313°K and in the presence of tannic acid as a stabilizing agent is more efficient that the dye solution alone. The dyeing systems tested are very complicated and need further studies for us to better understand the processes that take place in these systems.

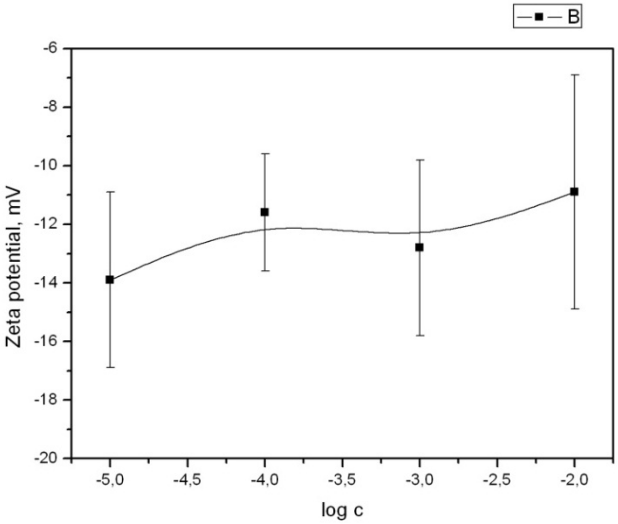


Fig. 20. Zeta potential of Leacril suspension in tannic acid solution determined by electrophoresis.

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7

The Future of Dye House Quality Control with the Introduction of Right-First Dyeing Technologies

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1. Introduction

The manufacturing of a textile begins with the fiber input, whereby each processing step results in an added cost to the final product. As dyeing of a textile is often the last step in the manufacturing of a fabric, it requires extra caution to get it right by avoiding waste and maintaining cost control. Only under favourable conditions is it possible to get it right the first time. In the past, it was not unusual for a dyer to re-dye until the target shade was reached. A typical strategy was to start with a base recipe that undershot the target shade. After each dyeing the missing dye component was added to the bath until the shade was matched. The smaller the number of reformulation, the more skilful the dyer was considered.

The Right-First-Time (RFT) dyeing concept was introduced in 1970 and became a desired feature of textile dyeing. This concept meant that at each dyeing the target shade was achieved the first time, hence not requiring re-dyeing. However, the successful evolution of the concept depended on work carried out over many years by a relatively small number of organizations. Many application research and development projects were carried out mainly by the laboratory, pilot-plant and bulk-scale equipment of the major users and manufacturers of dyes and equipment, as well as by universities.

Since the end of 20th century, with the increased competition, dye houses are asked to meet more exact requirements while they are under pressure to reduce the cost of manufacturing. In order to stay competitive and be in business, they were required to exercise tighter quality control and seek ways to optimize dyeings. This necessitated the understanding of a) dyes, chemicals and substrates and their compatibilities; and b) the parameters that influence the rate and extent of dye uptake by the substrate (Park & Shore, 2007).

The variables that are objectively measured and monitored during a dyeing for quality control purposes have traditionally been limited to time, temperature, pH, and conductivity. Measurement of the fabric shade reflectance is only utilized in the development of new recipes/procedures and the verification of the dyed fabric shade. The development of recipes/procedures and the debugging of dyeing problems continue to rely on indirect information obtained by ad-hoc trail and errors, subjective observations, and visual assessments of dyers.

The first prototype system (Beck et al., 1990; Keaton & Glover, 1985) to measure the dye build up directly in real-time during a dyeing was developed in 1990's. However, due to technological limitations such as; a) the high cost of spectrophotometers, b) the low computation speed that is not sufficient to process the data generated by the spectrophotometer, and c) the insufficient computer memory restricting the amount of data that can be manipulated for the accurate determination of dye amounts, the adaptation of these prototype systems from the industry was delayed. For example, to determine the dye concentrations of a 3-dye combination precisely in real time (2+ decimal points), it is obligatory to have a computer with more than 500 MBs of memory. About eight years ago, computers with these configurations became available at low cost.

With advances in computation and electronics by the mid 2000's, the limitations listed above were overcome. As a result, two groups, one in England and the other in the US, began adapting dyebath monitoring systems (Dixon & Farrell, 2009; Ferus-Comelo et al., 2005). These systems became the back-bone of commercial RFT dyeing in select plants. The historical progress of these technologies were discussed in detail by Smith (Smith, 2007) in his acceptance of the AATCC Olney Award at the 2007 AATCC conference.

It was recognized that the successful practical dyer must achieve the following objectives:

- the material must match the target color (usually being color constant or isometric in different illuminants)
- the color must be applied uniformly and the processed material must have satisfactory fastness and physical properties
- the cost of production must be within the allowed budget
- the material must be delivered on time.

Important factors to achieve successful dyeing at RFT include dye standardization, compatibility of dyes and chemicals, catching dyeing problems earlier in the dyeing cycle, reducing or eliminating wasted textile and optimizing dyeing and quantifying end product quality. Early adapters of the RFT technologies reported reduction in time and cost while increasing overall product quality.

Another important aim of dyeing research was the optimization of dyeing recipe and procedures by:

- characterizing the performance of dyes, auxiliaries and substrates by identifying physio-chemical parameters,
- cutting extra time from the procedure,
- using compatible dyes and chemicals,
- avoiding unlevelness by controlling temperature and pH and limiting rate of exhaustion,
- eliminating chemicals that are not necessary,
- evaluating the performance of dyeing equipment and optimizing dyeing machine parameters such as flow rate or circulation time,
- developing procedures that reduce dyeing time with increased rate of exhaustion at under utilized dyeing steps

It is not the purpose of this chapter to discuss optimization strategies, although some of that optimization occurs with the quality control improvements discussed here.

It is perhaps somewhat surprising that no formal research and development program has yet to be undertaken to systematically develop RFT quality control and optimization procedures in practical dyeing processes.

In order to be consistent in communicating the analysis and interpretation of the dye exhaustion data, several new terms were introduced over the past several years by the

industry. With this chapter, the author defines and shares this emerging terminology with the academic researchers to facilitate communication.
New plots that are used regularly in the analysis of dye absorbance / concentration data are also introduced and discussed in this chapter for the first time.

2. Typical configuration and the setup of the dyebath monitoring system

A typical dyebath monitoring system such as shown in Figure 1 enables dyers to monitor each dye concentration in the dyebath while measuring the temperature, pH, and conductivity of the dyebath simultaneously.

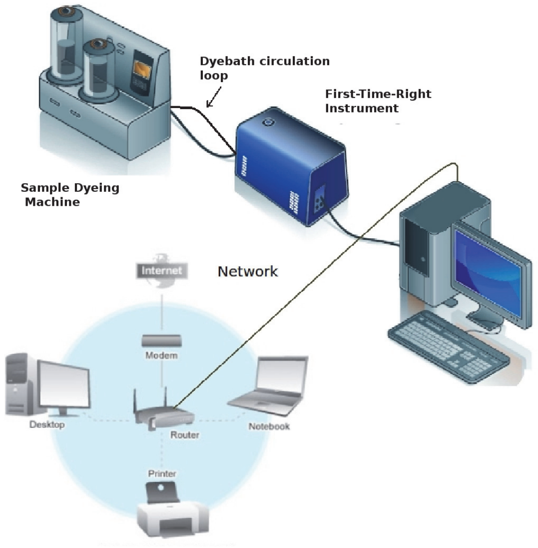

Fig. 1. HueMetrix Dye-It-Right Monitor.

The determination of dye concentrations in real-time works as follows once the dyes are calibrated:

1. Approximately every 90 seconds during the dyeing process, the instrument takes a micro sample of dyebath via a small dyebath circulation loop connected to the dye machine.
2. The sample is conditioned, both physically and chemically for optimum spectral analysis.
3. Each micro sample is read with the state-of-the art spectrophotometer and analyzed.
4. The resulting data set (includes dye concentration, exhaustion, temperature, pH, and conductivity) is recorded by the software.
5. The instruments post-processing software provides certain analysis features to aid dyers in determining dyeing performance.

The system determines individual dye concentrations according to the Beer-Lambert law (McDonald, 1997):

$$A(\lambda) = l\epsilon(\lambda)c \tag{1}$$

and the additivity of individual dye spectrums when they are mixed (Johnson, 1989).

In Equation 1, ϵ : molar absorbance [mol/L], λ : wavelength, A : absorbance [Au], and c : dye concentration [g/L].

Existing systems (Dixon & Farrell, 2009) are now capable of measuring dye concentrations of almost any dye class, including water insoluble disperse dyes. They can even measure multiple dyes of the same colors.

The determination of dye amounts may be done *manually* or *automatically*.

Manual mode; requires the injection of dye solution via syringe from the luer-lock syringe port of the instrument. Following injection, the technician may choose to re-sample or inject a new sample.

Automatic mode; is selected during the dyeing process where, every ninety seconds or so, a dyebath sample circulating in the circulation loop connected to the dyebath is automatically taken from the dyebath by the opening and closing of the solenoid valve.

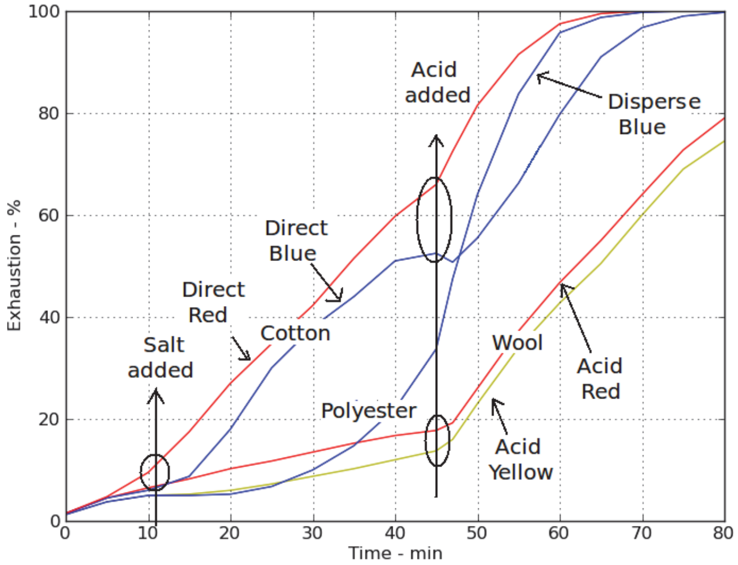

Fig. 2. The monitoring of dye uptake by the fabric for individual dyes during a dyeing cycle.

Regardless of the choice to run in manual or automatic mode, a micro sample is enough to calculate the individual dye amounts in the solution. This data may then be correlated with the temperature, pH, and conductivity sensor measurements if they are attached. The results are then presented to the dyer in real-time at various overlay graphs.

When the dyeing is completed, the technician may save the results in a database. The data stored may then be analyzed by an engineer following the methodology suggested in this paper.

3. Data processing and tools to analyze and interpret real-time dye monitoring data

Establishing a standard for quality attributes against which assessments will be made is critical in dyeing quality control.

The quality attributes that have practical importance are:

- concentration
- exhaustion
- temperature
- pH
- conductivity
- strike rate [maximum rate of exhaustion]
- strike temperature [the temperature at which exhaustion accelerates]

Among these attributes, concentration, temperature, pH, and conductivity are measured directly, and the exhaustion, maximum rate of exhaustion (strike rate) and the temperature at which the exhaustion accelerates (strike temperature) are the derived attributes of those measured.

Figure 2 shows the % exhaustion of red, yellow and blue color dyes on a fabric made of polyester, cotton and wool blended fibers versus time. On this substrate, the acid dyes color the wool, the direct dyes color the cotton, and the disperse dyes color the polyester fibers. The chart plotted in Figure 2 shows that, during the dyeing, the addition of salt triggers the cotton fibers to absorb the direct dyes, the addition of acid triggers wool fibers to absorb acid dyes, and the rise of temperature eventually starts the dyeing of polyester with heat driven disperse dyeing.

Furthermore, Figure 2 shows that the citric acid also interacts with direct dyes, resulting in the exhaustion of these dyes by the cotton fibers. The capability to capture such detailed information on dyes and their interactions with chemicals, fabric, and process variables enables the dyer to develop the proposed quality control schema below for a dye-house.

In the evaluation of quality attributes one has to be aware of the limitations of the technology which are discussed by Günay and Jasper (Günay & Jasper, 2010). However, note that the effect of these limitations on the conclusions drawn is often insignificant.

In addition, note that using equipment for solution and dispersion preparation in conjunction with the low-cost electronic dispensing pipette for dyebath preparation increases confidence in results and improves repeatability of tests.

Definitions of the critical attributes and their determination methodology are given below:

Exhaustion: is the percent amount of dye that has migrated onto the substrate. % Exhaustion is a function of the initial and current concentrations and calculated as follows;

$$\%Exhaustion = 1 - \frac{C(t)}{C(t_s)} * 100$$

Final exhaustion: is the value of the exhaustion at the end of a dyeing.

Strike time - t_s and temperature - $T(t_s)$: are the time and the corresponding dyeing temperature at which the dye starts to go onto fabric with an increasing rate. Especially in synthetic fibers at glass transition temperature, fiber relaxes and expands and eventually allows dye molecules to penetrate into amorphous regions. Knowing the time and temperature of this point may permit fiber manufacturers to compare different fibers for blending and quality control purposes. It may also provide data on the comparative information on fiber morphologies and crystallinity.

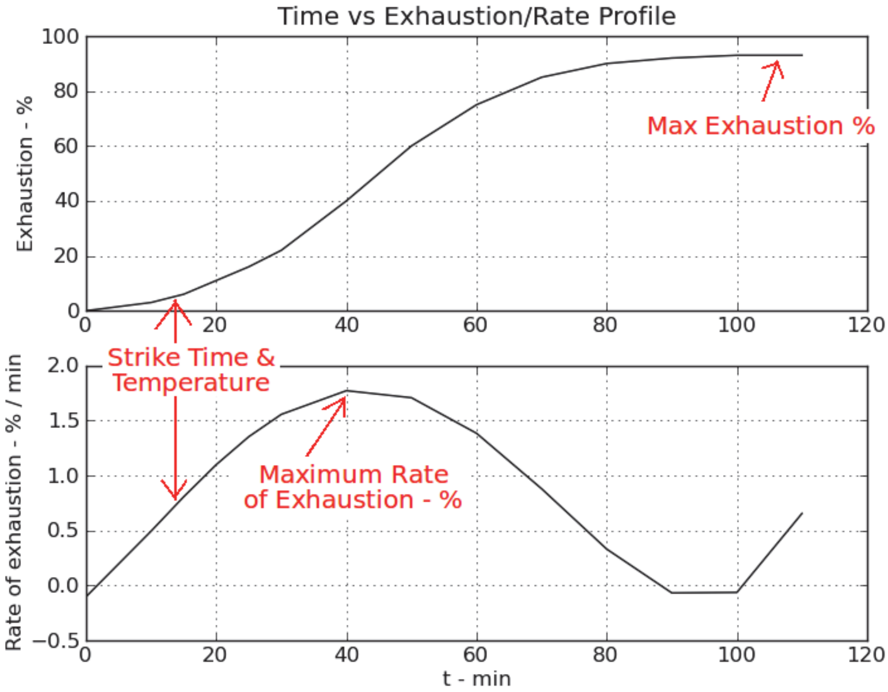

Fig. 3. Display of critical attributes on exhaust profile for a typical dyeing.

Equilibrium time - t_e: is the time when exhaustion of dye slows down and begins to level of as it reaches its ultimate exhaustion, $E(t_e)$.

% Rate of exhaustion - $\frac{\Delta E}{\Delta t}$: is determined by calculating the average exhaustion rate between the strike and equilibrium times as follows:

$$\%Rate \quad of \quad Exhaustion = \frac{E(t_e) - E(t_s)}{t_e - t_s}$$

Maximum exhaustion % rate: is the value of the maximum rate of % exhaustion. This is a critical value often effects the levelness of the dyeing.

Temperature for maximum exhaustion % rate: is the temperature at which the maximum rate of % exhaustion occurs. Near this temperature the exhaustion rate is decreased to prevent unlevelness.

Figure 3 demonstrates the definitions of critical attributes on exhaustion versus time and the rate of exhaustion versus time plots. For this dyeing, the final exhaustion reached was about % 90. The % strike time is around 16^{th} minutes.

4. Comprehensive quality control strategy

Several factors which must be monitored or controlled to achieve RFT dyeing were identified with the combined efforts of researchers at universities and the technical staff of dyers and their suppliers (Koksal & Smith, 1995; Park, 1987).

It was concluded that the shade variation in a dye-house may be minimized by a comprehensive quality control strategy that adapts:

- tight dye-house input quality control,
- last checks right prior to a dyeing,
- monitoring of dye uptake during the dyeing, and
- post dyeing quality confirmation.

Of note in this chapter is the author's proposal and discussion of new testing methods emerging with the introduction and advances in right-first-time dyebath monitoring technologies.

4.1 Variables that needs to be monitored for RFT dyeing

The principal factors in obtaining dyeing reproducibility are listed in Table 1.

These factors are grouped and ordered accordingly with respect to the stages of dyeing. A typical dyeing is considered to begin in the laboratory with shade matching and sample dyeing, continues with the final checks before dyeing, and reaches completion with the post dyeing quality confirmation.

The remainder of this chapter is a detailed analysis of tests to monitor and control the factors listed in Table 1. It is vital to apply these tests into routine testing and operating procedures in both in the laboratory and in production.

The failure to monitor these factors, due to fatigue or a lack of standard operating procedure (SOP), prevents dye houses from achieving a high level of right-first-time production.

4.2 Quality control in the laboratory

Even though dye manufacturers provide services for determining a matching recipe for a given shade, these can only be used as a starting point for in-house laboratory work by the dye user. The reason for this is due to the fact that the dyeings carried out in different locations are not comparable unless the same dyes, chemicals, substrate and water supplies have been used (Park & Shore, 2009).

4.2.1 Color matching

Even when visual assessment of color is carried out by standardized methods, the results obtained can be subjective and unreliable, as decisions may be affected by the age, sex, and sensitivity in color discrimination as well as the current physiology of the observer (McLaren, 1970). To make visual assessment of color more consistent, a set of observers may be asked to evaluate samples.

An improvement in the quality of color matching in terms of accuracy, consistency, and reproducibility can only be achieved by the use of instrumental methods based on spectrophotometry (Park & Shore, 2009). Color-difference equations such as $DE_{CMC(2:1)}$ and $CIEDE_{2000}$ provide a single number while effectively compensating for the visual non-uniformity of the color space. The numbers obtained from these equations, especially the CMC equation, have been widely adopted in setting tolerance limits for color-differences between the reference and manufactured fabrics.

Many dye houses rely on external color matching and recipe formulation laboratories. However, quick response, just-in-time, and right-first-time dyeing can only be achieved by a basic in house dye house laboratory.

In the laboratory	• Color matching – Determination of metamerism index • Dyes: – Hue of dyes – Strength of dyes – Moisture content of dye when powder – Physical form of dyes, liquid at national have greatly improved accuracy – Fastness properties – Ease of dissolving or dispersing dye – Dye compatibility (Heat, blocking effect) • Dyeability of substrate: – Evaluation of heat-setting conditions; (polyester): time, temperature, tension – Substrate contraction evaluation – Evaluation of yarns for blending – Construction – Substrate content variations – Substrate preparation: a) Degree of bleaching, Degree of mercerization, b) Cleanness c) existence of chemicals, Size content, etc • Evaluation of water quality – Hardness, pH, purity, chlorine amount, etc. • Evaluation of recipe/procedure in dyeing: – Maximum exhaustion determination – Dye compatibility evaluation for heat and blocking effects – Dye instability and Dye-Dye interactions – Evaluation of chemicals and auxiliaries pre dyeing
Pre-dyeing	• Verify dry weight of substrate / Moisture content of substrate may vary • Verify weight of dyes / dyebath color (dye check) • Liquor-to-ratio • Salt amount (cotton dyeing) • Weight of chemicals and auxiliary product
During dyeing	• Dyebath temperature • Dye concentration • Dyebath pH • Conductivity • Exhaustion profile vs. standard • Time of dyeing
After dyeing	• Shade match confirmation and levelness evaluation • Color fastness confirmation (Wash/Light) and waste water examination

Table 1. Important factors that need to be monitored for RFT dyeing

Currently, both Datacolor and Hunter Labs provide customer tailored turnkey systems that integrate computer color matching with the plant dye and substrate inventory. Today, even dye houses with a few dyeing machines are equipped with low-cost hand-held color measurement spectrophotometers. It was essential for the automotive industry to adapt these technologies where tolerance limits are low and tight, while the visual limit of the trained observer is only 0.6 DE_{CMC}.

The ability to measure reflectance of a substrate and correlate it with the visual assessment of trained color observers was the critical step in achieving recipe/ procedure prediction. Sophisticated computer programs based on non-linear equations were developed so that close recipe predictions may be achieved. These predicted recipes were often modified to obtain the final product shade and quality attributes that satisfy customer requirements. Afterwards, the modified recipe can be adjusted for the bulk production as an RFT dyeing.

Two specimens having identical tristimulus values for a given reference illuminant and reference observer are metameric if their spectral radiance distribution differ within the visible spectrum (Schanda, 2007). As a result, a sample may look different at different lighting conditions. This could be an issue especially for a manufacturer where a garment is assembled from various parts that are supplied by different manufacturers. The metamerism index is a single number which indicates how well two materials that match one illuminant will match under another illuminant. Using a spectrophotometer determining L, a, b values, one may calculate the metamerism index as follows:

$$Metamarism \quad Index = \sqrt{(\Delta L_{i1} - \Delta L_{i2})^2 + (\Delta a_{i1} - \Delta a_{i2})^2 + (\Delta b_{i1} - \Delta b_{i2})^2} \qquad (2)$$

where $\Delta = X_s - X_r$, $i1$ is illuminant 1, $i2$ is illuminant, s is standard and r is reference.

4.2.2 Incoming dye shipment test

Dye standardization makes a major contribution to dye selection and the ability to achieve RFT dyeing. Researchers (Park & Shore, 2007) listed the parameters for dye selection and their responses to environment and behavior in the dye-fiber system. Even though all parameters listed in the publication (Park & Shore, 2007) are important, only a number of factors are considered critical and are included in the routine evaluation of dyes, either in the assessment of deliveries or in the evaluation of competitive products at the plant. The parameters that may be monitored practically are:

- Dye hue test
- Dye solution strength test : a) moisture content of dye when powder, b) Physical form of dyes; liquid versus powder.
- Dye stability and sensitivity to chemicals in particular pH
- Determination of strike temperature for dye database
- Dispersion performance for disperse dyes
- Fixation for reactive dyes
- Fastness

Among all the variables, perhaps hue and strength are the most important control parameters that need to be evaluated for each incoming dye (Park & Shore, 2007).

Commercially, absorption spectrophotometry is frequently used in assessing dye strength. Despite time and experience, there are significant variations in measuring dye strength even within the same lab. These variations are often caused by differences in weighing methods such as a) errors in weighing, b) variability in the solution making, and c) variability in wait time before absorbance measurement, and d) evaporation of the dye solution. To ensure accurate and comparable results between laboratories, it is essential to have standard test procedures to estimate hue and the relative strengths of dyes (Günay & Jasper, 2010; Park & Shore, 2007).

4.2.2.1 Dye hue test

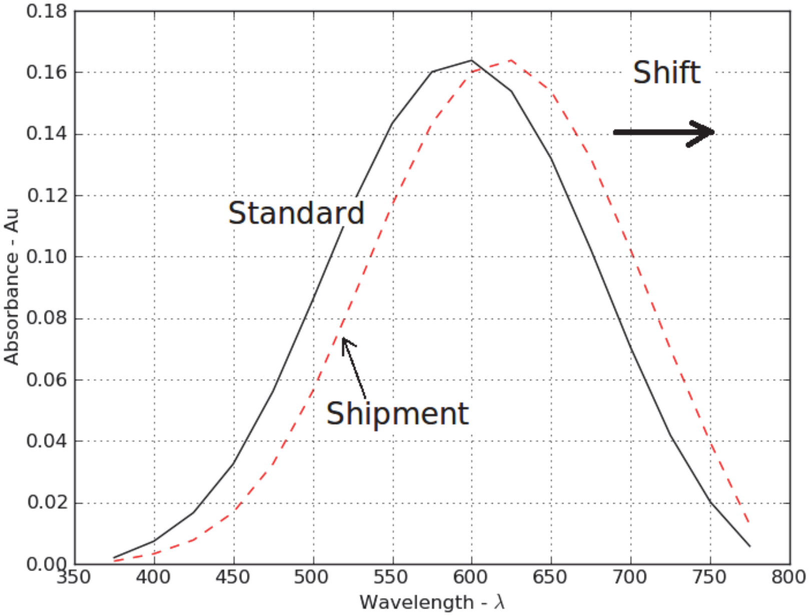

Fig. 4. Significant spectral differences between the standard and shipment dyes.

The dyes which determine the shade of the fabrics are shipped to dye houses lot-by-lot, sometimes from different plants, and occasionally from different countries. After being stored in a warehouse for some time, they are used in production as needed. Even though attempts are made to manufacture dyes that are exactly the same, this is often not an easy task to achieve. There may be spectral differences among dye shipments. These may be caused by either color chemistry differences between the dye shipments or unfavorable stocking conditions such as heat and humidity which modify the chemistry of the dye at the warehouse.

Spectral shifts such as shown in Figure 4 cannot be easily corrected. In such cases, it is highly recommended to avoid those dyes that exhibit these spectral shifts in manufacturing. To quantify the spectral shifts, a dyer may measure the absorbance of the dyes in the inventory and graph them as a function of time. Later using Equation 3, the dyer can determine the storage stability of plant dyes.

$$= \frac{\sum_{380}^{780} |A(t)_\lambda - A(0)_\lambda|}{\sum_{380}^{780} A(0)_\lambda} \tag{3}$$

4.2.2.2 Dye solution strength test

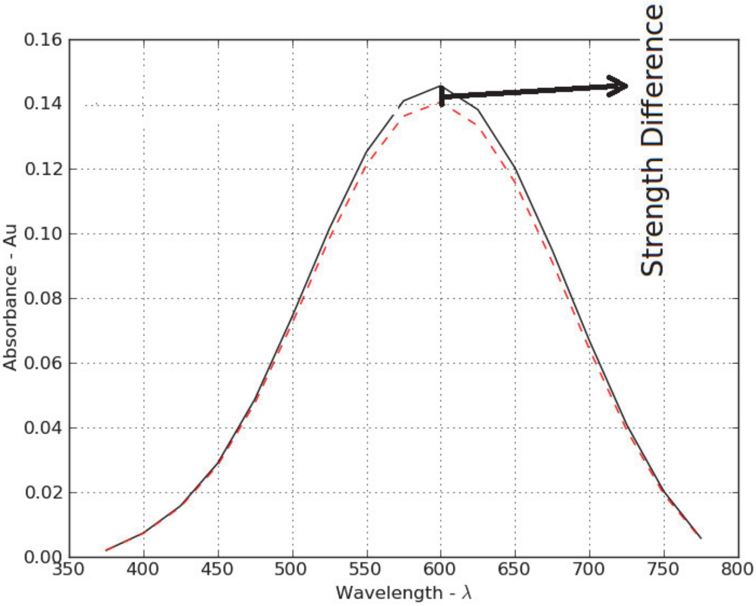

Fig. 5. Strength differences in dyes.

When a partnership is established between dyer and dye supplier, the latter provides the customer with a certificate of conformity to the standard for individual deliveries. However, it is still good practice to verify dye strength differences between the shipments of dyes and their standards.

The storage conditions of dyes in use must be carefully controlled, as the effect of ambient conditions on moisture content can significantly impact dye strength (Gaunt & Moffitt, 1991) which in turn may cause severe color differences in depth and hue in dyeing. Consequently, it may be good practice for a dyer to check dye strength prior to each dyeing.

This could be especially important for disperse dyes, as these contain different diluents that vary in hydroscopicity.

Figure 5 shows the strength differences in spectra between the standard and shipment dye. This difference may be quantified by determining the maximum absorbance at λ_{max} for each dye and calculating the ratio between them as given in Equation 4.

$$\%Strength_{dye} = \frac{A_{\lambda max}^{shipment}}{A_{\lambda max}^{standard}} \times 100 \tag{4}$$

Figure 5 demonstrates that the strength of the shipment dye is only % 96 of the standard one. If the result obtained in Equation 4 is less than % 100, the result is due to a weaker dye. If the shipment dye is above % 100, the dye is stronger than the standard one. To match the same shade using the new shipment dyes, the recipes have to be corrected accordingly. For example, if one of the shipment dye's strength is 96%, instead of simply adding 4% of that dye, the proper correction would be calculated as follows:

$$= \frac{100}{\%Strength_{dye}} \times Amount_{dye} \tag{5}$$

Knowing the spectral strength deviations from the standards increases one's chances of successful dyeing.

Using the method suggested above, it is possible to achieve dye standardization to within +/- 0.05% tolerance. With currently available dye strength determination based on dyed sample reflectance measurement technology, tighter tolerances less than +/- 3% can not be reached (Park & Shore, 2009). Hence, the proposed method has clear advantages over the existing dye strength determination based on reflectance measurements.

Note that as moisture content and dye solubility are key parameters in determining the dye strength accurately, it is particularly important to establish SOP (Standard Operating Procedures) for storage and handling of the dyes.

Furthermore, some dyes are available in both liquid and powder form. Liquid dyes may be preferable for accuracy reasons and for health and safety due to reduced exposure of operators to dye dust.

4.2.2.3 Determination of strike temperature for dye database

Heat sensitive dyes such as acid and disperse class dyes do not begin exhausting significantly until the temperature reaches a certain level. When this level is reached, the dye starts migrating into fiber as polymer expands and allows dye molecules to penetrate. While dyes with high molecular volume may require higher temperatures to begin exhaustion, the dyes that are small in molecular size are likely to exhaust earlier.

A database of dye and strike temperature may be populated for each dye in the inventory, and when a recipe is formulated, dyes close in strike temperature may be selected for efficient and level dyeing. Refer to section 3 for the determination of strike temperatures.

4.2.2.4 Dispersion breakage of disperse dyes

Dispersions are not stable and over time dye particles coagulate and settle in the machine and/or on the fiber (Ferus-Comelo, 2008). Even though dispersion breakage increases with liquor flow velocity in the machine, it is still dye specific. Once the dye is no longer dispersed, it deposits on any available surface; fiber, metal or glass, for example, leading to uneven dye distribution in the machine and on the substrate. Dispersion breakage is therefore undesirable but, to some extent, unfortunately also unavoidable. It is possible that deposited dye is re-dispersed or dissolved during later stages of the dyeing so that dispersion breakage might not always be noticeable on the final product (Ferus-Comelo, 2009).

A quantitative indication of the extent of dispersion breakage can be obtained by comparing exhaustion values calculated by dye concentration measurements in the dyebath with those

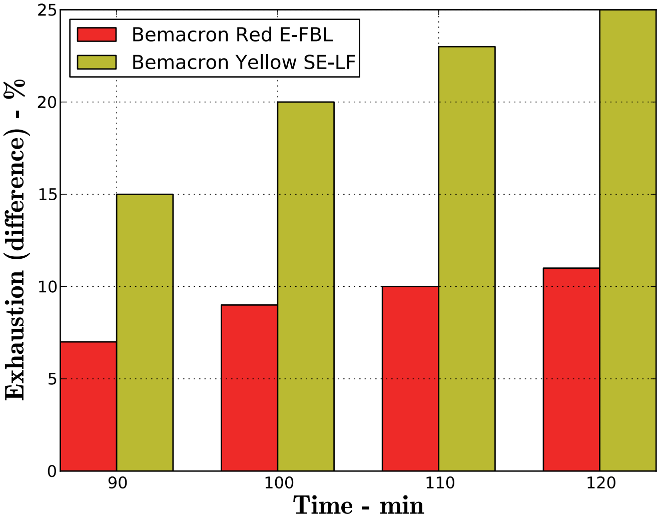

Fig. 6. Dispersion breakage for 2 dyes calculated from exhaustion differences.

calculated from fiber reflectance measurements. When the exhaustion values obtained from dyebath measurements are significantly higher than those obtained from the washed substrate, the difference is probably caused by dispersion breakage since the deposited dye is neither taken up by the fiber nor present in the dyebath. Exhaustion values calculated from the solution measurement are in this situation, therefore systematically too high (Ferus-Comelo, 2009).

Figure 6 shows dispersion breakage for 2 sample dyes calculated as the differences between the measured exhaustions using a real-time dyebath monitoring system and the calculated exhaustions from the reflectance measurement of the substrate. There are significant differences in dispersion breakage for given dyes. The exhaustion measured is on the average 12% more for the Bemacron Yellow SE-LF than that of Bemacron Red E-FBL. Furthermore, the dispersion breakage increases for Bemacron Yellow SE-LF more rapidly than that of Bemacron Red E-FBL. Consequently, the dispersion breakage of former dye is less than the latter, hence has a higher tendency to produce uneven dyeing.

4.2.2.5 Fixation efficiency for reactive dyes

Since fixation efficiency of reactive dyes varies, it is recommended that dyes with higher fixation are identified and prefered in recipe formulation in plants. The methodology to determine fixation efficiency of reactive dyes using RFT monitoring technologies is rather straightforward. Determination could be achieved by dyeing a few different kinds of substrates with the same dye and recording their final exhaustion when dyeing is completed. Since fixation is the amount of dye covalently bonded to the substrate, it is critical to remove excess dye from the substrate upon completion of the dyeing by means of successive rinses. Successive rinses should be performed until no significant dye is bleeding into the rinse bath. Following each rinse the amount of dye flushed from the substrate should be accounted for and deducted from the final dye exhaustion by means of basic book keeping using Equation

6.

$$\%Fixation = \%Final \quad Dye \quad Exhaustion - \sum_{i}^{n} \%R_i \tag{6}$$

where R_i is the percentage of dye flushed at the ith step of the rinse and n is the number of rinses.

4.2.2.6 Fastness

Fastness is the ability of fabric to retain color in use. There are three types of fastness tests : a) wash fastness, b) rubbing fastness, and c) light fastness. These test methods are discussed in detail at AATCC test methods 61, 8, and 16, respectively. Briefly,

wash test: is done by stitching the shaded fabric between the two white fabrics and laundering the specimen. After drying the degree, the stained white fabrics are evaluated against a standard stain scale.

rubbing test: is performed by rubbing the shaded fabric under pressure to a white fabric specimen. The degree to which the white specimen is stained determines the rubbing fastness of the fabric.

light fastness: Light fastness is the degree to which a dye resists fading due to light exposure. Different dyes have different degrees of resistance to fading by light. The test is often conducted under Xenon light and standard condition for a determined duration. After the test, the level the sample fades is compared against a standard scale to quantify light fastness.

In order to grade and quantify loss of color, reflectance measurements may be employed.
This section provides several quality attributes about dyes. Due to complexity in dye quality attributes, simple product substitution using the so-called equivalent dyes is not an easy option. It requires a great deal of study to assess all the factors which impact dyeing, some of which are given in this section.

4.2.3 Dyeability of substrate - substrate evaluation

Both natural and synthetic fiber properties may vary between different shipments of bales or lots. Variations in fiber properties caused by changes in manufacturing inputs/ parameters for synthetic fibers or environmental factors for natural fibers may produce textile products that do not satisfy customer requirements such as strain/strength, shade consistency, or levelness. The variation in textile physical properties may affect the performance of dyeing and the final product significantly. Hence, it is important to develop tests to determine, evaluate and control:

- substrate content variations,
- yarns for blending,
- variations caused by heat-setting conditions; (polyester): time, temperature, tension,
- variation in substrate preparations such as a) degree of bleaching, b) degree of mercerization (size content), c) existing of chemicals and d) cleanness,
- effect of construction in dyeability,
- expected contraction after dyeing.

This section provides examples to demonstrate that monitoring the performance of dyeing may lead one to determine the dyeing quality attributes of fibers and in turn: a) improve fiber properties, b) develop new fibers, and c) verify fiber quality for new crop and merge.

4.2.3.1 Substrate content variations

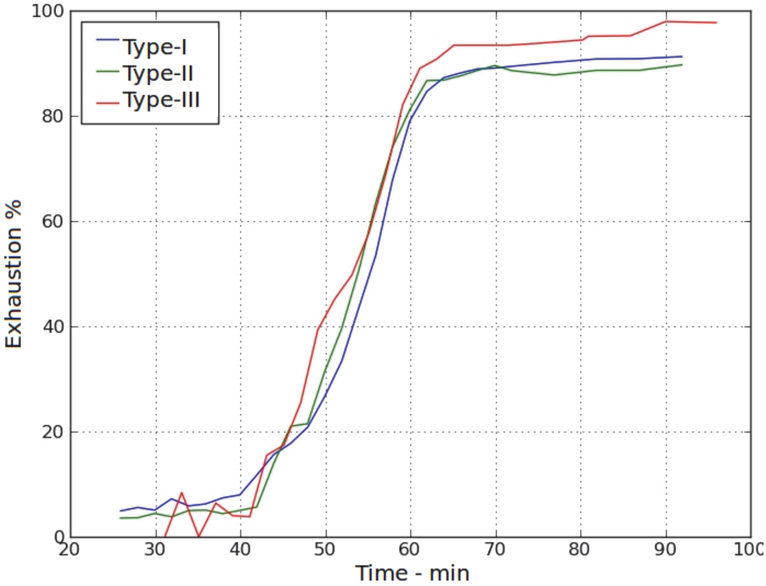

Fig. 7. The exhaustion curves of three shipments of the polyester fiber.

Figure 7 shows the exhaustion performance of disperse dyeing of Red 167 on three different polyester fibers. In Type-I and Type-II, recycled polyester fibers were blended into yarn. The pure polyester fiber, Type-III, has a 10% greater final exhaustion than the others. As a result, the foreign matters present in the recycled polyester fiber blends negatively affect the dyeing performance of the yarn. If Types I, II and III fibers were combined in a fabric, it would come as no surprise to observe barre effect in the constructed fabric, as some parts of the fabric would uptake more dye than others.

4.2.3.2 Evaluation of yarns for blending

A common source of frustration and blame is barre in blended fabrics. The dyer will usually blame the barre on micronaire or yarn texturing differences, and the fiber producer then blames the dyer for bad procedure or faulty dyeing.

Figure 8 shows three different exhaustion profiles of two different polyester fibers blended into a final fabric. The single fibers and blended fabric were dyed individually with a single disperse dye. The key to the graph is as follows: 767 is a Drawn Textured Yarn (DTY), 769 is a Semi Drawn Yarn (SDY), and 771 is the blended fabric produced from both yarns. Ideally, the exhaustion profile for each yarn would overlay and dye exactly the same, and so would the blend. This is not the case however, as the base fibers dye differently. And when the fibers are blended, the overall exhaustion profile for the dyeing of the combined yarns is different than either fiber. Consequently, when there are three or more total dyes for a shade, the shading between the yarns can become quite significant because of the differences in the fibers dyeability.

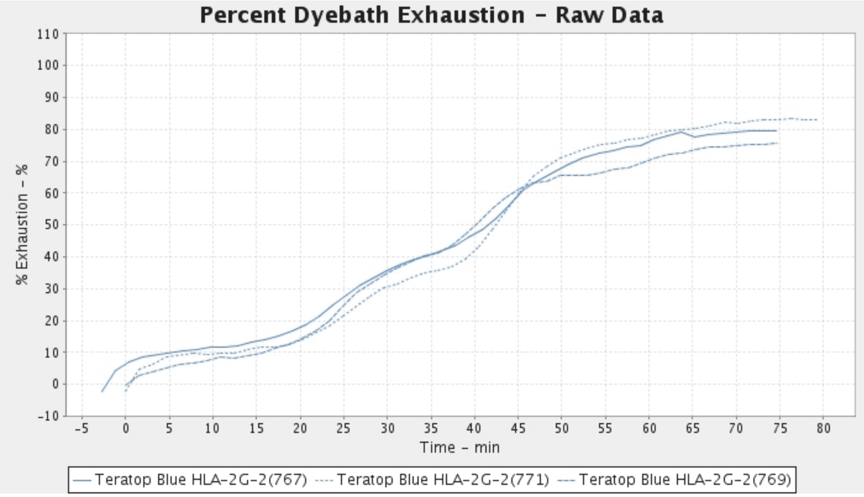

Fig. 8. Dyeings of individual and blended polyester yarns with different exhaustion profiles.

4.2.3.3 Evaluation of fiber properties on dye uptake

Fiber characteristics may be impacted by heat treatment conditions such as temperature and tension at which drawing is applied, as well as the heat treatment history.

Figure 9 shows dye exhaustion performance of the same substrates of different yarns. As seen from the graph, the matching characteristic exhaustion curves indicate that the absorption and/or migration of dyes to substrate behave the same way. The morphological differences due to different yarn cross-sections contributed to strike temperature differences between these two dyeings.

4.2.3.4 Evaluation of substrate construction on dye uptake

Figure 10 shows dye exhaustion of different substrates that use the same yarns. As seen in the picture, both dyeings have the same strike temperatures, indicating the yarns have the same physical and chemical properties. However, the time of dyeing, $t_e - t_s$, for both substrates varies significantly. This is perhaps due to differences in surface area affecting dye absorption and migration.

4.2.3.5 Evaluation of pre dyeing treatment of the substrate

Many coloration problems arise as a result of inadequate preparation of the substrate. Substrate preparations such as a) degree of bleaching, b) degree of mercerization (size content), c) existence of chemicals, and d) cleanness may not only significantly affect the accuracy of concentration measurement but also dyeing performance. Therefore, in order to reduce the shade variation between lots that may have been caused by inconsistent substrate treatments in pre dyeing steps, it is highly recommended to wash off the substrate before the dyeing.

4.2.3.6 Determination of contraction after dyeing

It is not uncommon to observe fabric contraction after a dyeing. In order to meet customer requirements, it is highly recommended to do a lab dyeing prior to batch dyeing to estimate %

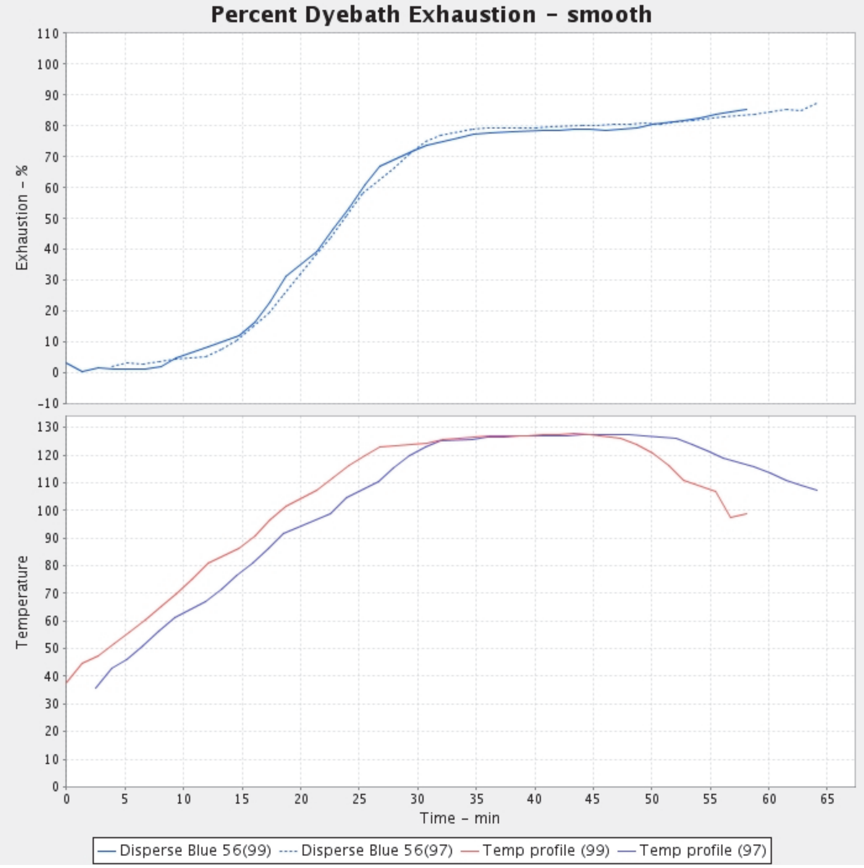

Fig. 9. Different yarn used in same fabric structures.

contraction. Final fabric dimensions may be set by adjusting tenter frame width and overfeed to accommodate % contraction.

4.2.4 Dye house water quality control

The quality of textiles produced by any manufacturing operation which employs wet processes, such as preparation, dyeing and finishing, is profoundly affected by the water quality (Smith & Rucker, 1987a).
Dye house water may be supplied from;

collected rain water filtered by sand bed. It is pure, but limited in supply, availability, and varies with weather conditions and contents deviate depending on air pollution.

collected surface water from lakes and rivers. May contain dissolved organic and inorganic matters such as chloride, sulphate, carbonate, bicarbonate of sodium, potassium, calcium an iron. Often dependable and consistent supply. Variation may occur gradually.

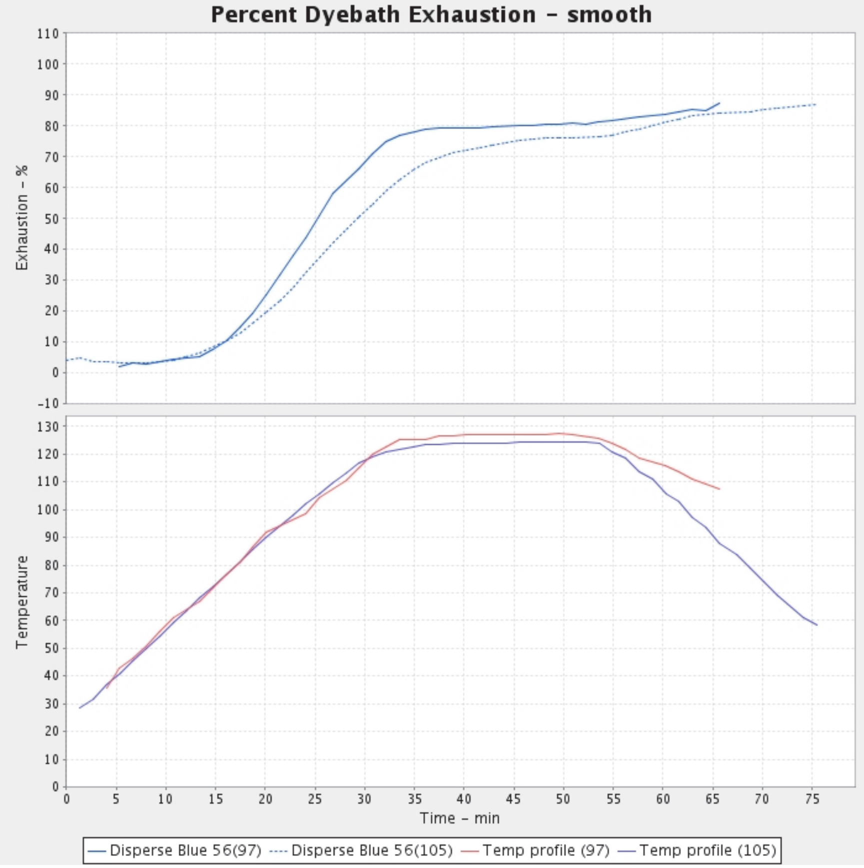

Fig. 10. Same yarn used in different fabric structures.

well water below the surface. May contain soluble organic compounds, ammonium salts, nitrates. Often dependable and consistent supply with gradual variation over time possible.

city water. Consistent supply but not necessarily dependable composition. Chemicals may vary with season and occasionally even by day.

Choosing the correct water supply consistency is critical in RFT dyeing. For the ease of the dyeing process, dye plants are located accordingly. For example, if plant water has hardness, scale could form in boilers and pipes and could result in increased energy use due to reduced thermal conductivity. High CO_2 concentration may cause boiler corrosion when CO_2 reacts with iron in the presence of O_2.
Using hard water has often produced serious negative results on dyeing performance, such as:

Wastage of Soap & Detergent: Ca and Mg salts react with soap and lather is not formed easily.

Reaction with Dyestuff: The reactive groups present in dyes react with Na, Ca, Mg, and Fe in hard water. This causes wastage of dye, and produces duller shade and faulty dyeing. A sequestering agent is added to prevent this.

Deposition on Textile Material: Soap reacts with hard water and produces insoluble salts which deposit on the fabric during scouring. These salts harden and reduce flexibility in the fabric.

Ideal water has the following properties (Heetjans & Tindall, 1995):

1. Color: Water must be colorless by which the dyeing will be carried out.
2. Odor/ Smell: Water must be odorless.
3. pH: Value would be 7 to 8.
4. Water Hardness: Less than 90 ppm (90 milligrams of $CaCO_3$ per litre of water).
5. Dissolved Solids : <1 ML/L
6. Solid Deposits: < 50 Mg/l.
7. Organic Substance: < 20 Mg/ L.
8. Inorganic Salt: < 500mg/L
9. Iron : < 0.1 Mg/l.
10. Copper: < 0.005 Mg/L.
11. Nitrate: < 50 Mg/ L.
12. Nitrite: < 5 Mg/L.

Water contaminants, especially metals, can have a substantial effect on many textile wet processes. The effects are not always adverse, but it is not desirable to have variance in processes and product quality due to water quality changes. Because these variations in the quality of water make process and machinery optimization and control difficult (Smith & Rucker, 1987b).

There are many quick qualitative tests for detection of trace quantities of ions and elements in water. There are also quantitative tests for determining the exact concentration of cations such as calcium, magnesium, iron, copper, and manganese in water (Smith & Rucker, 1987b).

In addition to regular testing for pH and the hardness of the incoming water, a standard sample dyeing with single dye without chemicals may be chosen and monitored using RFT technologies every so often, and exhaustion profiles may be compared with the standard ones. Although not conclusive, the deviation from the standard exhaustion profile may indicate variation in the incoming plant water.

4.2.5 Evaluation of recipe/procedure in laboratory dyeing

Even though researchers developed techniques and sophisticated algorithms to predict recipes and procedures using color matching instruments and historic dyeing databases, it is still cost-effective to repeat bulk production dyeing in the laboratory. It has been shown that a bulk correction of a 300-kg production batch may cost as much as 25 laboratory dyeings depending on the process and dye house infrastructure (Hildebrand & Hoffmann, 1993).

It is important for staff to follow SOP to minimize errors caused by inconsistent procedures within the lab between operators.

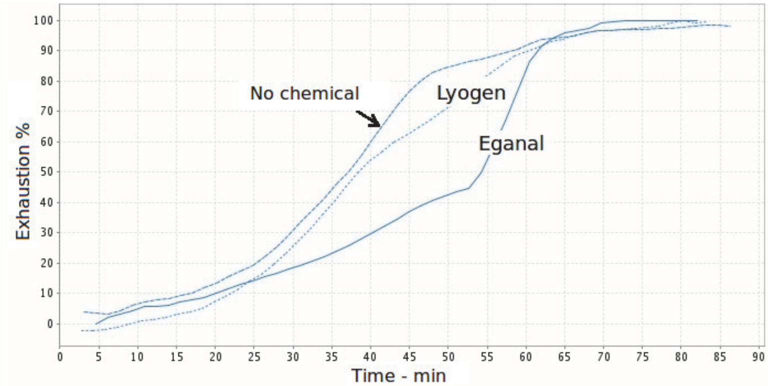

Fig. 11. Effect of leveling agent on dyeing

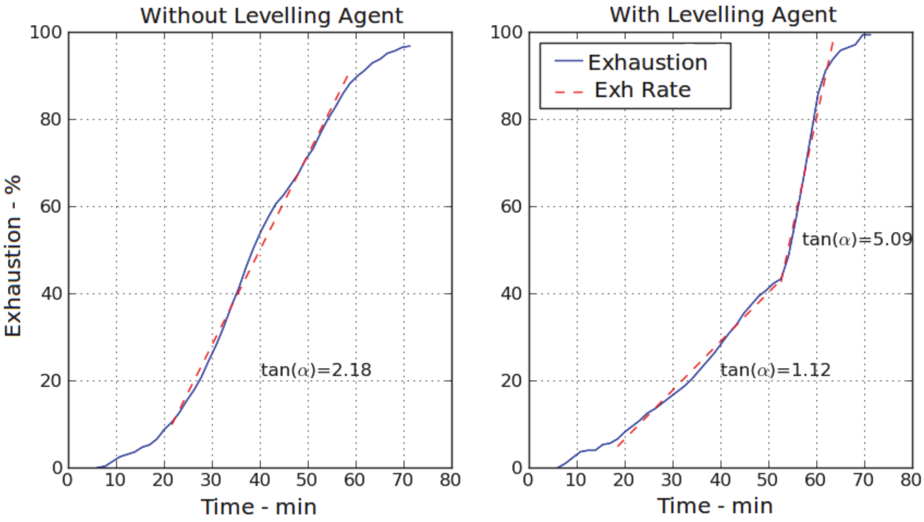

Fig. 12. Effect of leveling agent on dye strike rate

4.2.5.1 Evaluation of chemicals and auxiliaries pre dyeing

Different chemicals may produce different results on the same dyeing. Sometimes the same chemical may act differently in another dyeing. To determine the effect of chemicals on dyeing performance, it is best to monitor the dye exhaustion profile and determine strike temperatures and rates.

Figure 11 demonstrates Lyogen and Eganal leveling agent's effect on two different dyeings using the same disperse dye *Terasil Blue RBS*. Both leveling agents delay the dye exhaustion differently as demonstrated in their dye exhaustion profiles shown in Figure 11. For this particular dyeing, the absence of a leveling agent did not cause any dyeing unlevelness. On the contrary, the leveling agent was the cause of shade levelness observed on the fabric. This was explained by the increased rate of exhaustion in the presence of levelness agents at the exhaustion phase.

Figure 12 shows the exhaustion trends during the exhaustion phase. In the absence of chemicals, the average rate of exhaustion was calculated to be at 2.18 % / min using Equation 7.

$$tan(\alpha) = \frac{\%Dye \quad uptake}{Time} \tag{7}$$

In the presence of a leveling agent, the chemical Eganal blocks the dye uptake until the 53^{th} minute. Up to that point the average dye uptake is around 1.12 % / min. Once the blocking effect of the chemical disappears, 50 % of the exhaustion occurs in the next 10 minutes with an average exhaustion rate of 5.09 % / min. If the fabric in the dye machine circulates at a slower paste, then observation of shade unlevelness would come as no surprise.

Consequently, different leveling agents produce different results on dyeing performance. In some cases, it may be even better to avoid using a leveling agent.

4.2.5.2 Dyebath stability and sensitivity to chemicals

Dye instability may occur when:

- dyes in dyebath interact with each other,
- one or more dyes interact with chemicals in the dyebath,
- dyes change with temperature or time.

When two or more dyes are mixed together with no chemical interaction among them, the sum of the spectra of the individual dyes should equal the spectrum of the mixture. Dyes with this property obey the law of spectral additivity (Günay, 2009). A number of investigations with direct and VAT classes of dyes in mixture have proven this statement invalid. Neale and Stringfellow (Neale & Stringfellow, 1943) concluded that for certain direct dyes, the spectra of the mixtures in water were not additive. In an aqueous solution, pairs of dyes interact with each other, possibly through the operation of resonance bonds or residual valency forces similar to those responsible for anchoring the dye onto the hydroxyl groups of cellulose.

Using a dyebath monitoring system, one may determine the absorbance profile of each dye and the dyebath. Figure 13 shows the absorbance spectrums of Solophenyl Bordeaux 3BLE, Solophenyl Blue FGLE 220% and Solophenyl Scarlet BNLE 200% shade direct dyes at concentrations of 2.60 g/L, 1.00 g/L and 0.90 g/L respectively. When these three dyes are mixed together, the dye interaction between the Blue FGLE dye and the other two dyes shifts the spectrum compared to a spectrum comprised of the linear sum of the absorbance spectra, as shown in Figure 14. Such shifts due to spectral additivity (or super position) may cause concentration estimation and dyeing problems.

A pair test of the dye mixture indicated that the Blue FGLE of the mixture interacts with both the Bordeaux and Scarlet dyes. It was therefore recommended that the Solophenyl Blue FGLE 220% dye be substituted with another blue dye (DF Blue FGL) to reduce or eliminate dyeing problems.

4.2.5.3 Dye compatibility evaluation for heat and blocking effects

It is not uncommon for certain dyes to block each other when combined and consequently lower the exhaustion of the other dye. This is often caused by differences in dye molecular sizes. In other words, when a smaller molecular sized dye is combined with a larger molecular sized dye, the dye with the smaller molecular size may penetrate into the structure of the substrate faster than the larger one, consequently exhausting faster. However,

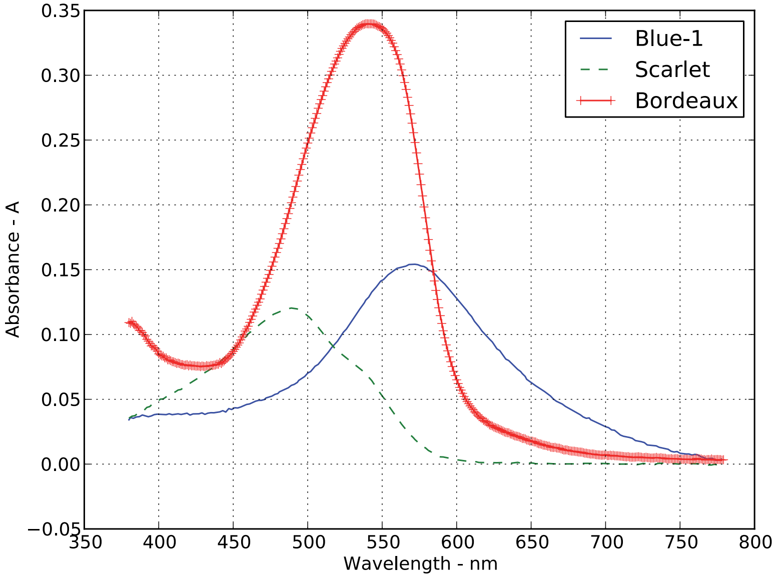

Fig. 13. Spectra of 3 different direct dyes

another possible scenario could have the larger molecular sized dye block entry points of the substrate and block the smaller molecular sized dye's penetration into the structure. Nevertheless, whether the former or latter phenomenon occurs, the dye incompatibility may create differences in strike temperatures and exhaustion rates. Level dyeing and high exhaustion may often be achieved only with compatible dyes.

Figure 15 demonstrates dyes that are not considered compatible when used together. As Orca Navy NRBL has a lower strike temperature than both the Lanaset Yellow S-L and Lanaset Red, it begins exhaustion before the others. Consequently, the substrate will first be dyed with the Navy shade dye, followed by the Red and Yellow shade dyes. As a result, even if the same amount of dye were exhausted onto the fabric, the shade obtained would be different when the dyes are incompatible, as opposed to when they are not.

4.2.5.4 Maximum exhaustion determination

One of the goals of optimum dyeing is reaching the maximum exhaustion efficiency possible. This may not be possible when dyes and/or chemicals are not compatible, or the recipe or procedure is not appropriate for the target dyeing. Nevertheless, it is still good practice to determine the maximum exhaustion of a dyeing for process optimization to lower cost and environmental waste.

4.2.6 Considerations to achieve lab-to-dye house correlation

In the past, nonreproducibility was so common that dyeings frequently needed follow up corrective dyeing. Consequently, the dyers subtracted 10-15% from the quantities given in

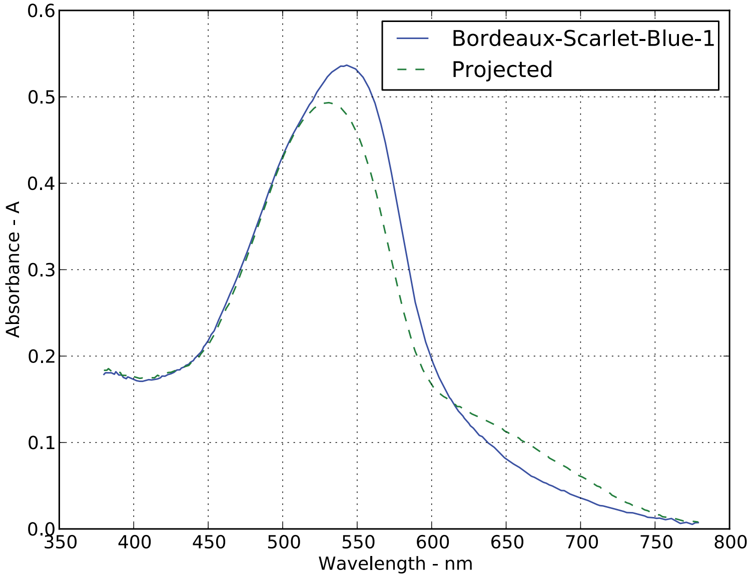

Fig. 14. Combined Spectrum of Bordeaux, Scarlet and Blue-1 Direct Dyes

the laboratory recipe before proceeding to mass production. This caused at least one color addition and removed any possibility of RFT dyeing.

As a result of numerous independent worldwide audits, it was found that many important factors varied between the laboratory and production. The dyeings carried out in the laboratory may not be comparable unless the same dyes, chemicals, substrate, and water supplies are used (Park & Shore, 2007). Since, high-accuracy laboratory dyeing is essential for dye evaluation and database preparation for shade matching. It is therefore critical for dyers to achieve Lab-to-Dye house correlation by replicating the conditions of the dye house in the laboratory. Achieving this would permit dyers to simulate dyeing and prevent production loss.

4.3 Pre-dyeing last controls

- Verify dry weight of substrate as moisture content of substrate may vary the weight
- Verify weight of dyes / dyebath color (dye check)
- Liquor-ratio
- Weight of chemicals and auxiliaries. Verify pH and conductivity

It was demonstrated by Sumner (Summer, 1976) that inaccuracies in weighing and measurement of volume in the drug room or dye dispensary were two of the principal causes of poor reproducibility in the dyeing process. It is therefore critical to verify the % amount of dye per unit fabric weight using RFT technologies described below.

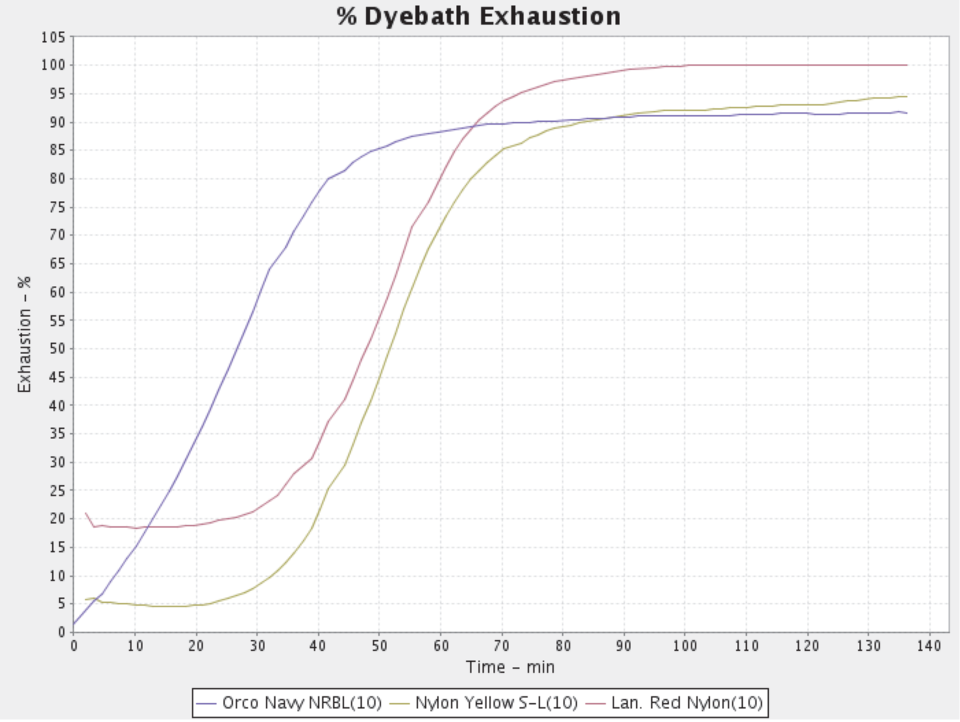

Fig. 15. Incompatiblities between dyes.

4.3.1 Dye amount check in the prepared dyebath

Even though instrumentation errors are rare in automatic dye/chemical dispensing, human weighing errors often cause varying dye amounts in the recipe. To prevent these errors, it is recommended to check dye concentrations in the dyebath mixture before they are transferred to the dyeing machine. This task can be achieved easily by injecting a sample of the dyebath to the RFT monitoring system and comparing the individual dye concentrations with the specified amount in the recipe. For this task, it is best to inject the dyebath sample up to 5 times and determine the average dye concentration. Once the average dye concentrations are determined, they are compared with the expected dye concentrations, and the absolute error for each dye is calculated.

$$E_s = |C_e - \bar{C_m}| \tag{8}$$

$$\%E_s = \frac{E_s}{C_e} \tag{9}$$

When evaluating solution errors - E_s:

- use Equation 8 at low concentrations (< 0.01 g/L) due to instrumental limitations
- use Equation 9 at high concentrations (> 1 g/L) for percent error.

where C_e and C_m are the expected and measured concentrations in g/L, respectively. This is due to limitations in dye concentration predictions discussed by the author in an earlier paper (Günay & Jasper, 2010).

4.4 Quality control during dyeing

4.4.1 Dyeing monitoring and procedure confirmation

During a repeat dyeing, pH, conductivity, temperature, and dye bath concentrations may be monitored and compared with the monitoring of the standard dyeing. The deviations from the standard profiles may be observed in real-time and corrected during the process. If it is not possible to take the corrective action during the dyeing procedure, the monitoring data collected may enable the dyer to determine the root causes of the problem and take the right corrective actions for the following steps and dyeings. Quantification of the departure from the standard would also allow one to employ statistical control charts to trigger alarms for out-of-control procedures.

4.4.2 Use of control systems

It has been demonstrated that RFT production can be achieved in dye houses where dye bath monitoring systems were deployed. As expected, major financial savings and other benefits have been observed from RFT processing. Further savings in labor may be obtained by introducing control systems at various levels of sophistication using semi-automated (SAC) or fully- automated (FAC) systems and by increasing accuracy and consistency. The installation of robotic systems can convert blind dyeing into a lights-out operation; however, a slight increase in labor qualifications may be necessary (Park & Shore, 2004). Commercially available control systems have been available since 1979 (Ziv et al., 1979), and these control systems, including dispensing, have recently been discussed (Jahmeerbacus et al., 2004; Jasper & Joshi, 2001).

4.5 Post dyeing checks

4.5.1 Shade confirmation

The difficulties associated with visual assessment were eliminated with the availability of optimized color-difference equations which allowed for the development of standards and tolerance limits. The total color difference formulas such as DE and DE(CMC) enable dyers and customers to objectively communicate closeness of color match by a single number. Whether visual or instrumental methods are used, a standard operating procedure (SOP) is required which must include factors such as preparation, handling, and measurement of samples. Conditioning of samples for illuminant, humidity, and temperature is essential, and the variations obtained as a result of differences in moisture content alone have been reported. Inappropriate storage conditions can also lead to significant color changes (Park, 1991).

The small color differences [within the range of DE(CMC) 0.3-0.5] demanded by automotive manufacturers and textile retailers cannot be achieved consistently by dyeing processes based on visual matching and correction; these small color differences can only be measured using the instrumental color assessment methods.

4.5.2 Levelness

Uniformity of fabric appearance is critical in the manufacture of high quality products. Irregularity is normally not acceptable, with the exception of stone-washed, acid- washed or pigment-dyed textiles, where an effect is sought to comply with a fashion trend (Chong et al., 1992). Uniform distribution of a shade within a dyed fabric is affected by several factors (Shivramkrishnan, 1983). The causes of shade variation may be the result of materials, equipment, controls, procedures, human factors, and logistics. These factors affect the distribution of dye in the dyebath and/or the ability of a dye to migrate on the fabric for uniform fabric appearance. For example, the mass variation of yarn could create non-random periodic irregularities that cause visible streaks on the woven fabric appearance (Günay et al., 2007). Furthermore, the high rate in dye uptake could lead to unlevel dyeing of the textile (Shamey & Hussein, 2005; Smith, 2007). It is therefore critical to monitor and control the dyeing and to evaluate the resulting textile appearance as objectively as possible to achieve optimum dyeing.

The common practice for evaluating color levelness today is based on the visual assessment of one or more observers. While in some cases the grading is simply a pass or failure, in others it is finer tuned by assigning a number such as 5 for the most level and 1 for the least level (Chong et al., 1992; Yang & Li, 1993). Visual assessments are highly dependent on the judgment of the observer; therefore, significant deviations occur in human assessment estimates. In addition, visual assessments often fail to quantify levelness. Communication of levelness data is therefore difficult to assess among suppliers, laboratories, and manufacturers.

Due to the shortcoming of visual assessments, several colorists have suggested objective methods to measure color levelness (Cardamone et al., 1995; Chong et al., 1992; Yang & Li, 1993). Scientists have previously used the colorimetric data of fabric obtained from a spectrophotometer. While some have calculated the standard deviation of the reflectance measurements of the spectrophotometer (Chong et al., 1992), others have instead suggested using K/S values (Yang & Li, 1993). In both approaches, levelness is derived from the variation of reflectance after the spectrum is adjusted with the spectral limunus efficiency function (Wyszechki & Stiles, 2000). Cardamone et al. demonstrated that colorimetric analysis with reflectance and K/S offers limited descriptions of color uniformity. They additionally suggested levelness evaluation based on digital image analysis (Cardamone et al., 1995). Tavanai and et al. furthermore confirmed that the common defects of a dyed fabric are better detected by using the gray scale format over the colored format (Tavanai et al., 1997). Cardamone et al. (Cardamone et al., 1995) obtained the histogram of the digitized image at a particular gray scale. They then calculated the levelness index as the standard deviation of the gray scale histograms.

While the above methods are useful in quantifying levelness objectively, they do not take into account;

- the 2-dimensional aspects of the levelness,
- the scale or extend (micro to macro) of levelness.

4.5.2.1 Measurement of levelness

In an earlier study by the authors, it was demonstrated that the between-area variance curves may be employed to analyze and quantify fabric appearance irregularities where the signal contains periodic irregularities (Günay et al., 2007; Suh et al., 2007).

The first task in determining the levelness of a dyed fabric using between-area variance curves is the identification of representative areas for imaging. This is critical, as the confidence level of the conclusions will depend on the number and nature of the sampling.

Next, the dyed sample images may be captured using an instrumentation setup that consists of a light-box (Gretag Macbeth Spectra Light III), a digital camera, and a tripod. While the illuminant D_{65} is incident upon the surface of the specimen by an angle of 45^0, the camera should be perpendicular to the plane of the specimen, as suggested by the AATCC Technical Manual (Evaluation Procedure 9-2007 Option C).

The distance between the camera and the sample and the size of the sample may be adjusted so that the effect of lighting variation is minimized. This relatively simple and inexpensive setup allows one to capture sample images without the shadow of the camera on the sample. Each image is converted into gray scale as it is captured. Depending on the size of the fabric and the desired scale of levelness (micro or macro), users may adjust the sample size and/or resolution.

Finally, each captured image is uploaded into custom developed software to determine the levelness of the sample in an automated fashion. The software auto partitions the fabric image into different grid sizes, calculates the coefficient of variation at different scales, plots coefficient of variation as a function of grid size, and reports a surface irregularity index. The approach summarized above is subjected to a detailed analysis in the sections that follow.

4.5.2.2 Between-area variance curves

Simply put, the between-area variance curves are obtained by calculating the variances of gray scale pixel values, while varying rectangular unit areas within the 2-D gray scale matrix. This 2-D gray scale matrix is constructed from the actual fabric image that is captured using a standard digital camera as described above.

Although there are many ways to choose rectangular unit areas having equal area sizes (Günay, 2005), these unit areas may be considered squares for the purpose of levelness.

Let m be the pixel length and n be the pixel width of the entire virtual fabric matrix. The fabric is first partitioned into unit areas of size A_{1x1} as shown in Figure 16. The between-area variance curve, CB(A_k), is the plot of the coefficients of variation between the varying unit areas $A_{k\times k}$. This relationship is mathematically formulated with Equation 10.

$$CB(A_k) = \frac{100}{\bar{F}_k}\sqrt{\frac{1}{m_k n_k}\sum_{i=1}^{m_k}\sum_{j=1}^{n_k}[F_{i,j} - \bar{F}_k]^2} \tag{10}$$

where CB(A_k) is the between-area variance among the unit areas of size $A_{k\times k}$,

m_k is the number of segments in the x direction, that is $m_k = m/k$,

n_k is the number of segments in the y direction, that is $n_k = n/k$,

$F_{i,j}$ is the value of the property at the cell of at row i and column j (ex; the gray scale pixel value at the cell),

$\bar{F}_k$ is the mean value of the property for all unit areas;

$$\bar{F}_k = \frac{\sum_{i=1}^{m_k}\sum_{j=1}^{n_k} F_{i,j}}{m_k n_k}$$

$m_k n_k$ is the total number of unit areas within a designated fabric matrix.

When the size of each unit area (A_k) increases, the variance within the unit areas increases. Consequently, the coefficient of variation between areas, CB(A_k), decreases asymptotically to zero. While the initial values of the CB(A) curve indicate the level of overall irregularity, the rate with which it drops asymptotically is determined by the correlation among the neighboring unit areas.

Non random appearance defects will exhibit patterns that are easily identifiable by the observer. Defining and measuring levelness as the departure of visual appearance of a dyed fabric from randomness will produce results in agreement with the user's expectation.

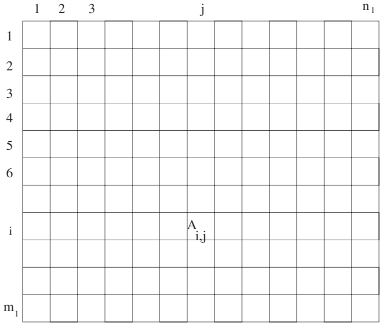

Fig. 16. Fabric matrix unit area 1x1

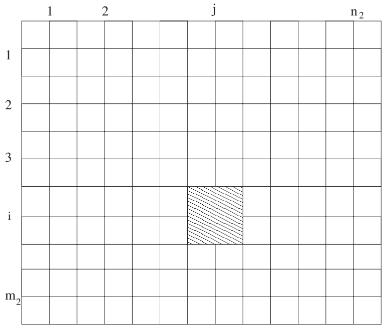

Fig. 17. Unit area 2x2

As a first step, the dyed RGB fabric image is converted into gray scale using the standard RGB to gray scale conversion protocol [GSV = 0.3*Red + 0.59*Green + 0.11*Blue]. It must be noted however that variation in chroma may occasionally be lost during this conversion. The resultant image is then mapped to a fabric matrix as shown in Figure 16. The CB(A_1) is then calculated using the Equation 10. Let $F_{i,j}$ be the gray scale value of a cell located at row i and column j where $i = 1, 2, ...m_1$ and $j = 1, 2, ..., n_1$. If μ is the expected value and σ^2 is the variance of the unit cells whose size is 1×1 and value $F_{i,j}$, then the CB(A_1) is simply:

$$= 100\frac{\sigma}{\mu} \tag{11}$$

If the gray scale values of the neighboring unit cells are independent from one another, when they are merged to obtain unit cells of size $k \times k$ as demonstrated in Figure 17 for 2×2, CB(A_k) equals to:

$$= 100\frac{\sqrt{k^2 \cdot \sigma^2}}{k^2 \cdot \mu} \tag{12}$$

$$= 100\frac{\sigma}{k \cdot \mu} \tag{13}$$

$$= \frac{CB(A_1)}{k} \tag{14}$$

The coefficient of variation between areas will decrease as the unit area size increases for a completely random and isotropic irregular fabric. This is also the theoretical limit when $\sigma > 0$.

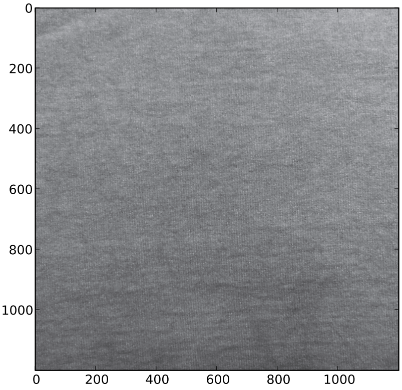

Fig. 18. Gray scale image of fabric sample 8

On the other hand, the CB(A_k) of a real fabric gray scale image matrix would likely produce a CB(A_k) curve above the theoretical limit.
Since levelness is considered a departure from randomness, one can obtain surface irregularity by calculating the ratio of the CB(A) curves of the actual fabric appearance and its theoretical limit as follows:

1. take k as $1, 2, 3, ..., N$ where $N \leq floor(minimum(m,n)/2)$
2. calculate CB(A_k) for each k
3. define surface irregularity (SI) as:

$$SI = \frac{\sum_{k=1}^{k=N}(100\frac{\sigma}{k\mu})}{\sum_{k=1}^{N} CB(A_k)} \tag{15}$$

Note that unless the fabric is completely random $SI > 1$.
Equation 15, k is regarded as the scale factor and N depends on the resolution of the image. Even though k was chosen to be one of $1, 2, 3, ..., N$ in this study, another set of scales may be chosen for optimum results as needed.
Figure 18 shows the gray scale image of a brown colored fabric sample 8. As seen from the image, the levelness information of the dyeing was not lost with the gray scale transformation. Actual and theoretical CB(A) curves corresponding to this fabric sample are overlaid as shown in Figure 19. Due to appearance irregularities that span over several pixels, the actual CB(A) curve does not decrease rapidly despite the increase in the measurement area. The surface irregularity suggested as the ratio of the area underneath the theoretical CB(A) curve over the actual one accounts for the nature of the irregularity demonstrated in Figure 18.
Figures 20 and 21 are the gray scale images of fabric samples 3 and 5. >From the gray scale image of fabric sample 3, it is clear that the dye was not evenly distributed. Overlaid CB(A) curves for these fabrics are shown in Figures 23 and 22. The theoretically projected

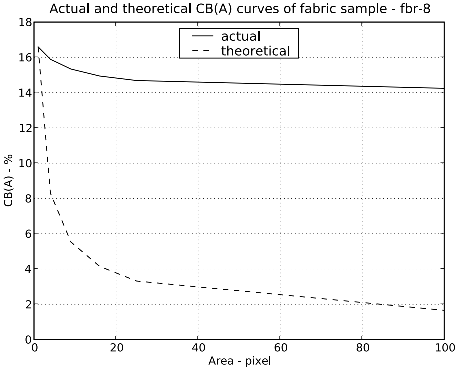

Fig. 19. CB(A) of fabric sample 8

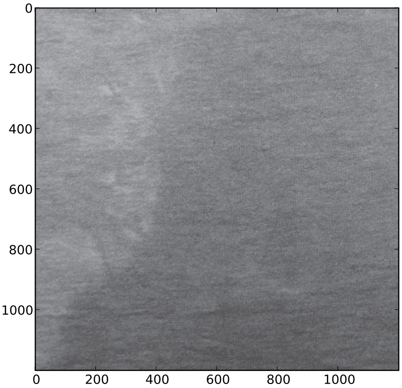

Fig. 20. Gray scale image of fabric sample 3

CB(A) curves do overlay perfectly on top of each other as shown in Figure 22; however, the calculated actual CB(A) curves shown in Figure 23 differ significantly due to practically the same levelness or irregularity of both fabrics at the micro level. But as grid size or scale increases, the levelness becomes more pronounced for fabric sample 3 shown in Figure 20 than fabric sample 5 shown in Figure 21. In other words, fabric sample 3 has irregularity that spans over many more pixels. The increase in the measurement area does not drop the corresponding CB(A) as rapidly as for fabric sample 5. If only the coefficient of variation for unit area size CB(1), 39.97 and 39.74 were used in determining the levelness of fabrics samples 3 and 5 respectively, the conclusions drawn would likely be erroneous.

In order to compare the performance of the proposed levelness measurement with the visual assessment of experts, 8 dyeing samples are identified. Five experienced observers in the field are asked to rate the quality of dyeing for levelness. Currently, there is no standard to visually assess levelness of dyeing. Considering the need to be consistent with the earlier studies and

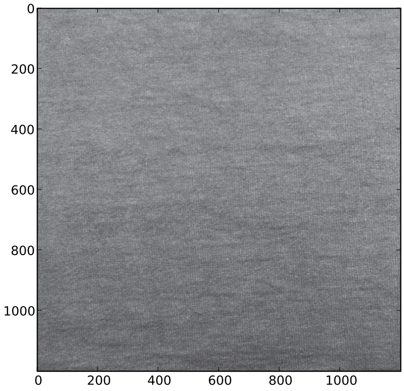

Fig. 21. Gray scale image of fabric sample 5

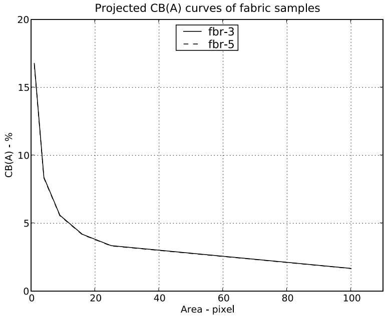

Fig. 22. Theoretically projected CB(A) curves

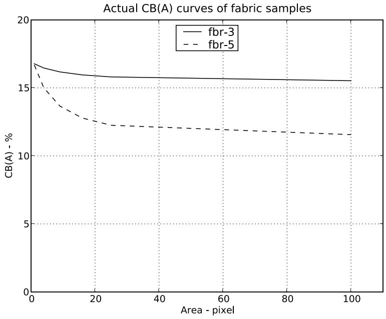

Fig. 23. Calculated CB(A) curves

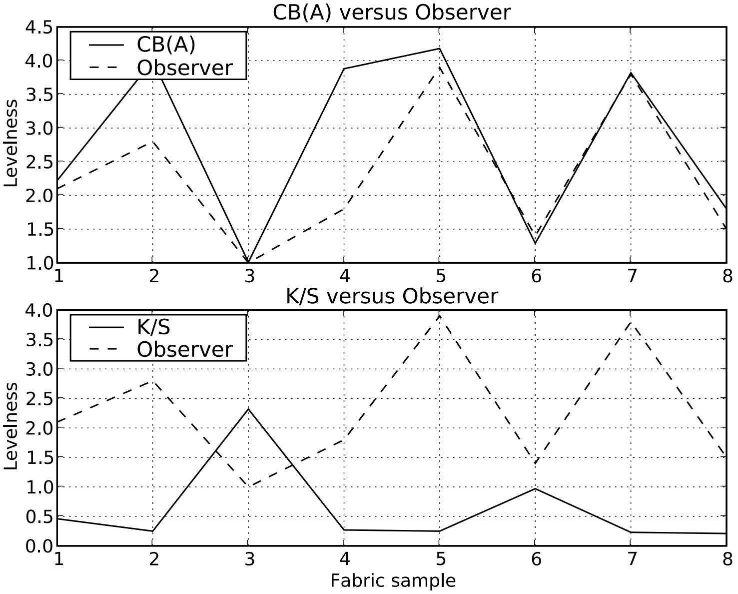

Fig. 24. Observer rating versus levelness calculated by CB(A) and K/S overlaid

to develop a method that is familiar to expert observers, it was decided that a grading system based on gray scale format similar to color difference evaluation would be appropriate.

Meanwhile, using a custom transformation function $44.12 * SI - 17.22$, the surface irregularity calculated using Equation 15 is mapped between 1 and 5 in order to approximate the visual assessment of the observers.

To evaluate performance of the K/S, reflectance measurement is made using a Datacolor spectrophotometer. Fabrics are read at 4 random locations over the visible spectrum ($\lambda = 400 - 700nm$). Levelness index (U) is calculated as follows:

$$U = \sum_{\lambda=400}^{700} S_r(\lambda) V(\lambda) \tag{16}$$

where $V(\lambda)$ is the luminous efficiency at λ, $S_r(\lambda)$ is

$$= \frac{\sqrt{\sum_{\lambda=1}^{n} [(K/S)_\lambda - (\bar{K/S})_\lambda]^2}}{n-1} \tag{17}$$

and $\bar{K/S}$ is the sample mean of K/S at λ.

The results are given in Table 2 and demonstrated in Figure 24. The results show that the observer's gradings agree more with the surface irregularity calculated based on the CB(A) than with the levelness index (U) determined based on the K/S values suggested by (Yang & Li, 1993). This is mainly because; 1) reflectance measurement with a spectrophotometer is highly sensitive to small changes in color, 2) the representative number

Sample #	Observer's Average	CB(1)%	U - K/S	Surface Irregularity
1	2.1	27.05	0.46	2.22
2	2.8	30.40	0.25	4.00
3	1.0	39.97	2.32	1.01
4	1.8	24.61	0.27	3.88
5	3.9	39.74	0.25	4.18
6	1.4	33.11	0.97	1.29
7	3.8	31.81	0.23	3.82
8	1.5	39.54	0.21	1.80

Table 2. Comparison of levelness obtained from the observer, K/S, CB(1) and SI

of sampling using a spectrophotometer is not as convenient as simply taking a picture of a fabric. Vast differences between the observer and the surface irregularity for samples 2 and 4 are due to outlier observer responses.

It is critical to note that the levelness for a large fabric could appear at different scales. Using the proposed methodology, technicians could tackle this issue in the following ways:

1. imaging of a much larger area of fabric using a higher resolution camera,
2. imaging of fabric at distant locations and merging them to form the fabric matrix shown in Figure 16,
3. imaging of fabric at distant locations, determining the levelness of these individual cells, calculating the mean and variance of the quantified levelness.

The methodology developed is practical and resistant to human subjectivity and fatigue since it involves:

1. capturing fabric images using a digital camera under standard lighting conditions,
2. analysis of the fabric sample images with software developed using the surface irregularity function suggested.

Unlike previous methods, the methodology suggested by the author (Günay, 2009) also deals with the issue of levelness at different scales; that is, at micro or macro levels. The superiority of the proposed approach is that the variation is plotted as a function of grid size. Varying grid size acts like varying resolutions or scales. The surface irregularity function proposed adds all these variations at different resolutions to produce a single number. Nevertheless, there will occasionally be cases where the surface irregularity obtained by adding variations at different resolutions will not be sufficient. This is because it is theoretically possible to arrive at the same surface irregularity index by adding a different set of numbers. Although this would seldom occur, researchers are encouraged to investigate and propose solutions to handle such cases.

4.5.3 Waste water check

After the dyeing is completed, collecting the waste water of the dyeing and rinses and measuring the dye amounts flushed allows one to determine the actual dye uptake of the fabric, or in dyers terminology, *the fixation*.

Table 3 shows the cumulative percent amount of dye flushed after each dyeing process for specific reactive dyeing. As given in Table, following the 5th rinse, 56% of the Yellow dye is wasted. By calculating fixation for each stage and analyzing it, one may be able to notice any significant deviation from the expected results and identify potential problems in dyeing.

Stage	Remazol Navy RGB	Remazol Red RB	Remazol Yellow RNL
Exhaustion	13.459	33.553	39.637
Rinse-1	18.513	44.042	51.709
Rinse-2	19.891	46.431	54.38
Rinse-3	21.388	48.215	56.41
Rinse-4	21.848	49.012	56.517
Rinse-5	22.001	49.451	56.09

Table 3. Cumulative dye wasted after each reactive dyeing process step.

5. Benefits of RFT quality control

The batch dyer incurs severe financial penalties if a proportion of batches are not dyed correctly the first time. A color correction added between 24% and 36% to the total dyeing cost of the initial dyed batch, depending on the dye substrate system and the stage of manufacture at which dyeing was carried out. Stripping and re-dyeing increased the initial dyeing cost by between 170% and 200%; however, these are direct costs that do not include indirect costs such as loss in revenue and profit (Park & Shore, 2007). Only a few dye houses worldwide have successfully achieved RFT production by implementing some of the quality control strategies mentioned in this chapter. Hence, there have been relatively few case studies published to describe these projects or to document the success achieved. A number of these dye houses in the US obtained more than 98% first-time-right dyeing by adapting the RFT technologies introduced here while achieving significant cost reductions. In addition to the cost savings obtained by RFT processing, there are several other benefits, including improved quality through shorter processing times, increased productivity from the same equipment and time frame, improved production planning, and less capital expenditure on processing equipment (Park & Shore, 2004). RFT processing is an essential prerequisite to the introduction of automation and robotics.

6. Conclusions

With the recent advances in spectrophotometer and computing technologies, it became feasible to practically and cost effectively measure the dyeing characteristics of dyes in a solution. In this chapter, methodologies are suggested to systematically monitor the quality of incoming materials, including dyes, chemicals, and fibers throughout the dyeing process. Being able to monitor quality control attributes during the dyeing cycle also increases profitability by reducing reworks.

Furthermore, by measuring and quantifying quality attributes, the dyer-customer relationships are likely to improve by fast troubleshooting, correct dispute resolution and accurate technical information exchange.

Although the concept of RFT was never the subject of formalized major R&D projects, it evolved through the foresight, determination, and ultimate success of a relatively few organizations over a considerable span of time in the dye- and machinery-making and - using industries. The author hopes this chapter will lead textile researchers and process engineers to develop additional quality control methodologies in the future, in addition to the ones suggested here.

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8

Commercially Adaptable Coloration Processes for Generic Polypropylene Fiber

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1. Introduction

Polypropylene (PP) fibers belong to the newest generation of large-scale, manufactured chemical fibers, having the fourth largest volume in production after polyesters, polyamides and acrylics [1, 2]. PP is one of the most successful commodity fibers, reaching a world production capacity of four million tons a year. Due to its low density (0.9 gm/cc), high crystallinity, high stiffness and excellent chemical/bacterial resistance, isotactic PP is widely used in many industrial applications such as nonwovens, industrial ropes, packaging materials, furnishing products, etc. PP fiber has potential, high-volume applications in the carpet, textile, apparel and industrial textile markets.

Due to its thermoplastic nature, PP fiber is manufactured using conventional melt spinning. Subsequent multistage drawing imparts tensile strength and enhances mechanical properties required for industrial applications. Synthesis of PP polymer involves stereo-regular polymerization of propylene gas using Ziegler-Natta catalysts [3]. Only isotactic polypropylene is useful for fiber applications among the three stereoisomers. Since only a simple monomer, i.e., propylene gas, is involved in the synthesis of PP, this fiber is relatively inexpensive to produce as compared to other high volume textile fibers such as polyesters, acrylics and nylons. The major products of PP fibrous materials are monofilaments, multifilament yarns, staple fibers and yarns, nonwoven textiles (spunbond, meltblown), tapes, split filament, ropes, carpet backing, etc. Crystallinity of isotactic PP is about 70%, and the molecular weight of fiber grade PP is in the range of 80,000 to 300,000 gm/mole. Since the advent of stereo-regular isotactic polypropylene (PP), the fiber has been used in many industrial applications, as well as in carpets and apparel, due to its high degree of crystallinity, good handle, strength and a high enough melting point for normal use. The potential commercial importance of unmodified polypropylene (PP) fiber in the carpet and textile industries has led to research to develop an aqueous dyeing process for the highly-hydrophobic fiber, consistent with the established coloration processes in use for other high-volume fibers (cotton, nylon, polyester and acrylic). Despite substantial research conducted around the globe, a commercially viable and sustainable aqueous dyeing process of PP based on demand-activated manufacturing has not been realized.

PP offers the advantages of exceptionally low price, good strength and aesthetic properties, along with many other desirable characteristics of a textile/carpet fiber, thus creating the impetus for manufacturing from PP fiber a variety of materials such as towels, floor coverings, sportswear and select technical products. Due to its nonpolar and hydrophobic nature, most of the production of PP fiber is colored by means of mass pigmentation. This route of coloration gives excellent fastness properties during end use; however, it restricts the producer in fulfilling the changing fashion demands of the market. An alternative way of coloring PP fiber exists in which the fiber can be made dyeable by means of post modification, creating active sites for dye association or adding hydrophilic comonomers, but this route has adverse effects on the mechanical properties and costs of the fiber. The development of a truly aqueous process for dyeing PP in its generic, unmodified form is of significant importance vis-à-vis the rising demand for this relatively inexpensive fiber. The developed batch exhaust dyeing methods for PP fiber by us were reported earlier [4-6] and the continuous pad steam and pad/dry heat methods are reported in our recent paper [7]. This chapter covers the state of the art in PP dyeing as well as our adopted approach to develop a commercially viable coloration process for unmodified PP fiber in conventional aqueous systems.

2. Coloration of PP fiber

The major portion of colored PP fibers is currently manufactured by melt pigmentation (called spun dyed fibers) [8]. Melt pigmentation involves the addition of pigment particles in the polymer melt prior to extrusion and fiber spinning. Melt pigmentation can be performed in various ways. Pigments can be added to the pre-melted fiber polymer, or it can be mixed with the chips (also known as chip pigmentation) in order to produce melt pigmented PP fibers.

2.1 Different methods to aqueous dye PP fiber

Three general approaches to aqueous color PP fiber are reported in the literature [9]:

a. Attempts to color unmodified PP fiber with modified dyeing methods.
b. Modification of the fiber surface to create dye receptive sites.
c. Copolymerization and graft copolymerization.

The influence of dyestuff constitution and auxiliaries in the dyeing of unmodified PP has been studied by Herlinger et al.[10] The authors determined that the use of toluene and p-xylene as carriers, together with some anthraquinone disperse dyes having longer alkyl groups, improved the fixation of dyes into PP fiber by increasing the intermolecular forces between dye and fiber.

Oppermann et al. [11] reported the synthesis of disperse dyes with alkyl substituents of varying lengths and dyed unmodified PP with them at a high temperature (125°C) for 150 min. Wash fastness of the dyed samples increased on increasing the chain length of the alkyl substituent; however, the levelness also decreased. An octyl substituent proved an optimum length for good fastness and levelness properties.

Stright et al. [12] reviewed different ways to dye PP including the development of new dyes which were fixed in the fiber by formation of dye-metal complexes on the metal-containing PP fiber, resulting in adequate dyeings in a variety of shades. Dye-metal complex forming dyes could be applied to a wide variety of materials utilizing standard dyeing techniques.

Reactive modification involves treatment of PP fiber with certain chemicals in controlled-conditions [9]. This type of modification increases costs in excess drying, handling, recovery of materials and operational steps. The treated fibers also showed ring dyeing and inferior physical properties. Reactive modification is thus not a commercially viable option.

Incorporating dye receptive groups in a polymer chain is known as copolymerization, whereas attaching a segment of a dye receptive group as a side chain is termed graft copolymerization [9]. Several disadvantages are associated with the copolymerization of PP:

a. Copolymerization of PP with polar compounds gives low efficiency.
b. Polar compounds impede the crystallization behavior of PP and also decrease the melting point of the polymer.
c. Copolymerization adversely affects the physical and mechanical properties of the polymer.

Graft copolymerization was more technically appealing in the case of PP, but the expensive technology was considered as a barrier to the commercial adaptation [9].

2.1.1 Addition of dye receptors

Addition of dye receptor additives prior to fiber extrusion has been explored by many researchers [9]. Three different classes of these additives are:

a. Metallic compounds
b. Polymeric additives
c. Low molecular weight organic and inorganic compounds

The additive approach can be divided into four major areas of research involving the development of:

a. Disperse dyeable fiber using major disperse, vat and azoic dyes
b. Disperse dyeable fiber using mordant disperse dyes
c. Acid dyeable fiber using anionic dyes used for wool
d. Basic dyeable fiber using cationic dyes

Brown et al. [13] reported disperse and acid dyeable olefin fibers. The dyeable olefin fiber was prepared in two ways: (a) formed a blend of alpha-monoolefin polymer and 1-5% by weight of a pyridine type polymer dye receptor which led to disperse dyeable PP fiber; (b) formed a blend of less than 97% by weight of alpha-monoolefin polymer, 0.5-5% by weight of pyridine type polymer dye receptor and 0.5-5% of hydrophilic compound containing ethylene oxide units. The resultant fibers were dyeable by both anionic and disperse dyes. The approach was to dye the uniformly-dispersed additives so that the whole fiber appeared colored. This approach was found much easier and efficient than fiber pretreatments, copolymerization or grafting, and also less harmful to the fiber's physical properties.

2.1.2 Disperse dyeable PP fibers

The advantages of disperse dyeable PP fibers were:

a. The availability of a wide range of disperse dyes, eliminating the requirement of developing new dyes.
b. The leveling properties of disperse dyes were excellent.
c. Vat and azoic dyes could also be used after a slight modification in the process.
d. The result was excellent wash fastness due to water insolubility.

Grafting of dye enhancers to the polyolefin polymer has been reported by Negola et al. [9, 10]. A mixture of amorphous PETG (glycol-modified polyethylene terephthalate) was grafted onto polyolefin. Maleic anhydride was added to increase the cohesion and dispersion of amorphous PETG in polyolefin polymer. A formulation of 50% PP, 48%

amorphous PETG and 2% maleic anhydride was used and the resultant pellets were extruded into fiber form. A 5% disperse dyeable mixture grafted onto 95% PP resulted, which upon dyeing yielded deep shades, whereas a 2.5% disperse dyeable mixture onto 97.5% PP yielded light shades.

Addition of polymeric dye receptors has been investigated by Farber et al. [14] and Dayioglu et al. [15]. Disperse dyeable PP fiber was manufactured to be consumed in the carpet industry. The approach involved addition of selected polymeric compounds into the PP melt prior to extrusion. Certain limitations of using polar polymeric compounds exist:

a. Subsequent spinning and drawing operations become difficult because most of the polar polymeric compounds lack compatibility with PP.
b. As the polarity of admixing compounds increases, their compatibility with PP decreases. Therefore, polyamides and polyesters with strong polar groups are less compatible with PP than polystyrene and ethylene copolymers.
c. The melting point of most polar compounds is higher which requires a high processing temperature, resulting in the degradation of PP.
d. Many polymeric additives suitable for processing purposes do not have enough polarity to give adequate wet- and dry-cleaning fastness.
e. Most of the polymeric additives require amounts over 10% to be incorporated into the PP fiber to achieve satisfactory dyeability. Large quantities of incompatible and partially-miscible additives adversely affect the physical and mechanical properties of the resulting fiber.
f. The fiber is more costly than the generic version.

In relation to the above challenges, the selection of an appropriate PP additive with all-round adequate properties becomes difficult. An ideal polymeric additive for PP should possess polar groups lying pendant to its chain, be slightly crystalline in nature, have partial compatibility with PP, have a melting point greater that 140°C and have a glass transition greater than 90°C. Polymers such as saturated linear copolyesters, copolyamides, copolymers of vinyl pyridines with styrene, copolymers of ethylene with vinyl acetate and alkyl acrylate may work as such ideal additives.

In conclusion, disperse dyeable PP fibers are comparatively easy to produce and result in level dyeings, although they are more expensive than the generic fiber (usually >$1.00/lb. premium). However, the fastness properties of the dyed materials do not meet all the requirements of the textile and apparel businesses, especially due to their poor dry-cleaning fastness to perchloroethlene (PERC). In addition, a similar chlorinated solvent (trichloroethylene) is commonly used as a spot cleaning agent in carpets, both in manufacturing and in residential/commercial use. The shades obtained by acid and basic dyes are also brighter than those obtained with disperse dyes.

FiberVisions recently launched CoolVisions® (a disperse dyeable PP fiber) [16] having a dye receptor as an encapsulated additive in the polymer matrix. The dye receptor additive is an amorphous, low molecular weight copolyester. A compatibilizer is finely distributed and encapsulated in the microstructure of PP [17]. The modified PP fibers are manufactures by sheath-core bicomponent spinning consisting core as dye receptor and sheath material as PP.

2.1.3 Acid dyeable PP fibers

The advantages of acid dyeable PP fibers include [9]:

a. Acid dyes are inexpensive, offering a wide range of shades with bright colors.
b. Light fastness is excellent.

While most of the acid dyeable PP fiber versions have failed in the development stage itself due to their lack of commercial viability, some of them have shown limited commercial success. Those which have shown commercial success include acid-dyeable PP fiber from Montecatini (Mercalon D®), Hercules (Herculon® Acid Dyeable), Beaunit, Phillips and Toyobo. Out of these, Mercalon D® was dyeable with almost all anionic dyes up to dark shades. Mercalon D® is presently available as a staple fiber for carpets and knitting yarns. Merkalon D®'s use is increasing because its dyeing profile is similar to that of wool. Merkalon D® has a leveling problem in piece dyeing because of its high affinity to acid dyes and high rate of dyeing. Apart from a few limitations and high cost per pound, Merkalon D® fiber appears to have achieved the status of a commercial, general purpose fiber in the carpet and knitting industries.

Arkman et al. [18] reported the mixing of an additive in the PP polymer prior to fiber extrusion. The additive was synthesized by attaching long alkyl chains having substituents such as alkaline nitrogen to a rigid polymer backbone. They found a diffusion coefficient of dyeing in the order of 10-11 m^2/s, which indicated very fast diffusion of the acid dye molecules into the modified fiber driven mainly by the electrostatic interaction between the anionic acid dye and basic dye sites in the polymer contributed by the additive.

The use of Koprolene colors (dyes having a metal chelating group) for modified PP fibers containing nickel salt stabilizer has been reported by Baumann et al., [19] and has demonstrated attractive shades with excellent fastness properties to washing, dry-cleaning, crocking, light and gas fading. The scoured yarn or fabric was recommended to be dyed at 190 to 200^{o}F for one hour and finally to be washed.

2.2 Dyeing mechanism of PP fibers

Since none of the commercially-dyeable PP fiber was available long enough to explore its dyeing behavior [9], only a few scattered studies were reported. The dyeing of hydrophobic fibers with disperse dyes takes place through the solid solution mechanism, i.e., the dye forms a solution within the amorphous region of the polymer. The dye mass transfer from dyebath to the fiber phase is governed by the partition coefficient of the dye. Bird and Patel [20] have shown that the introduction of additional dye into the dye bath beyond the saturation point of the fiber phase did not increase the amount of dye inside the fiber.

Since generic, isotactic PP fiber has only ~30% amorphous mass accessible to dye molecules, the saturation value is low. The encapsulation of a suitable dye receptor additive into the PP matrix causes the amorphous regions of the fiber to increase, leading to the availability of more solvent for the dye to form a solid solution, and thus increasing the saturation values of the fiber. However, the physical properties of the PP fiber, e.g., the percent crystallinity, are lowered when additives are occluded in the solid state structure, and since the cost of the fiber is also increased, both factors detract from use of the modified fiber in textile/carpet products.

2.3 Dyeing of unmodified PP

Calogero et al. [21] reported dyeing of unmodified PP fibers using a colloidal emulsion of water plus long-chain, alkyl-substituted anthraquinone dyes dissolved in an organic solvent. Alkyl chains with carbon numbers from 8-18 were described, and the 18 chain length was found as ideal for PP. The ideal dyebath temperature was reported as 90^{o}C. The dyeing resulted in uniform coloration of the PP fibers with excellent fastness to washing, crocking and dry-cleaning.

Vat dyes captured a large part of the dyestuff market in the coloration of cellulosic fibers because they provide excellent all-round fastness, particularly to light, washing and chlorine bleach. Because of their insoluble nature in the oxidized form, vat dyes require a complicated application procedure involving the reduction of the oxidized form into first the leuco form and then with base into the more water-soluble alkaline leuco form. The soluble, reduced alkaline leuco form has high substantivity towards cellulosic fibers, and after levelness is achieved, the dyes are re-oxidized into the original, water-insoluble keto form inside the fibers.

Sodium dithionite and sodium hydroxide produce large amounts of sodium thiosulfate and sulfites as a byproduct, increasing the cost of effluent treatment. Roessler et al. [22] reported electrochemical methods for reduction of vat dyes which are environmentally friendly, thus providing an alternative to the use of sodium dithionite and sodium hydroxide.

A. V. Mishchenko et al. [23] investigated the batch exhaust dyeing of staple PP fiber at 100^{o}C and 80^{o}C with the acid leuco vat dyes thioindigo red S, thioindigo reddish brown Zh and thioindigo red S (actual chemical structures were not revealed). They plotted a dye exhaustion curve (dye adsorption versus dyeing time) and calculated the heat of dyeing and entropy of dyeing. The heat of dyeing was observed as negative, indicating the strong interaction between the acid leuco vat dye and the PP fiber. The measured heat of dyeing of acid leuco vat dye on unmodified PP was of the same order as that in the disperse dyeing of PP fiber.

The authors also investigated the effect of heat treatment [24] on the fixation of acid leuco dyes on PP fiber. The process sequence involved padding of PP fiber with the acid leuco vat dye solution, squeezing, drying and then treating with dry heat for 1 to 10 minutes. The authors noted that the heat treated fibers resulted in better fastness properties, and thus demonstrated that the heat treatment helped in the fixation of dye molecules via diffusion. The rate of dyeing increased on subsequent heat treatment.

Morozova et al. [25, 26] investigated the process of developing the leuco esters of vat dyes on PP fiber by a nitrite method and optimized the development conditions for maximum color yield:

Temperature: 60^{o}C; development time: 40 min.; liquor ratio: 50; liquor composition: 12.5% H_2SO_4, 2.2 g/l $NaNO_2$. The authors obtained satisfactory light and weathering fastness for the PP dyed with leuco-ester of Vat Brilliant Green S [26].

Bird and Patel [20] studied the dyeing of unmodified PP yarn and film with disperse dyes and concluded that no fundamental difference existed between PP and other substrates in the diffusion mechanism. They showed the Nernst isotherm partition mechanism of dye adsorption between fiber and aqueous phase, which was similar to that followed in the disperse dyeing of polyester fiber. Unmodified PP is more crystalline, nonpolar and hydrophobic than other synthetic fibers [20]. Moreover, the absence of hydrogen bonding groups in PP also precludes the fiber from attaching to the diffused dye molecules, resulting in the poor saturation values. Further, diffusion coefficients of disperse dyes in PP were higher than in cellulose acetate fibers, indicating that diffusion of the dyes inside the PP fiber was not the reason of poor saturation. Weak intermolecular interactions between disperse dyes and PP were concluded to be the reason for the poor saturation values.

According to Ulrich et al. [27], vat dyes when applied in their oxidized or vat acid forms in a colloidal state of dispersion under proper temperature conditions diffuse into highly hydrophobic fibers. Three methods of vat dye application on unmodified polypropylene fibers were employed: Exhaustion, pad-steaming and printing with steam fixation. Burkinshaw et al. [28] investigated dyeing of textile fibers including: segmented polyurethanes, segmented polyurethane ureas and segmented polyetheresters; polyesters including poly(tetramethylene terepthalate); polyamides including poly(hexamethylene adipamide); and polycaprolactam with acid leuco vat dyes utilizing alpha-hydroxyalkylsufinic acids, their salts and 1, 2, 4-trithiolane as additional reducing agents. The authors reported excellent depth of shade and wash fastness for the dyed materials.

Etters et al. [29] reported that several vat dyes in their acid leuco form exhibited substantivity to unmodified, knitted PP fabrics with C. I. Vat Blue 1, Vat Orange 1 and Vat Yellow 2. Gaehr et al. [30] reported that several Colloisol® vat dyes of BASF exhibited good affinity on plasma-pretreated PP fiber in a pigment pad-thermofix process at 120°C. The fixation of pigments was performed in a pad-steam or pad-dry heat process, and the processes were reported to be applicable for dyeing of fiber mixtures containing PP.

3. Literature review summary and scope of the research

From the literature review, the substantial volume of work conducted by researchers of different laboratories world-wide confirmed that the aqueous dyeing of generic, unmodified PP fiber is of significant importance for textile, carpet, apparel, sportswear and a variety of other product applications. Most of the work carried out by researchers included the modification of PP fiber in some form or another, paths which although they impart dyeability, increase the total fiber costs two to three times above that of generic PP because of utilization of a variety of modifying chemicals, additives, comonomers or components. Another disadvantage of the fiber modification route is that it adversely affects the mechanical and physical properties of the fiber. The low cost and good physical/aesthetic properties, the two basic motivations for utilizing generic PP fiber in textiles and carpets, have been outweighed by the disadvantages and limitations of modifying the fiber solely to impart aqueous dyeability.

The primary purpose of the aqueous dyeing of PP fiber in its generic, unmodified form is to exploit the advantages this fiber offers to the market place and, at the same time, create new product markets for this inexpensive fiber in high volume consumption areas such as tufted carpets, towels, apparel, sportswear and technical textiles. These product markets are governed today by demand-activated manufacturing, and hence can only be realized by developing flexible, aqueous batch and continuous dyeing processes for generic PP consistent with commercially-established coloration technologies already in use for other high-volume, commodity fibers.

4. Technical approach

The coloration of cellulosic fibers with vat dyes is well established [31]. However, hydrophobic fibers such as PP are not dyeable by the conventional, aqueous-based methods which are successful for cellulosic fibers in which the alkaline leuco, dianion form (completely water soluble) of vat dyes is utilized. Theoretically, acid leuco vat dyeing analogous to the disperse dyeing of polyester fiber may provide a method to aqueous color unmodified PP fiber. Etters et al. [29] among others [23, 24, 27] reported the acid leuco vat dye route as a potential path to aqueous dyed PP fiber in its unmodified form.

Recently, researchers [32, 33] investigated the process of dyeing polyester with indigo vat dye utilizing the non-ionic, acid leuco form of indigo (sparingly water soluble) to dye polyester fabrics and obtained good fastness results by optimizing the concentration of sodium hydroxide and sodium hydrosulphite. The authors noted that using excess sodium dithionite eliminated the need to back-titrate with acetic acid to achieve the acid leuco form of the vat dye [32].

The correlation between dye exhaustion and the solubility parameter for PLA fiber and disperse dyes has been reported by Karst et al. [34, 35] , who showed that the closer the solubility parameter of the dye was to the fiber, the better the exhaustion of the dye. Solubility parameter (SP) is the square root of the cohesive energy density. SP of the PP and commercially available vat dyes were calculated using the Fedors group contribution method [36]. Dyes having SP values closest to that of PP were given priority in this research. Calibration curves for each dye were prepared using UV/Vis NIR Spectrophotometry. The single stage, acid leuco vat dyeing process was utilized to dye the PP flat fabric. Various mixing parameters (Flory-Huggins interaction parameter and free energy of mixing) were predicted using Accelrys' Materials Studio® software. Dyes having the least free energy of mixing with PP were given priority in the experiments.

Exhaust batch dyeing experiments were conducted on a single bath Roaches Colortec® High Temperature Dyeing Machine at Georgia Tech, as well as on a Roaches Pyrotec Multi-Beaker Dyeing Machine at the University of Georgia, utilizing the optimized, single stage acid leuco dyeing procedure. Percent exhaustion was measured to evaluate the efficacy of each dye.

Dyed fabrics were evaluated for various fastness properties (washing, crocking and dry-cleaning) in order to certify the viable vat dye candidates. The impact of the dyeing process on the solid state structure of PP was investigated using X-ray diffraction and tensile testing. Rate of dyeing plots were prepared for the single dyeings as well as for combination dyeings. Adsorption isotherms were prepared to calculate the thermodynamic parameters of dyeing for single colorants. The K/S values of the dyed samples were determined.

In order to perform the continuous steam-pad dyeing, the PP fabric was dipped and squeezed into the solutions 2-3 times to perform the padding operations using dye pad and chempad formulations. The developed, optimized pad-steam process sequence for simulated continuous pad/steam coloration of unmodified PP fabric with acid leuco vat dyes was based upon the method first described by Ulrich et al. [27]. The fabric was padded into the dye pad formulation, dried in a convection oven, padded with the chempad formulation, steam-fixed in the lab box steamer and finally cold-rinsed, soaped, washed and air-dried.

The simulated continuous pad-dry heat process was based on the diffusion of acid leuco vat dye molecules into the swollen amorphous regions of the PP fiber at a temperature of 130°C. The PP fabric was padded into the vat acid formulation, the excess squeezed out by hand, and the saturated fabric placed into a forced convection oven at 130°C for 10 minutes.

5. Results and discussion

5.1 Solubility parameter calculations

The chemical structures of oxidized vat dyes were obtained from the Colour Index, 1971 Edition [37]. The chemical structures of the corresponding reduced acid leuco vat dyes were determined using the general hydrosulfite/hydroxide reaction. The Fedors group contribution method was applied after structural analysis of the acid leuco vat dyes to compute the solubility parameter. The table of atomic and group contributions to energy of vaporization and molar volumes from Fedors was used in this computation [36].

Table 5.1 shows the calculated solubility parameters (SPs) for oxidized and reduced vat dyes in which Vat Red 15, Vat Orange 7, Vat Yellow 2, Vat Blue 18 and Vat Orange 1 have the lowest values. The solubility parameter of PP was calculated to be 8.1 $(cal/cm^3)^{1/2}$. Since Vat Red 15 and Vat Orange 7 are cis- and trans- isomers, respectively, the two molecules yielded equal solubility parameters.

C.I. Name of Dye	C. I. Constitution Number	Calculated SPs $(cal/cm^3)^{1/2}$ for Keto Form	Calculated SPs $(cal/cm^3)^{1/2}$ for Acid Leuco Form
Vat Red 1	73360	13.9	16.0
Vat Yellow 2	67300	13.7	15.0
Vat Blue 6	69825	15.3	18.6
Vat Orange 1	59105	13.0	14.6
Vat Blue 1 (Indigo)	73000	13.9	16.7
Vat Brown 1	70800	15.5	19.3
Vat Red 15	71100	14.2	14.4
Vat Yellow 33	65429	14.3	16.0
Vat Red 13	70320	13.4	14.8
Vat Orange 7	71105	14.2	14.4
Vat Yellow 4	59100	13.6	15.6
Vat Violet 1	60010	12.1	14.8
Vat Violet 13	68700	14.9	16.6
Vat Black 27	69005	15.1	17.5
Vat Green 8	71050	15.3	19.1
Vat Orange 2	59705	13.4	14.8
Vat Blue 18	59815	13.1	14.5
Vat Green 1	59825	13.5	14.9
Vat Red 10	67000	15.1	18.4
Vat Orange 15	69025	14.6	16.7

Table 5.1. Calculated Solubility Parameters of Vat Dyes Using Fedors' Method [36]

5.2 Chemistry of acid leuco dyeing

The four stages of reduction of C. I. Vat Orange 1 dye (Fig. 5.1) indicate that excess sodium hydrosulphite acts as an acid in addition to being a reducing agent for the carbonyl groups, and the chemical thus converts the alkaline leuco form of vat dye (II) into first the monoioninc leuco form (III) and, with further addition of sodium hydrosulphite, into the nonionic (acid leuco) form (IV):

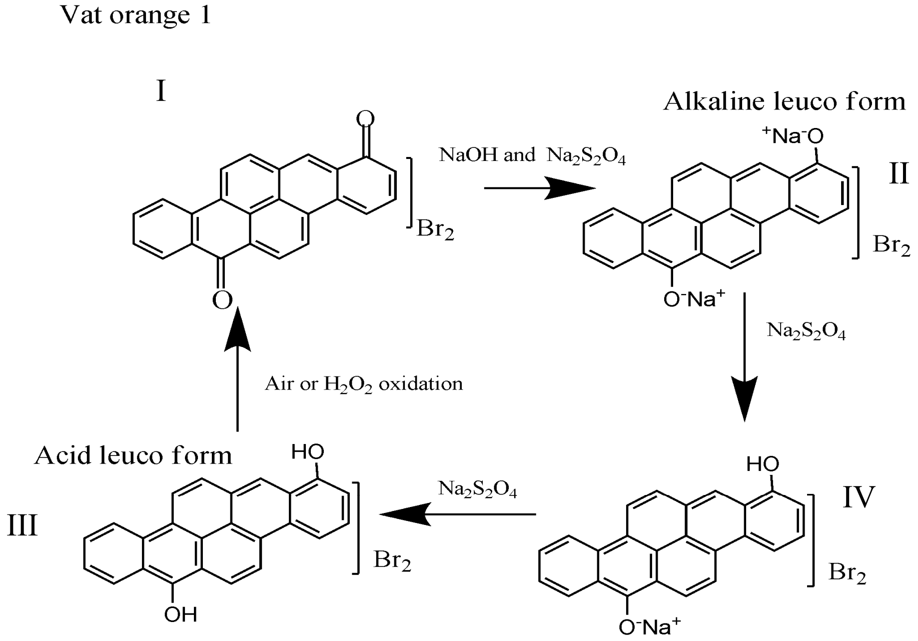

Fig. 5.1. Various Stages of Conversion of Vat Orange 1 from the Keto to the Acid Leuco Structure: (I) Original Keto Structure; (II) Alkaline Leuco; (III) Monoionic; and (IV) Acid Leuco

The neutral acid leuco form has been reported as having affinity with hydrophobic fibers such as polyester and PP [27, 32, 33].

5.3 Chemical structures of vat dye candidates for the PP single-stage, acid leuco vat dyeing process

Figure 5.2 shows the conversion of a vat dye into its acid leuco form with the action of sodium hydroxide and excess sodium hydrosulphite. The acid leuco forms were utilized to calculate the solubility parameters of the vat dyes using Fedors' group contribution method (Table 5.1).

From the Colour Index search, the chemical structure of C. I. Vat Blue 8 deemed it a candidate for the dye trichromatic series (Figure 5.2 e). The SP for Vat Blue 8 was calculated in its acid leuco form to be 15.4 (cal/cc)$^{1/2}$, which was lower than those of Vat Blue 6 (18.6 (cal/cc)$^{1/2}$) and Vat Blue 1 (16.7 (cal/cc)$^{1/2}$). The predicted mixing energy was also much lower for Vat Blue 8 (10.2 kcal/mole) than Vat Blue 6 (22.1 kcal/mole), further strengthening the theory that Vat Blue 8 could be a more viable performer than Vat Blue 6 in the trichromatic series. However, an exhaustive search of dye vendor sources revealed that Vat Blue 8 is currently not commercially available on the world market, thus precluding its experimental confirmation as a viable vat blue colorant for generic PP.

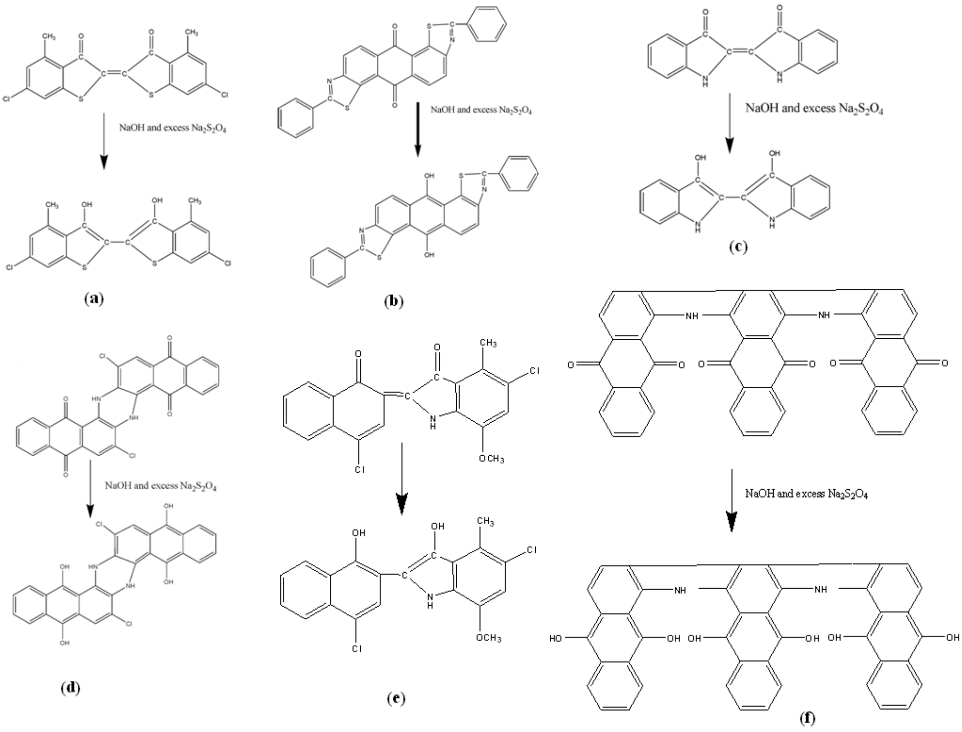

Fig. 5.2. Conversion of Oxidized Vat Dye Keto Structures into Reduced Acid Leuco Structures: (a) Vat Red 1; (b) Vat Yellow 2; (c) Vat Blue 1 (Indigo); (d) Vat Blue 6; (e) Vat Blue 8; and (f) Vat Brown 1

5.4 Predicted free energy of mixing of acid leuco vat dyes at 90°C using accelrys' materials studio® software

Mixing energies of different acid leuco vat dyes with isotactic PP chain of DP=10 were predicted using Accelrys' Materials Studio® (MS) software. The Blends Analysis Feature of the MS software was used to perform dye-PP mixing simulations. The results in Figure 5.3 demonstrated that the dyes C. I. Vat Blue 1, Vat Blue 8, Vat Red 1, and Vat Blue 6 had the lowest free energy / interaction parameters of mixing with PP. Vat Orange 1 and Vat Yellow 2 were intermediate in the parameters, while Vat Brown 1 had the highest free energy / interaction parameter of mixing. Vat Brown 1 was thus predicted to have poorer interactions with isotactic PP and resulting poorer exhaustion and color strength (K/S value) properties than the other dye candidates, predictions that were later confirmed by the exhaust batch dyeing experimental data.

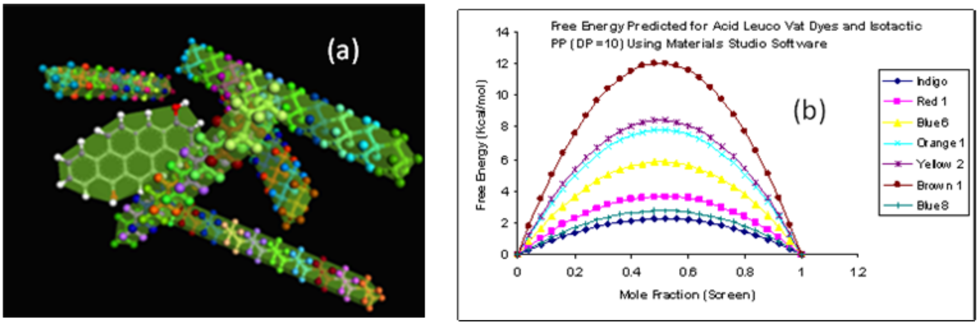

Fig. 5.3. (a) 3-D space Configuration of Vat Orange 1 Interacting with Isotactic PP in Materials Studio Workspace; (b) Free Energy vs. Mole Fraction of Different Dyes with PP at 363°K Predicted Using Materials Studio® Software

5.5 K/S value determinations

The Ultrascan XE sensor was standardized using a light trap and the standard white tile. The sensor was tested for accuracy before PP fabric measurements by scanning the diagnostic green tile, and then comparing the X, Y, Z tristimulus values obtained with the values printed on the green tile. Ten readings taken at different places were recorded for each of the dyed fabric samples, and the average of the ten readings was computed to derive the K/S value for each sample at the wavelength of minimum fabric reflectance. The K/S results in Table 5.2 revealed a correlation with the blend miscibility approach for the candidate six vat dyes, e.g., C. I. Vat Brown 1 gave the least color transfer onto the PP fabric due to its very high solubility parameter/mixing energy.

C.I. Name of Dye	Wavelength of Minimum Reflectance (nm)	K/S at Wavelength of Minimum Reflectance	SP (Acid Leuco Form) $(cal/cm^3)^{1/2}$
Vat Red 1	510	4.4	16.0
Vat Blue 6	600	3.9	18.6
Vat Yellow 2	420	2.1	15.0
Vat Orange 1	440	5.0	14.6
Vat Blue 1	640	6.1	16.7
Vat Brown 1	400	1.7	19.3

Table 5.2. Final K/S Values of PP Fabrics Colored by Single Stage Vat Acid Leuco Dyeing Method (8% owf)

The K/S versus % owf plot detailed that for all dyes, increasing the amount of colorant in the dyebath resulted in a gradual color buildup on the dyed fabric, followed by saturation (Figure 5.4). K/S values of the colored fabrics with the colorants of the trichromatic series plus orange exhibited similar K/S plots, whereas those dyed with Vat Blue 1 exhibited much higher K/S values, reinforcing the compatibility of the component colorants of the trichromatic series plus orange colorants in PP fabric dyeing, along with the incompatibility of Vat Blue 1 with the group.

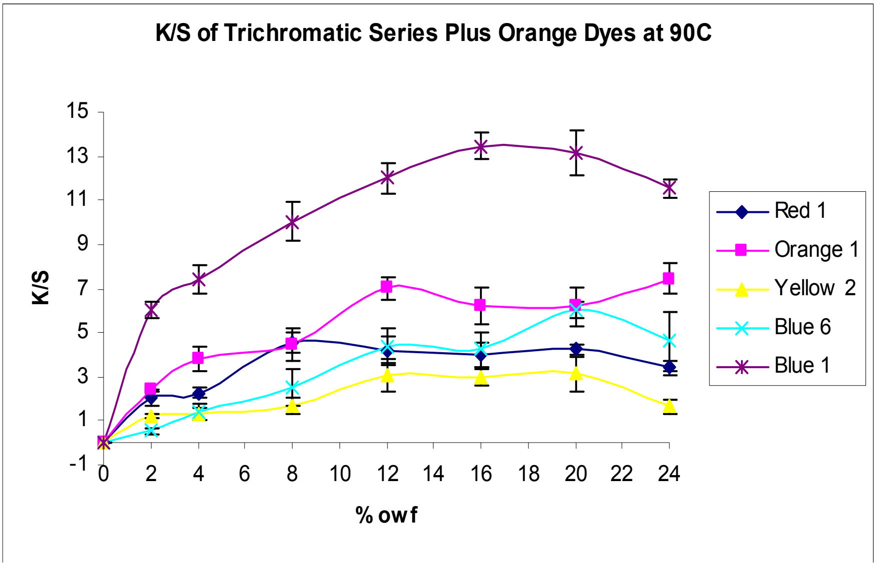

Fig. 5.4. K/S Values at Wavelengths of Minimum Reflectance versus % owf for Acid Leuco Vat Dyed PP Fabrics

5.6 Correlation of experimental K/S values with calculated acid leuco dye solubility parameters and predicted mixing energies

Figure 5.5 showed the correlation between K/S values of dyed PP fabrics and calculated SP/predicted mixing energies of six acid leuco vat dyes. Upon increasing solubility parameter and mixing energy from Vat Blue 1 to Vat Brown 1, the K/S value decreased. This correlation demonstrated the viability of the theoretical approaches (calculated SP and predicted mixing energy) to screening viable vat dye candidates for the coloration of generic PP.

The predicted mixing energy for Vat Orange 1 was high, but the corresponding high experimental fabric K/S value and low acid leuco vat dye SP value created an anomaly (Figure 5.5). The discrepancy was explained by the more complicated, high molecular weight chemical structure of C. I. Vat Orange 1 compared to the other certified dyes (MW = 468 g/mole, six fused aromatic rings in a benzenoid structure with a plane of symmetry running through the molecule, a dibromine salt, etc., Figure 5.1). Figure 5.3(a) models the difficulty in placing the Vat Orange 1 molecule within the polymeric chains of PP in the amorphous regions. In addition, utilizing the “like dissolves like” rule of organic chemistry and designating PP as the solvent and the Vat Orange 1 as the solute, the highly aromatic nature of the dye dictates poor compatibility with the aliphatic PP chains. Utilizing these two factors, the Materials Studio® Software predicted a comparatively high mixing energy between PP and Vat Orange 1 (Figure 5.3(b)). With the experimentally-observed high K/S value for the dyed fabric, however, the low SP of Vat Orange 1 (14.6 (cal/cc) $^{1/2}$) was a more accurate predictor of the good compatibility of the colorant with PP than was the mixing energy (Figure 5.5).

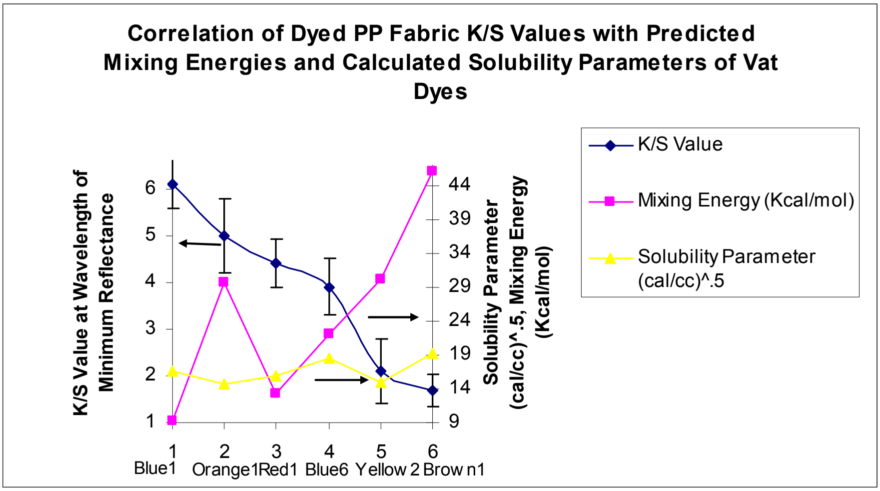

Fig. 5.5. Correlation of Dyed PP Fabric K/S Values with Calculated Acid Leuco Dye Solubility Parameters and Predicted Mixing Energies

5.7 Evaluation of fastness properties

5.7.1 Fastness to crocking

Crock fastness was determined using the electronic crock meter with 10 complete cycles in both dry as well as wet conditions according to AATCC Standard Test Method 8-2004. Vat Blue 6 exhibited less resistance to crocking as it stained the cotton cloth square to a rating of 3-4, whereas Vat Orange 1, Vat Red 1, Vat Blue 1 and Vat Yellow 2 all showed good to excellent crocking resistance (Table 5.3). The higher crock fastness ratings in the wet condition to that of the dry condition was attributed to the reduction in the frictional force between the low surface energy PP fabric and the rubbing finger of the crock meter caused by the lubricating effect of water at the interface.

C.I. Name of Dye	Staining Rating	
	Dry	Wet
Vat Orange 1	4	4-5
Vat Yellow 2	4-5	4-5
Vat Blue 6	3-4	4
Vat Red 1	4	4-5
Vat Blue 1	4	4

Table 5.3. Crock Fastness Ratings of PP Fabrics Dyed with Certified Vat Dyes

5.7.2 Fastness to washing

Wash fastness of the dyed materials was determined by AATCC Standard Test Method 61-2003, no. 2A. The fastness ratings (Table 5.4) revealed that Vat Orange 1 exhibited excellent wash fastness on the PP fabric, whereas the other vat dyes yielded good, acceptable wash fastness properties to the PP fabric.

C.I. Name of Dye	Change in Color	Staining on the Various Components of Multifiber Fabric Style # 10					
		Acetate	Cotton	Nylon 66	Polyester	Acrylic	Wool
Vat Orange 1	5	5	5	5	5	5	5
Vat Yellow 2	5	4-5	4-5	5	4-5	5	4-5
Vat Blue 6	5	4-5	4-5	4-5	4-5	4-5	4-5
Vat Red 1	5	4-5	4-5	4	4-5	4-5	4-5
Vat Blue 1	5	4-5	5	4	4-5	5	4-5

Table 5.4. Wash Fastness Ratings of PP Fabrics Dyed with Certified Vat Dyes

5.7.3 Fastness to dry-cleaning (Perchloroethylene)

Dry-cleaning fastness of the dyed materials was determined by AATCC Test Method 132-2004. The fastness ratings confirmed that all of the certified vat dyes imparted good, acceptable dry-cleaning fastness properties to dyed PP fabric (Table 5.5).

C.I. Name of Dye	Change in Color	Staining on the Various Components of Multifiber Fabric Style # 10					
		Acetate	Cotton	Nylon 66	Polyester	Acrylic	Wool
Vat Orange 1	5	5	4-5	4-5	4-5	4-5	4-5
Vat Yellow 2	5	4-5	4-5	4-5	4	4-5	4-5
Vat Blue 6	5	4-5	4	4	4	4	4-5
Vat Red 1	4-5	5	4	4-5	4-5	4-5	4-5
Vat Blue 1	4-5	4-5	4	4-5	4-5	4-5	4

Table 5.5. Dry-Cleaning Fastness Ratings of PP Fabrics Dyed with Certified Vat Dyes

C.I. Name of Dye Change in Color Staining on the Various Components of Multifiber Fabric Style # 10

6. Conclusions

Solubility parameter and molecular dynamics simulation approaches were developed to screen viable vat dye candidates for generic PP aqueous dyeing, and the dyes targeted as viable candidates by the theoretical techniques provided excellent experimental correlations, e.g., high color yields, in dyeing PP fabrics by the optimized acid leuco vat process.

A viable method to commercially aqueous batch dye generic, unmodified PP fiber textiles in a conventional process has been developed for a certified trichromatic series (red, yellow and blue) plus orange of vat dyes with adequate fastness properties to washing, crocking and dry-cleaning in their acid leuco forms: C. I. Vats Red 1, Yellow 2 and Blue 6 plus Orange 1. The same method was shown to adequately color PP textiles with C. I. Vat Blue 1 (Indigo) as a stand-alone colorant with adequate fastness properties to washing, crocking and dry-cleaning to produce the popular "denim" shade. The developed single-stage acid leuco method for dyeing generic PP fabrics at pH 7 provided good fastness properties and good color yields without fiber "ring-dyeing."

Of the vat dyes currently available on the commercial market, C. I. Vat Dyes Orange 1, Yellow 2, Red 1 and Blue 1, all possessing low solubility parameters closest to that of generic PP's 8.1 $(cal/cc)^{1/2}$, were demonstrated to be viable candidates for generic PP fiber coloration, while C. I. Vat Blue 6 was deemed a marginal candidate. However, Vat Blue 6 was the best-performing blue vat dye available outside of Vat Blue 1, and since the latter was so easily air-oxidized compared to the other candidates for the trichromatic series and was thus incompatible with them, Vat Blue 6 was judged sufficient in performance to move the technology forward into practice.

An exhaustive survey of blue vat dye structures in the Colour Index yielded one colorant that possessed the proper solubility parameter and heat of mixing with PP characteristics: C. I. Vat Blue 8. However, the colorant is no longer commercially available on the world market, but with the viable aqueous PP coloration process now developed, vat dye manufacturers will have incentives to bring Vat Blue 8 back into production.

7. Acknowledgment

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9

Substrate Independent Dyeing of Synthetic Textiles Treated with Low-Pressure Plasmas

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1. Introduction

The synthetic fibers are widely used in apparel and home furnishings due to their good physical and chemical properties. The synthetic fiber market is characterized by a trend towards ever-finer fibers. It is very difficult for these finer fibers to obtain very deep colours via the common dyeing processes. The increasing demand of polyester (PES) such as poly(ethylene terephthalate) (PET) in textile market for high performance applications in smart textiles, technical textiles, operation clothing etc. and more recently, for their potential applications as electronic textiles. It indicates that PET has the potential in research in the future due to the wide range of mechanical properties, relative high melting point and glass transition temperature, insensitivity to common solvents and moisture, chemical inertness. PET, an aliphatic-aromatic polymer composition and thermoplastic, shows a rather hydrophobic nature due to its rigid structure,

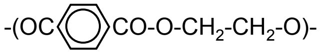

Fig. 1. Chemical structure of PET

The two carbonyl functions together with the aromatic ring provide the structural rigidity of the macromolecule; little flexibility arises due to the presence of the ethylene group in the repeating unit. The polar ester groups in the PET hold the PES into strong crystals. PET consists of a two-phase structure: crystalline (35 % in vol.) and non-crystalline (65 % in vol.). The most important phase in determining dyeability in the conventional dyeing process is the amorphous region. The PET becomes rubbery and swelling above its glass transition temperature. In this state the dye molecules are able to penetrate into the amorphous region and by cooling down the molecule can be trapped inside the PET macromolecules.

In recent years, consumers have shown an increasing preference for use of synthetic fibers blended with natural fibers to combine advantages of both materials. Due to the hydrophobic nature synthetics such as PES fibers are dyed at high temperatures around 130 °C and high pressure, this needs lot of energy and special equipment (Xu et al. 2002). Moreover, since polyesters are stronger than natural fibers, PES fabric blends containing wool, cotton etc. are very popular, since PES makes the fabrics more resilient and wrinkle free. Similar to PES, low priced polypropylene (PP) is frequently used in the technical textiles, home textiles, the automobile industry and to lesser extent in apparel textiles due to their special characteristics such as resistance to chemicals, low density etc. The dyeing of PP is difficult and the fastness properties are not good due to the highly crystalline molecular structure. However, dyeing of PES blends is a problem due to damage/reduction in the strength of natural fibers (cellulose degradation etc.) at high dyeing temperatures. Due to the hydrophobic nature of PES, its compact structure and cristallinity dyeing is limited to water-insoluble dyes such as disperse dyes, vat dyes etc. (De Girogi et al., 2000). The low and finite water solubility of these dyes is also a critical factor in determining levelling properties and dyeing rate (Kulkarni et al., 1986). Conventional polyester dyeing processes additionally require dispersing agent, dye carriers, and surfactants to obtain dye solubility in water. Due to dye reduction and migration, the fastness to washing was found to be on the satisfactory level when dyeing with these dyes (Son et al., 2004). The rate of diffusion of these dyestuffs in the fiber is relatively low. Therefore, the rate of diffusion in the conventional PES dyeing commercially may be raised either by working at higher temperature in the region of 130 °C and/ or in the super atmospheric pressure in the presence of accelerating agent or carrier or surfactants or dyeing auxiliaries.

Recently, research on the use of different surface modification techniques such as low pressure plasma (LPP) and atmospheric pressure plasma (APP) in order to improve the dyeability of polyesters has grown in interest, since they are environmentally efficient. An increase in hydrophilicity and dyeability of knitted PES textiles after the plasma modification in an O_2/CF_4 mixture was obtained, as reported by Aubrecht et al. (2006). The dyeability with basic dye is enhanced on PET/cotton blends by in situ polymerization of acrylic acid and water (Öktem et al., 2002). Sarmadi et al., 1993 observed that the dyeability with basic dye (dye bath temperature 100 °C and 2 hours dyeing time) can further be improved by an increase in the time it is exposed to CF_4 cold plasma, and found K/S values between 0.50-1.51 for a 2% owf (on the weight of fabric) dark shade dyeing with hydrophobic basic dye. A higher color yield was obtained on acrylic acid grafted PET fiber induced by Ar plasma. Barani et al. (2010) compared the dyeability of PES microfiber fabrics using various pre- and post-treatments. They reported that alkali, sol-gel and oxygen plasma treatments are able to enhance the color strength. Continuous modification of PES was carried out using DBD (dielectric barrier discharge) plasma at atmospheric pressure with a Ar/O_2 ratio of 10:1 (Zhongfu et al., 2007). It was reported that the spectral value (K/S) dyed with blue disperse dyes was found to be increased by 50% in comparison with that of untreated samples due to the formation of –COOH groups during plasma treatment. The work of Ferrero et al. (2004) has shown that the fastness to washing with basic dye on PET by in situ polymerization of acrylic acid using low temperature plasma was found to be unsatisfactory probably because of an unstable bond between grafted acrylic acid and dye molecules. Anti-reflecting coating layers have been deposited with organo-silicon compounds using APP plasma, which enhanced the color intensity on PET surfaces as explained by Lee et al. (2001). Okuno et at. (1992) studied the correlation between the crystallinity and dyeability of PET fibers using non-film-forming gases by cold plasma. They found that plasma-treated samples significantly reduced the dyeability due to the etching of macromolecules in the dyeable amorphous phase. Recently, Addamo et al. (2006) reported that the color depth of air LPP plasma treated PET fibers is related to their topographical characteristics and to their chemical surface composition. They observed that the color strength with disperse dye at a dyeing temperature of 100 °C can be increased by decreasing the fraction of light reflected from the treated surfaces.

Moreover, much research has also been done in the environmentally friendly dyeing of PET with disperse dyes in supercritical CO_2 which has the advantage of reducing the need for additional chemicals and waste water (Okuno et al., 1992; Montero et al., 2003; Özcan et al., 2005). The scaling of the supercritical fluid dyeing experiment from laboratory size to industrial scale is far from being a straight-forward procedure because it requires very high pressures (260-300 bar) and high investment cost. At low pressure K/S value is decreased, which yields low dye solubility (Özcan et al., 2005). Moreover, conventional textile dyeing is dependent on the substrate materials due to their specific chemical nature. In a specific dyeing condition, dye molecules chemically and physically bind with the textile fibers and thus, the dyestuff class is also limited to the chemical groups present in the fiber due to dye-fiber interaction. For this reasons, substrate independent dyeing is of particular interest not only for textiles, but also for the materials industries where coloration is needed. Barranco et al. was adding dyestuff molecules downstream in a film-forming plasma in order to obtain dye molecule containing nanocomposite coatings (Barranco et al., 2006). There has been very little attention focused on the application of hydrophilic acid dyes on hydrophobic PET fabrics. Milling acid dyes, which have excellent color brightness and very good wet fastness, can easily be applied to plasma-treated polyester or their blends with natural fibers at low dyeing temperature of 80 °C within an hour dyeing time, where plasma modification is used as an alternative to the required pre-treatment of PET textiles (Hossain et al., 2007a).

While some efforts have been devoted to study dyeability of PES by plasma treatments, very few articles have been reported about the application of acid dyes to PES. In this research, an attempt was made to solve some limitations of PET dyeing using hydrophilic acid dye by modifying the surface with a novel nanoporous plasma polymer coating. Since the dyeing becomes independent from the substrate material, this approach enables the dyeing of all kinds of synthetic fibers or blend fabrics. Surface modification of fabrics induced by ammonia/acetylene and ammonia/ethylene plasmas was carried out in order to incorporate amine end-functional groups into the hydrocarbon plasma polymer and consequently, provide accessible functional groups for the diffusion of hydrophilic acid dye molecules into the nanoporous structure of the plasma polymer.

Nitrogenated amorphous hydrocarbon films (a-C:H:N films) were deposited on PET fabrics by cold plasma using a pilot-plant plasma reactor. Tightly woven and washed polyethylene terephthalate (PET) fabric (76 ends/in, 76 picks/in, 43.5 g/m^2) from Sefar AG (Switzerland) was used in this study. The deposited-hydrophilic a-C:H:N films were characterized by contact angles (CAs). The mechanical stability of the plasma coating was examined by Abrasion & Pilling Tester. Dyeing of the plasma coating was examined by Datacolor Spectraflash, and the results of dyeing were compared for both plasmas (ammonia/acetylene and ammonia/ethylene), while a study was investigated to observe the influences of energy input in terms of power input per unit of gas flow W/F (J/cm^3), film thickness, and gas ratio.

2. Plasma treatments

A gas discharge allows the acceleration of free electrons when driven by an external source (e.g. RF generator). As a consequence, highly reactive and activated molecular species such as chemical radicals, ions, metastables, electrons etc. can be created by ionization, fragmentation (dissociation), excitation, UV radiation, etching reactions etc. These species chemically and physically react with the polymer surfaces, thus altering the surface properties and surface morphology in the topmost layers (Hossain, 2008).

The setup for RF excitation is well-established. In the case of a capacitively coupled RF discharge, two electrodes are mounted in a vacuum chamber as shown in Fig. 1. A process gas with a typical pressure of a few pascal is introduced while working in LPP conditions. When the RF voltage exceeds a certain value in the range of some hundred volts, depending on gas, pressure and reactor geometry, the discharge ignites. The energy coupling in RF plasmas via the electrons is well-defined enabling highly uniform discharges, a trait that is critical in treating irregularly shaped and large objects. RF plasmas are characterized by higher ionization efficiencies and can be sustained at lower gas pressures than DC discharges. Finally, in the case of RF discharge, the energy of the ions bombarding the sample is controlled by the (positive) plasma potential and the (negative) bias potential, which can be adjusted over a wide range of values.

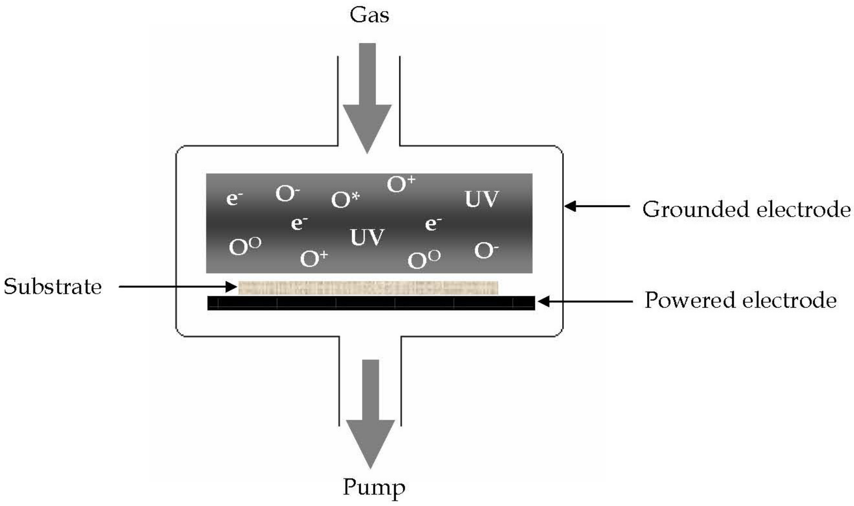

Fig. 2. RF plasma set up and illustration of active species present in oxygen plasma

Based on a wide range of applications and mechanism involved in plasma technology, plasma processes can be subdivided into two main categories:

- plasma modification referring to surface cleaning, activation, and surface etching >> non-film-forming plasma

Plasma activation generates radicals mainly by hydrogen abstraction from the polymer chain during collisions of reactive species with the polymer surfaces. Electrons, UV radiation or ion bombardment can generate radicals by C-C bond scission of the polymer. Non-polymer forming inorganic gases are used in this plasma activation process (Hossain et al., 2006a). Surface activation ranges from surface cleaning, radical formation and atom implantation to surface etching; it depends on different process parameters such as for example energy input. Surface cleaning is commonly used prior to other processing steps such as polymerization, metallization, dyeing, lamination etc. in order to increase the adhesion with textile surfaces.

- plasma modification referring to surface chemistry restructuring via deposition >> film-forming plasma, as described in the following section.

2.1 Deposition of plasma polymer films

In plasma depositions from the gas phase, which is commonly known as plasma polymerization or plasma enhanced chemical vapor deposition (PECVD), a very thin polymer layer (nm to µm) is deposited on the substrate surface. The layer is formed through polymerization of a monomer yielding film growth directly on the surface activated by the plasma (both in gas phase and surface reactions). In contrast to classic polymerization, plasma polymerization can use every monomer gas or vapor and is not limited to its reactivity. It is well known that plasma polymerization could be performed for almost any kind of monomer and it is mainly the elemental composition of the monomer, which is fed into the reaction that is important. The growth rate, mainly determined by gas flow rate and power input, varied depending on the monomer structure even if polymerized films showed similar characteristics (Morita et al., 1985).

In plasma polymerization, the monomer is fragmented under plasma conditions and builds up a plasma polymer. The plasma polymer does not contain regular repeating units; the chains are branched and randomly terminated with a high degree of crosslinking. Thus, it has a highly crosslinked and disordered structure without repeating units, as shown in Fig. 3. Structural preservation and gradients, with increasing degree of crosslinking over film thickness, can be controlled through process parameters, such as gas pressure, gas flow, and applied electric voltage, so that one can also construct so-called gradient layers. It is thus possible to obtain ultra-thin films with very useful properties for technological applications (Bismarck et al., 1999). A combination of polymerizable gases with non-polymerizable gases allows for the deposition of a variety of plasma polymer layers with many different functional groups possible. Thus, depending on the selection of the gas, monomer, process parameters, these thin coatings can be deposited with various physical and chemical characteristics. Consequently, functionalized surfaces with special properties can be obtained.

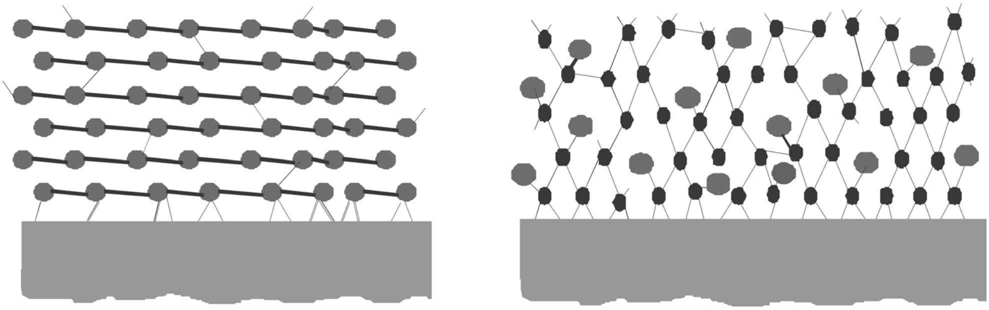

Fig. 3. Illustration of conventional polymer (left) and crosslinked plasma polymer (right)

The plasma treatments were carried out in a pilot-plant reactor, as shown in Fig. 4, in order to demonstrate the feasibility for industrial up-scaling. The reactor is described in more detail in the literature (Hossain et al., 2007b). The fabric samples were kept on the cylindrical electrode (65 cm width). The RF power (13.56 MHz) was connected to the electrode and the glow discharges were carried out for the required power (500-750 W), gas flow (NH_3/monomer ratio = 0.71-4.0), and duration (10-60 min), while the pressure was kept at 10 Pa for all experiments.

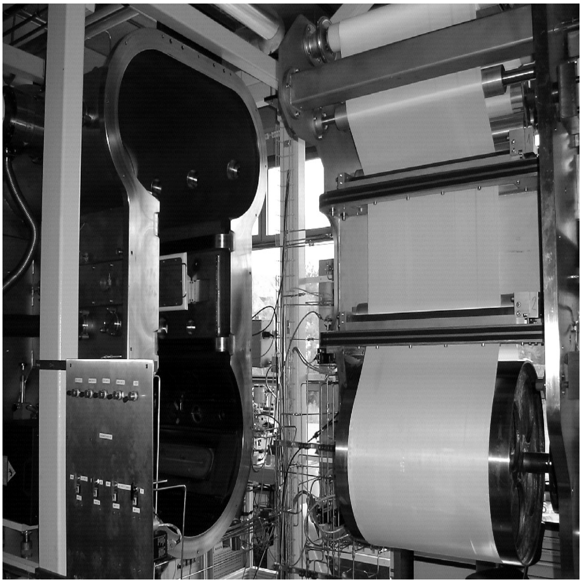

Fig. 4. Set-up of web coater

2.1.1 Nanoporous functionalized films

In this study, ammonia/acetylene and ammonia/ethylene gaseous discharges were performed in order to obtain nanoporous functionalized coatings. A RF plasma generator was used for the deposition of a-C:H:N films on PET textiles. In addition, since the plasma treatment is largely independent of the substrate material, this leads to the possibility to use a universal coating process instead of optimizing surface modification processes and plasma parameters for each different substrate material. However, special care should be taken in particular for textile substrates due to their 3-D structure and manufacturing residuals.

The structural modification of a-C:H films by the addition of nitrogen to the hydrocarbon precursor yielded hydrophilic functional sites (mainly amine functionalities) in a-C:H:N coatings (Hossain et al., 2007c). The a-C:H:N films become more graphitic and the density of voids increases with the incorporation of nitrogen and/or nitrogen functionalities in the coating (Cuong et al., 2005; Freire et al., 1995). As shown in Fig. 5, the AFM image indicates that the interconnected voids in the coating are below 25 nm. The dye molecules are thus small enough (about a few nanometer) to diffuse easily through the interconnected voids of the nanoporous structure into the plasma-polymer matrix and form dye-film bonds. Sufficiently large nanopores with a porosity of 10-20% strongly increase the specific surface area and provide a high functionality to attach molecules such as dyestuff.

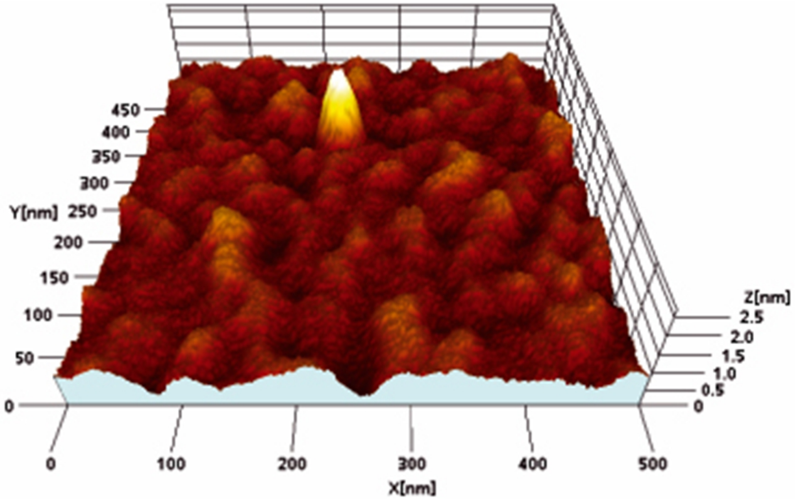

Fig. 5. 3-D AFM Imaging of a a-C:H:N plasma coating (W/F = 144 J/cm^3, NH_3/C_2H_2 = 1.2)

Previously, we examined the mass deposition rates for a wide range of NH_3/hydrocarbon ratio (Hegemann et al., 2005). It was found that plasma deposition, in particular radical-promoted plasma polymerization, was governed by the composite parameter: power input per monomer flow W/F. At moderate energy input ($120 \leq W/F \leq 144$ J/cm^3) a maximum in deposition rate can be achieved for a high NH_3/C_2H_2 ratio of 5:1, as can be seen in Fig. 6. Increasing the C_2H_2 content in the gas mixture leads to an increase of hydrocarbon radicals in the active plasma zone resulting in a gradual increase in a-C:H film character and enhanced deposition rates (Hegemann et al., 2005). Increasing the energy input yields more fragmentation and thus also more hydrocarbon radicals. However, modifications in film growth such as densification, degradation reactions of polymer chains, chemical and physical etching, and some temperature effects can be observed at higher specific energies ($W/F > 144$ J/cm^3) yielding a reduced deposition rate due to the transition between film growth and erosion regime (Hossain et al., 2007a; Hegemann et al., 2005). Moreover, higher energy input avoids the formation of voids, with high crosslinking of the amorphous network, and raises film rigidity due to the hybridization state of carbon atoms in a-C:H:N system. The presence of clustered carbon atoms decreases in the amorphous network connectivity. As a consequence, at high energy input inhomogeneous porous coating causes declination of dye molecules penetration into the coating during plasma dyeing process (Hossain et al., 2007a). In addition, at very low flow rates the film growth is limited by the availability of monomer supply (Waldman et al., 1995). Commonly, in LPP plasma more energetic particles and long-living radicals are generated compared to APP plasma. As a consequence etching effects can play a major role in low pressure plasma. However, the application of ammonia/acetylene plasma is very beneficial in avoiding strong etching effects during plasma polymerization, while coherent etching yield the formation of voids within the growing films (Hegemann et al., 2007; Jang et al., 1992). It can be concluded that the optimum chemical modification can be attained at moderate energy input, and suitable NH_3/hydrocarbon ratio (around 1.0) to obtain accessible amine-functional groups within a-C:H:N coatings (Hossain et al., 2007b).

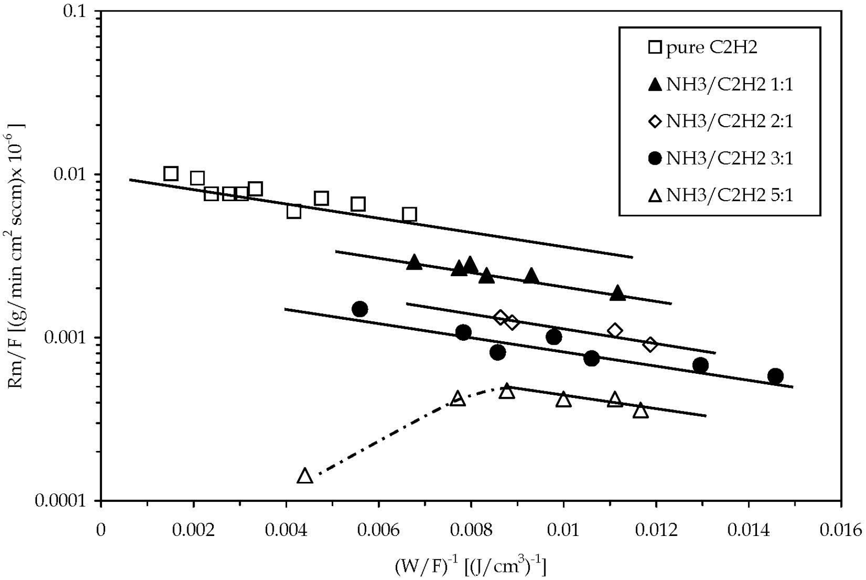

Fig. 6. Effect of energy input W/F (RF power/C_2H_2 flow) on the deposited film.

2.1.2 Wicking property improvement

The wicking property of plasma-coated fabrics was tested according to the water climbing time in the fabric at a certain height (strips size: 15 cm x 2 cm). The wicking times were recorded at fixed 2 cm water climbing height. Surface hydrophilicity was greatly enhanced, as shown in Fig. 7, due to the addition of polar functional groups (Hossain et al., 2007c). The

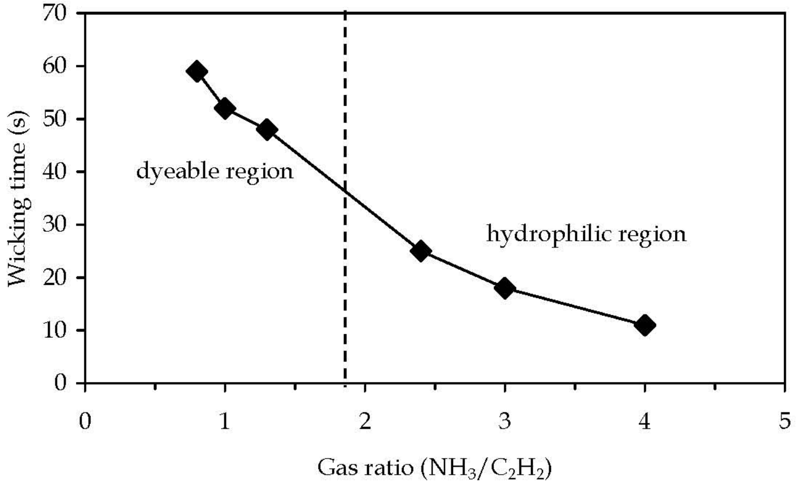

Fig. 7. Effect of gas ratio on wicking property of plasma-coated PET

wettability strongly depends on gas ratios rather than energy input etc. Higher NH_3/monomer ratios (> 2.50) were found to yield the lowest wicking times due to the formation of polar functionalities on the plasma polymer surface. Free radicals created on the plasma polymer produced polar oxygen functionalities, when the treated substrates were exposed to atmosphere, although no oxygen was used during plasma polymerization. On the other hand, higher gas ratios yield lower coloration, which is discussed in the following section.

3. Dyeing procedure

The dyeing of plasma treated samples was carried out in a laboratory-scale machine manufactured by Mathis, Switzerland (LABOMAT–8, Type BFA–8). Hydrophilic functional a-C:H:N films of the PET substrate were dyed with hydrophilic acid dyes (C.I. Acid Blue 127:1). The light-shade dyeing was performed using 0.5 % owf acid dye and 5 % owf sodium sulphate salt for exhaustion and the pH of the dye bath was adjusted to 4.5-5.0 by adding ammonium sulphate. The liquor to fabric ratio in dyeing was 1:100 and the following dyeing conditions were adopted: initial temperature 25 °C, followed by temperature gradient of 1.5 $°C\ min^{-1}$ up to 80 °C, then the dye bath temperature was maintained at 80 °C for 60 min. After dyeing, the dyed fabrics were washed with soap (Ultravon W) at 60 °C for 30 min (L:R = 1:100), then rinsed with warm and cold water and dried at room temperature. Substrate independent plasma dyeing mechanism is described in the Fig. 8. Due to the presence of sulfonic acid groups ($-SO_3H$), acid dye is water-soluble which is transported to the coating on the fiber by the motion of dye-liquor or the textile or simultaneous movement of both in the exhaustion dyeing process. By adsorption process, dye molecule comes on the coated surface; it is then diffused into the nanoporous coating. The basic amino group of coating is decisive important for acid dyeing which can be protonated in the acid medium and becomes fiber-cation (ammonium group). On the other hand, dye-molecule dissociates in the Na_2SO_4/H_2O solution and which gives rise to dye anions, as a consequence they interact with the ammonium groups of the coated fiber mainly by the formation of ionic bonds. Secondary bonds such as dispersion, polar bonds and hydrogen bonds can also additionally be formed between fiber and dye. As a result, dye molecule is fixed in the plasma coating which is independent from the substrate materials.

i) Protonation and cation formation:

$$\text{Film -NH}_2 \longrightarrow \text{Film -NH}_3^+$$

ii) Dissociation of dye molecules:

$$\text{Dye -SO}_3\text{Na} \longrightarrow \text{Dye -SO}_3^- + \text{Na}^+$$

iii) Film-dye bonding:

$$\text{Film -NH}_3^+ + \text{Dye -SO}_3^- \longrightarrow \text{Film -NH}_3^{+}\ {}^{-}\text{O}_3\text{S -Dye}$$

Fig. 8. Film/dye interaction

CIELAB color values of the dyed fabrics were determined using a Datacolor Spectraflash interfaced to a PC. Each fabric was folded twice so as to give four thicknesses, and an average of six readings was taken for each measurement. The reflectance (R %) value of the dyed fabrics was measured over the wavelength range of 360-750 nm. The illuminant type was D65 and the observer angle was 10°. The color strength values (K/S values at 490 nm) of the fabrics were calculated from Kubelka-Munk equation (1), where K is the absorption coefficient, S is the scattering coefficient, and *R* is the decimal fraction of the dyed fabrics.

$$K/S = (1-R)^2/2R \qquad (1)$$

3.1 Dyeing of plasma films

In order to obtain nanoporous thin films, different modifications were employed by varying the important plasma parameters such as discharge power and gas flow ratios. It was found that a gas ratio of NH_3/C_2H_4 around 0.70 - 1.0 and NH_3/C_2H_2 around 1.0 - 1.25 and a discharge power of around 500 - 600 W yield the optimum regarding amine functionalities (Hossain et al., 2007b). The amine functionalities were accessible by dye molecules. Fig. 9 demonstrated the dyeability of plasma-treated PET textiles with different coating thicknesses. The relative color strength value was increased gradually with the increase in coating thickness (i.e. plasma exposure time) (Hossain et al., 2007b; Balazs et al., 2007). It is noteworthy that with increasing plasma process time the penetration of reactive plasma species yielding plasma polymerization goes deeper into the textile structure, even in the inter-filament or inter-yarn spaces, resulting in better dyeability, i.e. number of amine-end groups. On the other hand, the reduced film thickness at very low flow rates led to a lower K/S value of the PET fabrics. Thus, dye molecules are able to penetrate into the nanoporous films and facilitate the dyeing of a-C:H:N thin films by forming chemical bonds mainly with amino groups within the plasma coatings (Hossain et al., 2009; Siow et al., 2006). Since the dyestuff used specifically binds with amine groups, dyeing can be used as a specific chemical tracer to

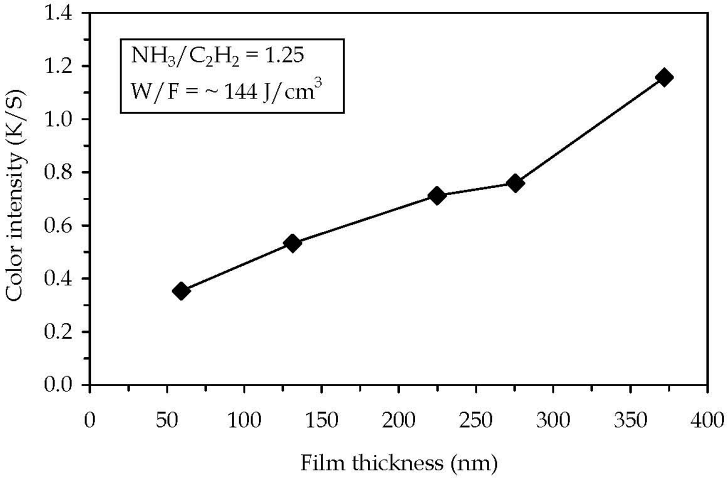

Fig. 9. Relative color strength values (K/S) depending on film thickness and exposure time (light-shade dyeing with 0.5% owf acid dyes).

detect the amount of amine groups inside the coatings. It should be mentioned that untreated PET textiles were not dyeable with acid dye, since they do not contain functional groups in their structure needed for ionic bond (dye-fiber interaction).

The gaseous mixture (suitable NH_3/C_2H_2 ratio ~ 1.25 and NH_3/C_2H_4 ratio ~ 1.0) helped to build up voids in the deposition resulting in a nanoporous plasma polymer coating which was accessible to dye molecules throughout the entire film volume (Freiere et al., 1995; Hammer et al., 2001). Higher ammonia flow to monomer gases indicates an increase nitrogen content, as can be seen in Fig. 10. Moreover, NH_3/C_2H_2 plasma yields a lower nitrogen content compared to NH_3/C_2H_4 plasma owing to an increased carbon content , which can be seen for equal gas ratios (ammonia/monomer = 1.25). The previous study also confirmed the chemical composition of the a-C:H:N deposited films discussing the XPS spectra elaborately (Hossain et al., 2007a). It can be assumed that higher NH_3/C_2H_4 produce more amides, cyanides, imines etc. within the coating rather than simple amine functional groups. Highly reactive ammonia, on the other hand, generates a high number of surface free radicals at higher nitrogen content (i.e. high NH_3/C_2H_2 = 2.70) as compared to a lower ratio (NH_3/C_2H_2 = 1.70). These reactive radicals contribute to form oxygen-containing polar functional groups by post-plasma reactions in the atmosphere. As a consequence, superhydrophilic coatings can be achieved with high ammonia content by incorporation of polar functional groups into the surface within a cross-linked hydrocarbon network. Likewise, the highest nitrogen content reveals the lowest color difference due to a lower number of amines (Table 1). The color difference was compared to non-plasma treated fabric. Thus, the dyeability of the plasma coatings was found to be low at a gas ratio > 2.50. Thus, coloration does not depend on the surface wettability, but on the density of amine-end group. The color intensity in different positions for each dyed sample was measured and the value was found to be almost identical and thus confirming a level dyeing.

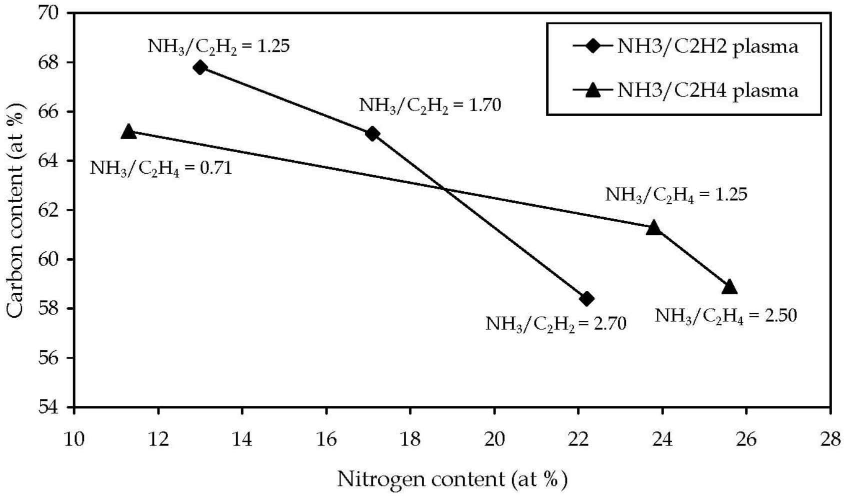

Fig. 10. Nitrogen and carbon contents of a-C:H:N films in different gas ratios

Power input (watt)	Film thickness (nm)	N-content in % [N/(N+C)]	Color difference (ΔE)
650	52	13	33.0
600	54	20	43.0
500	30	30	26.0

Table 1. Color difference of dyed a-C:H:N films at different plasma power, film thickness, and nitrogen concentration (NH_3/C_2H_4 plasma).

3.1.1 Rate of dye-uptake

Uptake of acid dyes onto the plasma coated fabric enhanced remarkably even in a very short dyeing time (5 min), as shown in Fig. 11. It is very interesting to see that the dye uptake remained similar from a short dyeing time (5 min) to a very long dyeing time (120 min), since no significant difference in dye uptake was found at longer time periods. The observed enhancement of dye uptake can be attributed to the deposition of nanoporous thin films which provide amine groups easily accessible to dye molecules within a short time. This demonstrates that the dye diffusion coefficients are quite high; in general these values are quite low when traditional dyeing processes are used (Banchero et al., 2005). In addition, since ultrathin films were dyed, the dye uptake reached to "dyeing equilibrium" very fast. Moreover, the uniform shade obtained certainly proved the regular distribution of dye molecules throughout the entire film thickness. The low internal diffusion time seems to be responsible for preventing non-uniformity problems along the film thickness. In fact, a high dye uptake rate represents a certain advantage since the total dyeing time can be shortened ten times over using plasma-enhanced dyeing, whereas, faster dye uptake kinetics is apt to cause non-uniform dye distribution in the final product when dyeing is done traditionally.

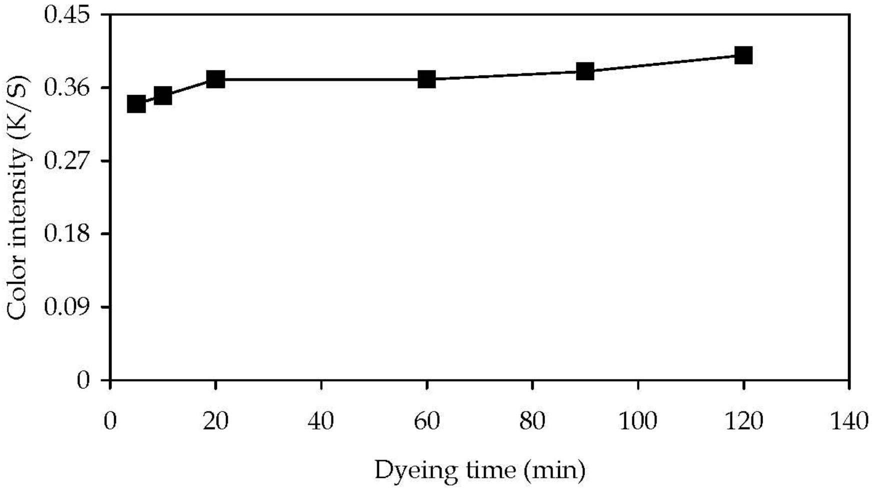

Fig. 11. Effect of dyeing time on dyeability (dyeing temperature 80 °C) (600 W, NH_3/C_2H_4 = 0.84, 20 min) and light-shade dyed PET (0.5% owf)

3.1.2 Temperature and pH effects

The dyeability was found to strongly depend on the dye bath temperature in the plasma dyeing process, as shown in Fig. 12; this is also a common phenomenon in traditional dyeing processes. Results show that the amount of dye absorbed on the coating decreases with decreasing dye-bath temperature. The low reduction in dyeability at lower temperature (< 80 °C) is probably due to dye aggregation and a low degree of adsorption. The differences, however, became very small especially at higher temperatures within the range of 80-120 °C. By increasing the temperature, dye uptake can be enhanced because of the increased solubility and mobility of dye molecules in water. There may be another reason for that, which is commonly seen in traditional synthetic dyeing processes: the enhanced color yield, which gradually increases with increasing temperature, can be attributed to a corresponding increase in the amount of accessible volume available for dye diffusion (Burkinshaw et al., 1995). The highest color yields were found to be at ~100 °C implying that the dye uptake reached the "saturation level" resulting in maximum acid-base intermolecular interaction between dyes and amine functionalities. At this level, the dye molecules occupied most of the incorporated amine functionalities in the film volume yielding maximum dyeability. Thus, substrates such as PES, PP, aramid, glass textiles etc. can be dyed at low temperatures similar to wool dyeing, since good coloration was obtained at levels as low as 80 °C.

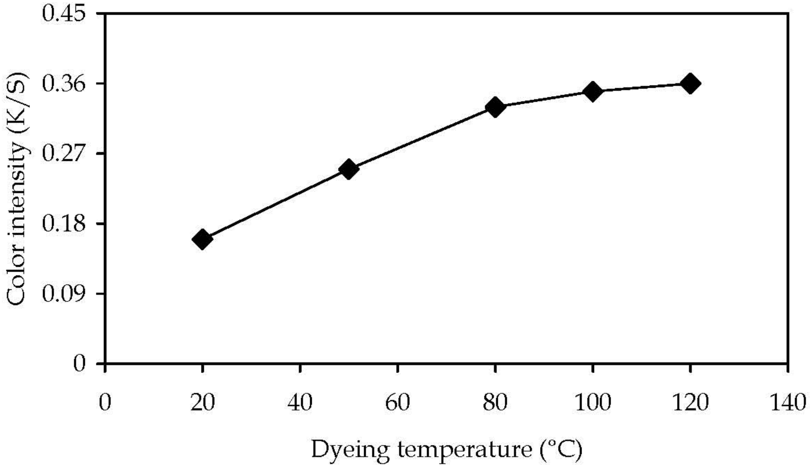

Fig. 12. Effect of dyeing temperature on dyeability (dyeing time 60 min) (600 W, NH_3/C_2H_4 = 0.84, 20 min) and light-shade dyed PET (0.5% owf)

The pH value of the dye bath was found to be very important in order to achieve level dyeing and to increase dye affinity to the functionalized films. The optimum level dyeing and color strength were obtained at a pH in the range of 4.5-5. However, the color intensity was increased at pH 2.5-3.0 due to improved exhaustion, but uneven shade was observed. On the other hand, dyeability was reduced at pH 6.0-7.0 due to low substantivity or low affinity of dyes to the film resulting in weak dye-film interaction.

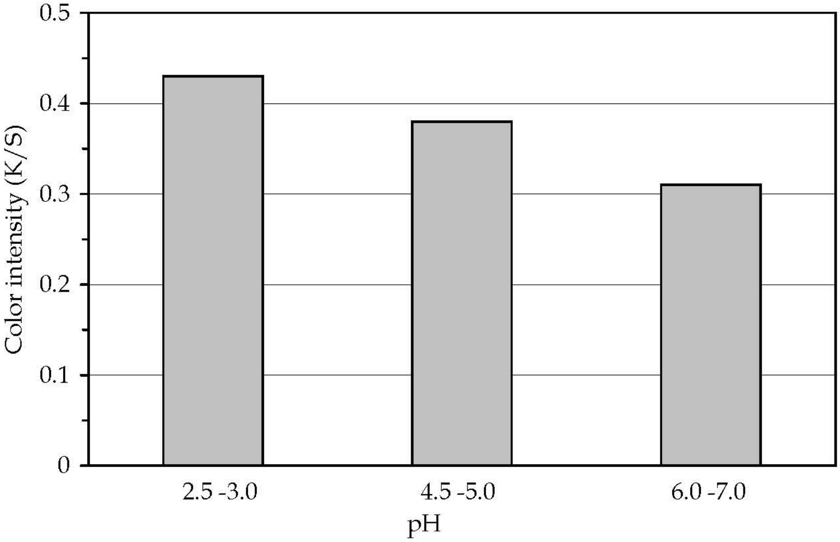

Fig. 13. Effect of dye bath pH on dyeability (dyeing time 60 min and dyeing temperature 80 °C) (600 W, NH_3/C_2H_4 = 0.84, 20 min) and light-shade dyed PET (0.5% owf).

3.1.3 Fastness properties

Table 2 shows summarized results of plasma-dyed PES that were assessed using an ISO test method (ISO 105-X12 for color fastness to rubbing and EN ISO 105-C06 for color fastness to washing). Under D65 illumination color changes, staining and rub were evaluated using grey scales: ISO-105-A02 grey scale for assessing change in color; ISO-105-A03 grey scale for staining and rub. All plasmas show almost comparable fastness properties after washing at 60 °C for ammonia/acetylene and ammonia/ethylene plasmas dyed PET. The acid dyeing

Gas ratio (vol.)	Wash fastness			Rub fastness	
	Color change	Staining (PET)	Staining (wool)	Dry	Wet
$NH_3/C_2H_2 = 1.00$	3	5	4	4-5	4-5
$NH_3/C_2H_2 = 1.25$	3	5	4	4	4
$NH_3/C_2H_2 = 1.50$	3	5	4	4	4-5
$NH_3/C_2H_4 = 0.71$	3	5	3-4	4	4-5
$NH_3/C_2H_4 = 1.00$	3	5	3-4	4	4-5
$NH_3/C_2H_4 = 1.25$	3	5	3-4	4	4-5

Table 2. Wash (at 60 °C) and rub fastness of a-C:H:N films deposited on PET fabrics

on a-C:H:N deposited plasma polymers exhibit acceptable fastness to laundering and rubbing. From these results, it is concluded that a nanoporous and functional plasma polymer enables permanent dye-fiber bonding with hydrophilic dyestuff. The coating was well adhered with the textile surface. No damages of the coating were detected after 60,000 rubbing cycles.

4. Commercialization

A considerable amount of basic research has been devoted mostly in laboratory scales to incorporate functional groups on the textile surfaces by plasma modification. Besides plasma parameters, the reactor geometry complicates the process scaling-up (Hegemann et al., 2007). Another fundamental problem at this moment is the lack of adapted plasma systems and the transfer of the laboratory findings into textile industry. Textilveredelung Grabher GmbH/Austria is using LPP plasma reactor (vol. 11 m^3) in obtaining permanent hydrophilic and hydrophobic surface modification on textiles. The roll-to-roll system has a 15 m long plasma passage and is able to treat substrates up to 1.60 m in width (Fig. 14). Sefar AG/Switzerland is one of the pioneering companies in high-performance filtration solutions and uses the world largest APP systems, consisted of a high voltage power supply, for industrial applications (Fig. 15). The machine is installed inline textile processing and is capable of treating textiles, nonwovens, polymer webs etc. up to 4.0 m wide and materials speed up to 25 m/min (depending on the hydrophilization effect). The developed processes offer a range of cost-effective, and environmentally sound solutions to problems faced in screen printing. As a process gas He/Ar, and CO_2 etc. have been successfully used in their system at modifying textiles.

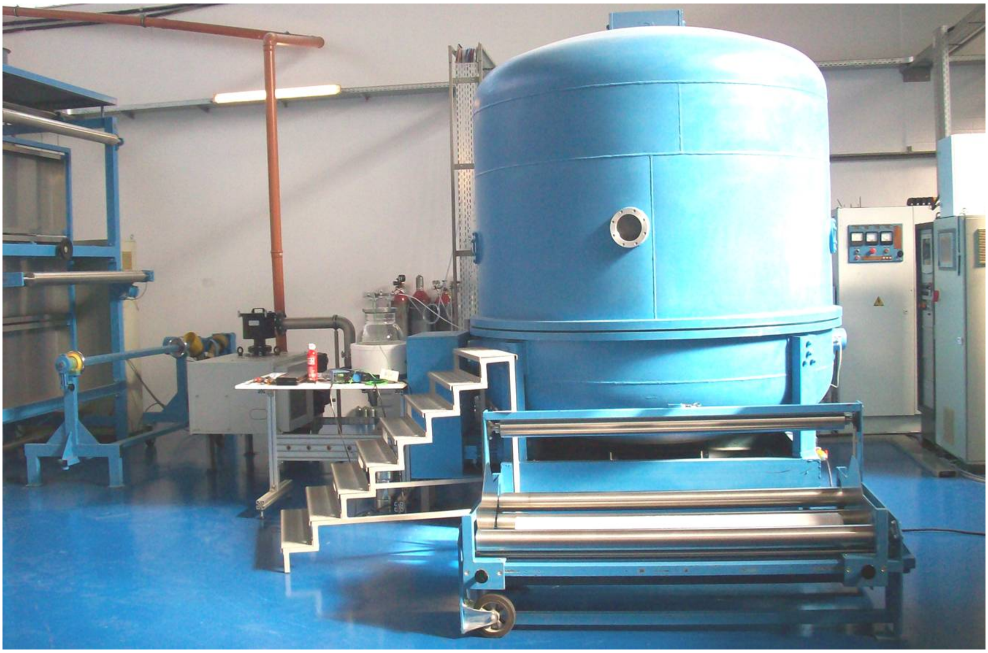

Fig. 14. Industrial plasma reactor at Textilveredelung Grabher GmbH/Austria

Fig. 15. The continuous plasma system at Sefar AG/ Switzerland

They reported that an oxygen containing gaseous mixture (Ar/He with O_2 and ratio 20:1) was found to be more efficient compared to pure inert gases (Ar, He etc.) to remove organic contaminants by oxidizing polymer surfaces and to implant polar functional groups on the textile surfaces (Oyama et al., 1998). The use of gaseous mixtures facilitates cross-linking und better hydrophilicity. In this process, oxygen plasma causes reactions with surface contaminants resulting in their volatilization and removal of the degradation products as water vapor, CO, CO_2, H_2, etc. (Hossain et al., 2006b). Moreover, oxygenated functions such as –OH, -C=O, -COO, -COOR etc. are grafted onto the surface as can be seen in XPS analysis (Fig. 16). Thus, functionalized and activated surfaces can be obtained, which can be used for the subsequent wet processing such as lamination, coating, dyeability, printability etc. The grafted surfaces can also lead to covalent bonds suitable for further attachment of coatings, matrices etc. These new reactive sites can be used to improve adhesion and prevent delamination of the subsequent coatings, thus supporting the formation of abrasion resistant coatings.

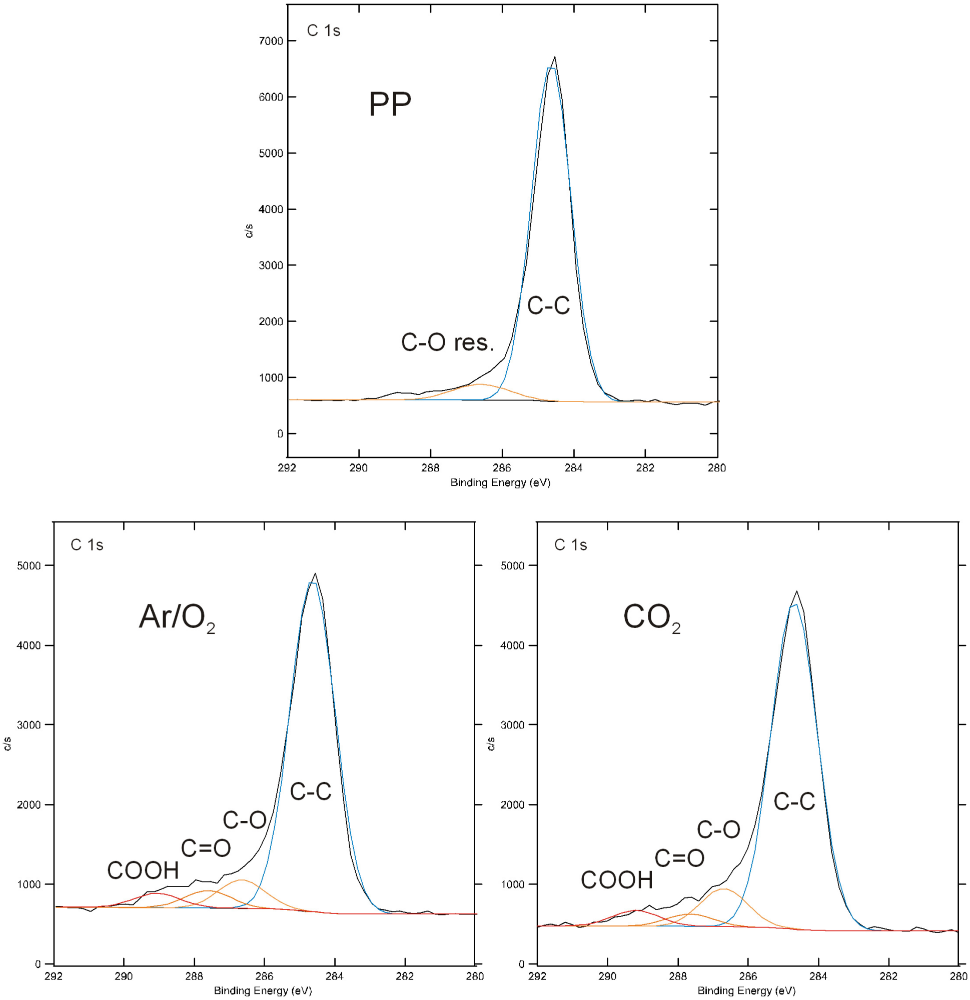

Fig. 16. XPS analysis of plasma-activated polypropylene (top: control, and bottom: Ar/O_2 and CO_2 plasmas)

4.1 Cost analysis

While plasma processing represents a dry, eco-friendly technology requiring a small amount of resources, it also has to prove its economic feasibility. Plasma activation processes without deposition of a film are state of the art in order to improve e.g. adhesion and can also be conducted using APP plasmas. Textile industry is thus using corona discharges operated in air for decades. However, the treatments are prone to aging effects (hydrophobic recovery) and show a limited uniformity. For more sophisticated applications such as the discussed (substrate independent) dyeing process, but also for the formation of permanent hydrophilic or hydrophobic surfaces, plasma polymerization processes are required. Thus, a large amount of research and development has been done to explore both LPP and APP technologies. Nowadays, both systems are industrially available as mentioned above, which enable a comparison of special processes also regarding the costs.

Certainly, LPP offers more and different possibilities such as physical and chemical vapor deposition utilizing energetic particle interactions (sputtering, ion-induced etching, ion implantation, subplantation and densification). Moreover, LPP are able to penetrate deeper into complex material structures such as textiles. Finally, LPP processes are well established, reliable and robust. For plasma processes based on plasma-chemical reactions, however, it could be shown that both LPP and APP processes can be compared (Sawada et al., 1995). For instance, the incorporation of polar groups in ultrathin plasma polymer films might be examined yielding a permanent hydrophilic surface (Herbert et al., 2009). The deposition rate is mainly determined by the monomer flow rate due to a comparable energy input into the plasma phase. As reactive gases N_2, NH_3, H_2, O_2, CO_2, H_2O etc. might be added, again at a comparable flow rate. APP in addition requires a "filling gas" to reach atmospheric pressure, where helium (He) shows the best characteristics regarding plasma stability and energetic UV radiation (used for crosslinking). LPP on the other hand, requires (expensive) vacuum technology and the corresponding pumping system leading to the common assumption that APP may be advantageous. APP might be operated with a simple housing, but requires high flow rates of the filling gas in order to provide a sufficiently defined plasma atmosphere and to obtain a drift of the reactants to the surface, since convection processes have to be overcome.

Assuming that additional costs might be comparable in both technologies, i.e. personal costs, infrastructure, maintenance and (low) energy costs, a cost analysis can be performed on the basis of the investment and the running costs. While the investment is certainly higher for a LPP system, the running costs are actually higher for the APP system due to the high amount of required filling gas. Beside the already mentioned technological arguments, now also the costs can be estimated and compared for both plasma processes, which supports industry in selecting the best technology for their requirements.

For comparison, we selected a hydrophilic plasma treatment based on the deposition of an ultrathin (25 nm) plasma polymer film containing functional polar groups such as the one described in this chapter (LPP). For the comparable APP process, He at a flow rate of 100 slm is considered as filling gas. Both processes enable coating of 150 cm in width at a comparable process velocity in order to obtain the same amount of produced functional textiles per day. Fig. 17 displays the evolution of the costs with time. As it can be noticed, the break-even of the LPP system with the APP process is already reached after 14 months of operation due to the high running costs by He use. Even when recycling of He (recovery around 80%) can be considered causing increased investment costs, the break-even is reached after around 3 years. A similar analysis holds for the use of Ar or N_2 as filling gas as well as for hydrophobic treatments, again showing that LPP is beside many further advantages the more cost-efficient technology.

For the presented dyeing process thicker coatings might be required (see Fig. 9) which reduces the amount of functionalized textile per day and should be regarded for the cost analysis. Process optimization can still be expected. Also note that a 4 m wide plasma system as used by Sefar with APP might not be feasible using LPP. A well-based cost analysis, however, should be done by potential applicants giving good reasons for LPP systems as used by Textilveredelung Grabher.

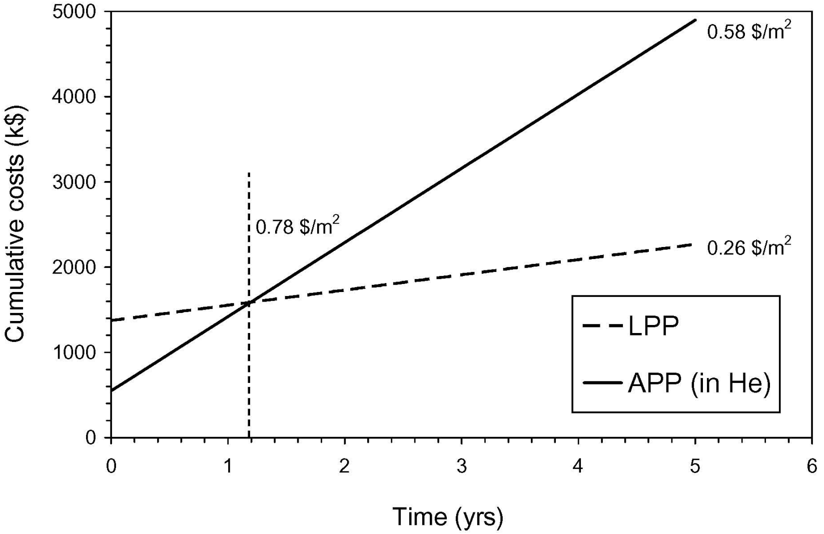

Fig. 17. Cost analysis for the comparison of LPP and APP processes for the permanent hydrophilization of textiles for 1.5 m in width and 5 km output per day showing the investment (at time zero) and the (constant) running costs. After 14 months both processes were producing 1500 km of functionalized textiles at a total cost of 0.78 $/m^2, which is further reducing with time.

5. Conclusion

This study investigated an alternative procedure to dye synthetic textiles, namely polyester, polypropylene etc., at low temperature using two different plasma polymerization methods, based on an original process of plasma deposition of nanoporous coatings. LPP discharge was performed for the modifications which avoid heat generation to the surface and additionally, it delivers high activation energy. The plasma modification alters the surface properties of textiles from hydrophobic to hydrophilic and to enable the dyeing of synthetics at low temperatures. Ammonia/hydrocarbon mixtures were investigated within a RF plasma using a web coater in order to deposit a-C:H:N coatings on PET textiles. Pure hydrocarbon discharges at low pressures can be used to deposit crosslinked a-C:H coatings. In particular, high deposition rates can be obtained with unsaturated hydrocarbon monomers such as acetylene and ethylene by producing the divalent radicals. Admixture of ammonia to the hydrocarbon discharge influenced the plasma polymerization mechanism depending mainly on gas ratio and energy input. Amine terminating groups, NH_2 and eventually NH, were embedded in hydrogenated carbon films (a-C:H films) using ammonia/hydrocarbon plasma. In addition, nitrogen incorporation in a-C:H films facilitated in forming crosslinked and branched plasma polymers. Thus, a nanoporous structure with a large specific surface area was achieved that contained functional groups inside the coating volume, which were accessible to e.g. acid dye molecules, thus facilitating substrate independent dyeing. It was found that dyeability is strongly influenced by both plasma parameters and fabric structure.

Besides plasma parameters the gas ratio plays a very important role in determining high color yields. Higher gas ratios were found to be less colored due to fewer amino functional groups, while they show higher hydrophilicity owing to the addition of polar functions on the surfaces during post plasma reactions. At gas ratios of around 1.25 for NH_3/C_2H_2 and 1.0 for NH_3/C_2H_4 crosslinked and branched a-C:H:N coatings were produced, which posed high number of accessible nitrogen functional groups, i.e. amino groups, resulting in high color intensity. Although their wetting properties were less pronounced as for higher ammonia content, dye molecules could easily enter the nanoporous film structure and chemically bound with the nitrogen functionalities. Thus, high K/S values per film thickness have been obtained. The uniformity of plasma polymers provides information about the even dyeing. Moreover, the plasma-deposited and dyed PET fabrics showed a good rubbing and washing fastness demonstrating the coating-functional permanency. The excellent abrasion resistance confirmed that the coating was permanently adhered to the substrate. Hence, the same dyeing principle can also be applied to all hydrophobic synthetic textiles and their blends with natural textiles which are difficult to dye.

A thorough cost analysis based on existing plasma processes were performed showing the ecological potential of plasma processes, in particular of low pressure plasma systems due to low running costs.

These findings demonstrate that plasma polymerization provides an eco-friendly multi-functionalized surface modification, since the use of chemicals; waste water etc. can be eliminated. Furthermore, since the coating thickness is in the nanometer range (<300 nm), the materials, architectural porosity, touch, and comfort etc. are not affected. The nanoporous plasma polymers can be effectively used as a foundation for multifunctional applications such as fiber-reinforced composites, superhydrophobicity, cell-adhesion etc. Thus, the developed nanoporous coatings that incorporate accessible functional groups are most promising candidates for technical textiles.

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10

Dyeing with Disperse Dyes

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1. Introduction

Before the First World War, almost all dyes were applied from solution in an aqueous dyebath to substrates such as cotton, wool, silk and other natural fibres. However, the introduction of a man-made fibre, cellulose acetate, with its inherent hydrophobic nature, created a situation where very few of the available dyes had affinity for the new fibre. Water-soluble anionic dyes had little substantivity for the fibre and the alkaline conditions required for the application of vat dyes brought about a loss in tensile strength and deterioration in fibre appearance due to the rapid hydrolysis of acetyl groups.

The development of disperse dyes for dyeing secondary cellulose acetate fibres in the early 1920s was a major technological breakthrough although their major use today is for the coloration of polyesters, the most important group of synthetic fibres (Broadbent, 2001). The first systematic study of dyes that was suitable for application to cellulose acetate by a direct dyeing process was carried out by Green. The presence of hydroxyl and amino groups, a low relative molecular mass and an almost neutral or basic character were found to be advantageous. As a result of these investigations, in 1922, Green and Saunders developed the Ionamine Dyes (British Dystuffs Corporation) for application to acetate fibres (Green & Saunders, 1923; Green, 1924) (Fig. 1). These water-soluble dyes were hydrolyzed in the aqueous dyebath to produce the sparingly soluble free base in a very fine suspension that was then absorbed by the fibre. This discovery, that aqueous dispersions of almost water-insoluble dyes were highly suitable for the dyeing of secondary acetate, lead to the rapid development of other such dyes for dyeing cellulose acetate.

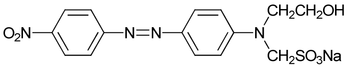
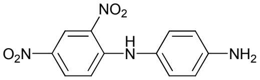


Fig. 1. An Ionamine dye.

In 1923, aqueous dispersions of dyes were examined independently by the British Celanese Corporation and the British Dyestuffs Corporation and Ionamine dyes were superseded by ranges of disperse dyes, such as SRA (British Celanese Corporation) and Duranol (ICI), that were devoid of ionic solubilising groups (Fig. 2). These sparingly water-soluble acetate dyes were applied to cellulose acetate in the form a fine aqueous dispersion (Burkinshaw, 1995).

The advent of other man-made fibres, such as nylon in 1938 and acrylic in the early 1940s, both of which possess a significant hydrophobic nature, further increased the use of disperse dyes. However, it was the discovery in 1941 and subsequent commercial introduction in

1948, of polyester fibres that triggered an intensive research effort into disperse dyestuffs. Due to the highly crystalline and hydrophobic nature of polyester, the fibre is only slightly swollen by water up to the atmospheric boil which, in the 1950s was the maximum practical temperature available for dyeing. Consequently, new methods of application had to be developed. These new methods involved opening up the fibre structure temporarily so as to facilitate dye penetration (Fourness, 1979).



SRA Golden Yellow IX

Fig. 2. SRA range dyes by British Celanese Corporation.

When cellulose acetate is dyed at 85-95°C, small molecular size dyes are required which have an adequate solubility to dissolve and diffuse into the fibre. Such dyes possess high vapour pressure that did not normally cause a problem as the resulting dyeings were not usually subjected to high temperatures. However, with the advent of polyester fibres, problems with fastness arose due to dye sublimation during the subsequent heat setting and pleating processes. The vapour pressure of disperse dyes is related to the relative molecular mass of the dye and can therefore be decreased by increasing the relative molecular mass of the dye and by incorporating polar substituent groups into the dye molecule, such as benzoyl or amide groups. Incorporation of polar groups into the dye molecule causes a slight increase in water solubility in addition to increasing the relative molecular mass, thus giving rise to slower rates of diffusion. The decrease in rate of diffusion means that dyeing times have to be increased. However, the use of higher temperatures or carriers leads to increases in the rate of diffusion of dye molecules into the fibres.

2. Disperse dyes

Disperse dyes are traditionally non-ionic chemicals with sparing solubility in water which, consequently, are able to retain comparatively better substantivity for hydrophobic fibres, such as polyester, nylon and acetate. For the sake of efficient diffusion into textiles, the particles of disperse dye should be as fine as possible comprising low molecular weight molecules in the range of 400 – 600. It is essential for disperse dyes to be able to withstand various dyeing conditions, pH and temperature, resulting in negligible changes in shade and fastness (Aspland, 1992, 1993).

Disperse dyes are often substituted azo, anthraquinone or diphenylamine compounds which are non-ionic and contain no water solubilising groups. The dye particles are thus held in dispersion by the surface-active agent and the dyes themselves are called disperse dyes. They are marketed in the form of either an easily dispersible powder or a concentrated aqueous dispersion and are now the main class of dye for certain synthetic fibres (Ingamells, 1993).

2.1 Classification

In the 1970s, ICI developed a method for the classification of disperse dyes according to their sublimation fastness and dyeing properties, placing them into categories named A to D. Class A dyes had low relative molecular masses and hence poor sublimation fastness, but desirable dyeing properties, whereas Class D dyes had high relative molecular masses and therefore good sublimation fastness, but somewhat poorer dyeing properties. Classes B and C were between these two extremes. Other dye manufacturing companies such as BASF soon introduced their own similar systems of disperse dye classification.

The Disperse Dye Committee of the Society of Dyers and Colourists has now classified the dyeing characteristics of disperse dyes according to the results of several tests which can be performed on the dyes. These tests assess characteristics such as the build up, levelling properties, rate of dyeing and temperature range properties of the dyes on a range of hydrophobic fibres. Small dye molecules with low polarity are levelling, rapid dyeing dyes with poor heat resistance. These are called low energy disperse dyes. More polar, higher molecular weight dyes have low dyeing rates, poor migration during dyeing but good heat and sublimation fastness. These constitute the high energy disperse dyes (Broadbent, 2001).

A chemical classification by chromogen is very useful to dye chemists, particularly those who intend to synthesize dyestuffs, while the latter classification is more valuable for dyers. The Colour Index listed around 1,150 disperse dyes in 1992 by chemical class. i.e. azo, anthraquinone, meethine, nitrodiphenylamine, xanthene, aminoketone, quinoline and miscellaneous.

2.1.1 Azo disperse dyes

Azo dyes are defined as compounds containing at least one azo group attached to sp^2-hybridized carbon atoms, such as benzene, naphthalene, thiazole and thiophene. Under normal conditions, azo dyes exist in the more stable planar tras-form so that the carbon-nitrogen bond angle is approximately 120° (Fig. 3) (Gordon & Gregory, 1983).

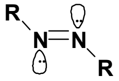


Fig. 3. The trans-form of an azo dye.

Azo dyes are by far the most important class and account for more than 50% of the total commercialized disperse dyes in the world. There are several reasons why azo dyes have dominated the markets and have replaced many of the conventional anthraquinone dyes. In principal, the azo group is an inherently intense chromophore in terms of the tinctorial strength, when compared with the comparatively weak anthraquinone chromogen, normally 2 or 3 times stronger in tinctorial strength. By virtue of their simplicity and the ease of manufacture, unlike the other types of dyestuffs such as anthraquinone and styryl, the cost of manufacturing azo dyes is comparatively lower than the expensive anthraquinone dyes.

Azo dyes cover a whole gamut of colours, from yellow to blue-green hues, by varying the intermediates especially when heterocyclic diazo components are coupled to aminobenzene couplers substituted with powerful electron donating groups, giving bright blue-green colours. Although some deficiencies of azo dyes are not easily overcome, such as duller shades, lower fastness to light and breakdown into carcinogenic amines derived from the cleavage of the azo linkage, and have somewhat restricted their extensive usage against anthraquinone dyes, the cost effectiveness undoubtedly compensates for the drawbacks mentioned above (Gordon & Gregory, 1983).

Aminoazobenzene dyes, which can be represented by the general structure (Fig. 4), have been by far most important disperse dyes particularly during the early period of progress for the coloration of polyester fibres.

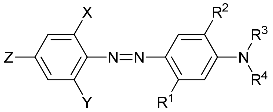
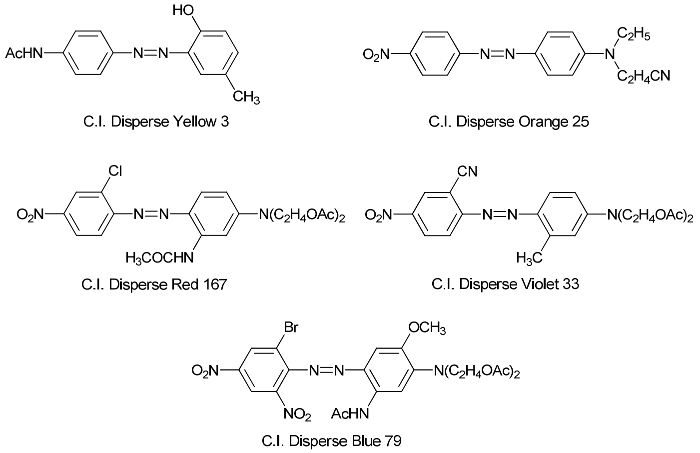


Fig. 4. General structure of aminoazobenzene dyes.

As a typical donor-acceptor chromogen, the electron-accepting substituents, X, Y and Z and the electron donating substituents R^1 and R^2 are favourably sited to create visible colors from yellows to reds, and more recently, blues (Fig. 5). In general, aminobenzenes are easily diazotized by normal diazotization reagents and the resultant diazonium salts are comparatively stable so that high yields of dyes of good purity are obtained.



C.I. Disperse Yellow 3

C.I. Disperse Orange 25

C.I. Disperse Red 167

C.I. Disperse Violet 33

C.I. Disperse Blue 79

Fig. 5. Some typical azo disperse dye structures.

2.1.2 Anthraquinone disperse dyes

Anthraquinone disperse dyes were among the early 'acetate' dyes and have made an important contribution to the violet and blue shade range. They produce bright dyeings of excellent light fastness and cause no dye stability problems during dyeing.

From a historical point of view, anthraquinone dyes are the oldest to mimic a natural chromogen. As seen from the Colour Index Classification, anthraquinone systems of basic formula (Fig. 6) are second only to the azo chromogen for the manufacture of disperse dyes.

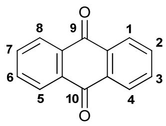
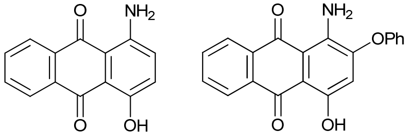


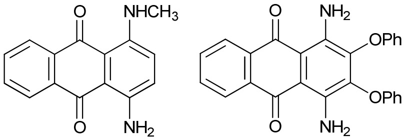
Fig. 6. Anthraquinone systems of basic formula ; 9,10-anthraquinone.

A whole range of colour shades from yellow to even turquoise blue can be provided by variation of the substituents in different positions. Thus, 1,5-dihydroxyanthraquinone has a yellow shade and an absorption maximum at 425 nm, whereas 1,4,5,8-tetraaminoanthraquinone absorbs maximally at 609 nm, giving rise to a greenish-blue color. The inherent brightness of anthraquinone dyes, which exceeds that of typical azo dyes, may be accounted for by their unique fluorescence emitted by the transition from the first singlet excited state to the ground state (Gordon & Gregory, 1983).

Simple anthraquinone disperse dyes containing alkylamino or hydroxy groups (e.g. C.I. Disperse Violet 4, C.I. Disperse Red 15) can be used for the coloration of cellulose acetate, although of limited color range and of moderate fastness. When more hydrophobic substituents are introduced to enhance the affinity for polyester fibre, various shades can be produced. Among these types of anthraquinone dyes, a bright red dye (C.I. Disperse Red 60) and a violet dye (C.I. Disperse Violet 26) have been widely used in the coloration industry, particularly C.I. Disperse Red 60 which acts as a basic colour for trichromic combinations in pale shades and is one of the best dyes available for heat transfer printing. These dyes show exceptional brilliance and high light fastness against similar colours of azo dyes (Fig. 7).



C.I. Disperse Red 15 C.I. Disperse Red 60



C.I. Disperse Violet 4 C.I. Disperse Violet 26

Fig. 7. Commercial anthraquinone disperse dyes.

Recent literature has revealed that more bathochromic shifts can be obtained by condensing various arylamines with 4-arylamino-5-nitro-1,8-dihydroxy anthraquinone or with 4,8-dichloroquinizarin or 4,5-dinitrochrysazin to give deep blush-green shades on polyester (Peters & Chao; Yu & Chao]. Although anthraquinone disperse dyes have many advantages such as bright shades, high light fastness, good stability in dyeing and excellent levelling, serious economic drawbacks and inevitable pollution problems ensure the continuing displacement of these dye by other types, such as benzodifuranone dyes and azo dyes having heterocyclic diazo components (Griffiths, 1984; Weaver & Shuttleworth, 1982).

2.1.3 Other disperse dye classes

Although anthraquinone, monoazo and disazo disperse dyes are the most important classes of disperse dyes in terms of market share, there are a number of other important classes as follows ;

- Nitroarylamino disperse dyes
- Coumarin disperse dyes

- Methine disperse dyes
- Naphthostyryl disperse dyes
- Quinophthalone disperse dyes
- Formazan disperse dyes
- Benzodifuranone disperse dyes

2.2 Constitution and fastness properties

Many attempts have been made to trace relationships between the chemical structure of a dye and its fastness properties. However, such inter-relationships can be very complex. Some general trends can be distinguished but, within these, more subtle interactions involving electronic and steric effects make it very difficult to set down hard and fast rules. In recent years, more precise information has been obtained by studying groups of very closely related dyes in which minor structural changes have been shown to influence fastness properties.

Satisfactory fastness to light, washing, rubbing, sublimation and (on acetate) burnt gas fumes, is particularly significant for disperse dyes (Dawson, 1984).

2.2.1 Fastness to wet treatment

The demand for environmentally friendly dyes of high wet fastness on polyester is increasing. As a result of current trends towards the increased use of finishing treatments, microfibers and stringent wash fastness test criteria, previously satisfactory colorants are no longer suitable and the performance of agents of relatively high fastness can be rendered ordinary (Choi et al).

Fastness to washing is similarly dependent on diffusion as it is unlikely during the limited time of a washing cycle or test that an equilibrium between the dye inside and outside the fibre will be reached. Consequently, the fastness will be subject to kinetic control: other things being equal, increases in size and polarity of the dye molecule will reduce its mobility within the fibre and be reflected in a lower diffusion coefficient and an attendant increase in wash fastness. The nature of the disperse-dyed substrate is also very important. Polyester tends to have better fastness to wet treatments such as washing and perspiration fastness than nylon and acetate with a given dye since its structure is more crystalline and hydrophobic. Both properties restrict diffusion, the former directly, by presenting a close-packed structure as an obstacle to movement, and the later directly by reduced fibre-swelling which serves to keep the structure tightly packed. Heat fastness/dyeing trade-off, changes in diffusion characteristics to improve wash fastness will have an opposite effect on dyeability.

In terms of providing satisfactory wash fastness on polyester, dye selection has become far more critical than it ever has been, because of the more demanding wash fastness tests employed currently and the now widespread use of aftertreatments. Before the 1970s, the universal wash-fastness trial for dyed polyester was the ISO 105 C03 wash test, which simulated domestic washing with soap and examined staining on polyester and cotton or wool. Nearly all disperse dyes gave very good to excellent results. However, from the 1970s onwards, achieving satisfactory fastness to washing became more problematic as the result of a customer-driven rise in standards being implemented in the guise of more severe testing protocols (Baldwinson, 1989). Stringent conditions were stipulated in the late 1960s by Marks and Spencer, who required their suppliers to use only those dyes that met criteria using adjacent nylon, which showed a greater tendency to stain than wool or cotton. Heat treatments made fastness more of a problem in the case of some dyes; the high temperatures lead to thermomigration where dye molecules tend to move from the core of the fibre towards the surface, and thus counteract the reduction clearing and lower the wash fastness. In the early 1980s, an official range of European wash test (the ISO 105 C06 series) was published that reflected the widespread adoption of detergents for domestic laundering, which with dyed polyester often gave lower ratings than with soap-based tests: any dye stripped from the fibre by the soap tends to remain solubilised through the powerful surfactant properties of the soap present in a relatively large concentration. Detergent, containing much less surfactant, is able to remove surface dye, but is not as effective at solubilising it, promoting staining although the inclusion of perborate bleaching agents can counteract this. This together with the now routine use of multifibre adjacent fabrics, has rendered many previously satisfactory dyes unsuitable and made dye selection far more important in this respect. An extreme requirement is that for polyester microfibres: the high surface area to mass ratio of these materials means that higher than normal depths of dyeing are needed for satisfactory shades. An investigation has suggested that planar dyes of low relative molecular mass (for satisfactory build up) and of high tinctorial strength may meet the challenge (Chao & Chen, 1994). During the 1990s, the development of novel wash test procedures has continued in order to counter perceived changes in the market such as innovations in detergent formulation. The appearance of a new generation of protocols like BS 1006 UK-TO and ISO 105:C08 is a sign that fastness criteria will keep evolving and so present fresh challenges to which disperse dye technology must respond (Choi et al, 2000).

A range of test has been devised to simulate the action of various other wet agencies including perspiration. Much effort has been expended on trying to find ways to mimic human sweat, which is a complex mixture containing salt and amino acids (Heir et al, 1946). Fresh perspiration is slightly acidic, but goes alkaline with bacterial action (Perspiration Fastness Subcommittee, 1952), hence the development of two test, one at pH 5.5, the other at pH 8. Disperse-dyed polyester generally performs well because its structure is still close-packed at body temperature (the level at which the test samples are maintained).

Recently, improved wet fastness was achieved by incorporating easily washable groups into dye structures. Thus, the modified dyes containing diesters, thiophenes, benzodifuranones, phthalimides and fluorosulfonyl group have been designed to improve the wash fastness (Fig. 8) (Koh & Kim, 1998a, 1998b; Koh & Greaves, 2001). The most often patented dyes with enhanced wash fastness and build-up properties were based on heterocyclic amines such as 2-aminothiophene, and 2-aminopyrazole, and were used separately or in combination (Freeman and Sokolowska, 1999).

2.2.2 Fastness to dry heat

Sublimation, or dry heat, fastness can be an important property of disperse-dyed polyester because of the use of heat treatments in the finishing of the fabric; disperse dyes must be small, non-ionic molecules of low molecular weight. As such, they often exhibit a significant vapour pressure. Therefore, if heat treatments during fixation, or subsequently, e.g. ironing, are involved, the dye may sublime and cause contamination of equipment or adjacent undyed material (Gordon & Gregory).

The heat fastness of dyeings of equal dye concentration on the same substrate will, at a specific temperature and time, be dependent on the size and polarity of the molecules of the dyes involved which in turn determine the rate of diffusion of the dye within the substrate and the volatility of the dye. Increases in size and/or polarity will tend to reduce the rate of diffusion out of the fibre and the vapour pressure of the dye and thus increase sublimation fastness. The same changes will tend to make application by exhaustion methods more problematical as the lowered diffusion coefficient will mean slower fibre-penetration, reduced levelling power and lower colour yields. Therefore, a compromise between the decrease in hydrophobicity (and consequent loss in fibre affinity) and polarity has to be made. Because of this property, disperse dyes have been classified into types of excellent dyeing properties but poor heat fastness (Class A) through to those with excellent heat fastness but poor dyeing properties (Class D) (Nunn, 1978).

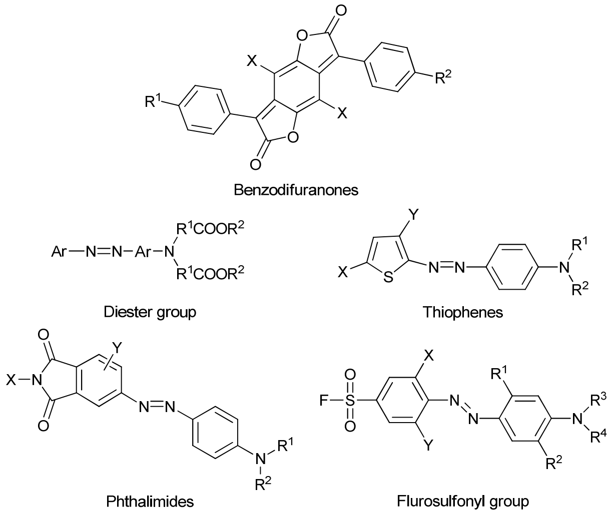
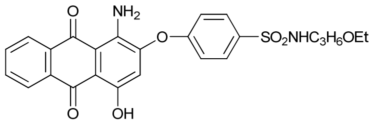


Fig. 8. Recently developed disperse dyes with high wash fastness

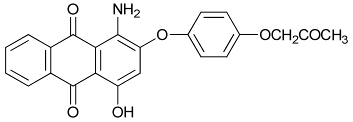
The structural changes useful in raising heat fastness include modification of the side chains of the terminal amino nitrogen (Hallas, 1979). However, other balances must be kept in mind; the hydroxyl group is a particularly effective group, but can have an adverse effect on light fastness on polyester. Increasing mass may also play a small part in the effectiveness of these groups. A 2-acetylamino group in the donor ring can have a beneficial effect on heat fastness (Gordon & Gregory, 1983), the tendency to sublime decreasing as the polarity and the number of potential hydrogen-bonding groups increases .

Generally the effects of substitution in the diazo residue are less marked. Replacement of either carbocyclic ring for a heterocycle can raise fastness, as well as substitution on the heterocycle itself, although in some cases, little difference has been found, for example between some thiazole and phenyl analogues (Peters & Cheung, 1985).

Improved sublimation fastness can be achieved by increasing the molecular size and by incorporating additional hydrophobic groups into anthraquinone ring. Thus, the modified dyes such as C.I. Disperse Red 92 and C.I. Disperse Red 229 have been designed to improve the moderate sublimation fastness of C.I. Disperse Red 60 by introducing additional substituents that leave the brilliant hue intact (Fig. 9).



C.I. Disperse Red 92



C.I. Disperse Red 229

Fig. 9. Modified dyes for improved sublimation fastness.

2.2.3 Fastness to light

Many dyes are known to fade when left exposed to sunlight for prolonged periods. Such photofading is a well known technological phenomenon within the textile industry (Zollinger, 1991). In particular, certain applications of textiles dyes require higher light fastness quality control than others and this has led to an accepted light fastness scale that facilitates selection of a dye for a give application (Oakes, 2001). Although a close relationship does exist between the chemical structure of a dye and its light fastness rating, it is important to remember that other factors are of relevance, the most critical of which are (Giles & McKay, 1963):

a. The inherent photostability of the dye molecule; in general, the chromophoric nucleus is the most important element in determining the light fastness of a dye, but nuclear substituents may alter the fastness significantly.
b. The concentration of the dye within the fibre; usually the fastness of a dyed fibre increases with increasing dye concentrations.
c. The nature of the fibre in which the dye is dispersed; different fibres contain different chemical groups and these substituents can have a significant effect on the light fastness rating of a dye on a given fibre.
d. The wavelength distribution of the incident radiation; not all the absorption are equally effective in starting a fading process.
e. The composition of the atmosphere; the moisture content of the atmosphere can have a marked effect on the fading rates of certain dyes.

A survey of commercial disperse dyes applied to various substrates has revealed that the average light fastness is highest on polyester, followed by di-, tri-acetate and then nylon, although this could simply be an artefact of commercial usage and research concentrating on dyes for polyester and acetate as these are the more important substrates for this dye class.

However, anomalously low fastness arises with *o*-nitro substitution. The deleterious effect has been ascribed to the proximity of the negative charge on the nearest oxygen of the nitro function to the azo group preventing electron delocalization, ultimately lowering the bond order of the α-nitrogen-carbon link and therefore increasing susceptibility to photolytic cleavage (Mehta & Peters, 1981).

In the 4-aminoazobenzene series, variation of the terminal amino groups provides an important means of increasing light fastness on polyester. The use of β-cyanoethyl groups appear advantageous, while that of β-hydroxyethyl groups, useful in dyes for diacetate, is here inexpedient, although *o*-acylation brings about a striking increase in fastness (Kassim & Peters, 1973)

Oxidation and reduction reactions are known as the two most important pathways for the fading of dyes. Although photooxidative processes are generally accepted as being responsible for fading on non-protein substrates, such as polyester and acetate, there is little direct evidence (Fig. 10).

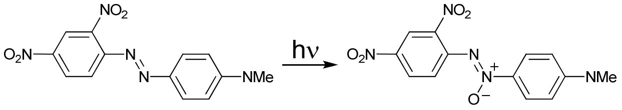


Fig. 10. Oxidative fading mechanism of azo dye : the conversion of the azo group to an azoxy group.

Deductions from Hammett plots provide indirect affirmation (Gordon & Gregory, 1983) as well as increased fading in the presence of oxygen. Direct evidence has however been obtained of an oxidative pathway, the dealkylation of 4-*N*,*N*-dialkylaminoazobenzenes on polyester and nylon in which dye-sensitized singlet oxygen attacks the terminal nitrogen lone pair electrons of the dye in the ground state. While the dealkylated products will not differ radically in colour, the creation of carbonyl species and peroxides may cause destruction of the azo group, leading to more significant fading.

Intensive investigations have concentrated on improving the molecular stability to light, and elucidating some empirical correlations between the electronic behaviour of substituents and their resistance to light. Anthraquinone dyes containing electron-donating substituents are more susceptible to fading than those containing groups, such as –NHCOPh, which contribute towards better light fastness (Dawson, 1983).

Further incorporation of less basic substituents, notably heterocyclic moieties, into β-positions of 1,4-diaminoanthraquinone leads to bright turquoise blue dyes, for example C.I. Disperse Blue 60 and Blue 87 that were originally developed by DuPont and BASF in 1955 and 1963, respectively (Fig. 11). The superior light fastness of these dyes is attributed to the electron-withdrawing effect exerted by the imide groups (Dawson, 1983). These two bright dyes are still preferred for the coloration of polyester in intrinsic turquoise shades and in a bright green by the addition of an appropriate yellow dye.

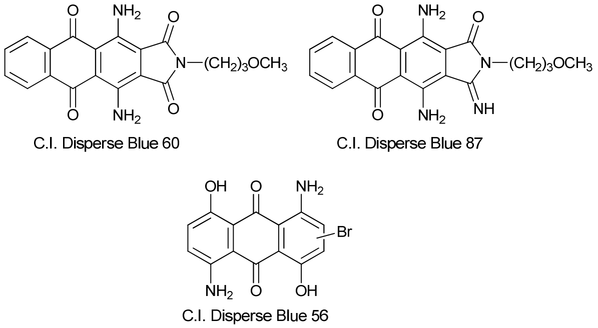


Fig. 11. Modified dyes for improved light fastness.

A classic anthraquinone dye, C.I. Disperse Blue 56 was first synthesized to dye cellulose acetate during the late 1950s, featuring a bright neutral blue shade and excellent level dyeing. However, the manufacture of this dye gives rise to environmental problems and is economically disadvantageous. Nevertheless, this dye remains of limited application in areas that require good light fastness in pale depths.

3. Hydrophobic fibres

Disperse dyes can be applied to a whole range of chemically diverse, hydrophobic man-made fibres, which include acetate, acrylic, modacrylic, nylon, polyester and polyurethane fibres. However, of these, the most important fibres for disperse dyeing are polyester and secondary cellulose acetate (J. R. Aspland, 1997).

3.1 Polyester fibres

Polyester fibre is a manufactured fibre composed of synthetic linear macromolecules having in the chain at least 85% (by mass) of an ester of a diol and benzene-1,4-dicarboxylic acid(terephthalic acid) (Denton & Daniels, 2002). Fibres of the most common polyester, Poly(ethylene terephthalate) (PET or PES) is generally made from either terephthalic acid or dimethyl terephthalate together with ethylene glycol (Fig. 12) (Lewin & Pearce, 1985).

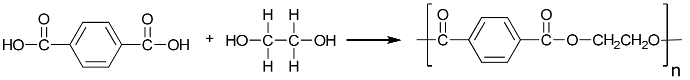


Fig. 12. Polymerization of poly(ethylene terephthalate).

3.1.1 Historical background

The first commercial fibre-forming polyester was developed by Dickson and Whinfield working at the Calico Printers' Association in England in 1941. It was produced by condensation of ethylene glycol and terephthalic acid. Rights to manufacture this product were bought by ICI and DuPont. The ICI product was named Terylene and the DuPont product Dacron (A. D. Broadbent).

Polyester fibres are produced as medium- and high-tenacity filament yarns and as staple fibres of various lengths and fibre colour to suit the kinds of spinning machinery found in the textile trade. Polyester fibre not only offers the typical features of a synthetic fibre, such as high chemical resistance, high moth-proofness, excellent wash and wear and permanent press characteristics, but also, when blended with cotton and wool, gives rise to fabrics of high quality. These unique properties make it the largest commodity fibre in the synthetic fibre world, in 1990, polyester production exceeded the total production of both polyamide and polyacrylic fibres (Brunnschweiler & Hearle, 1993).

Recent developments include new polymer compositions, physical characteristics improvement, enhanced aesthetic quality and improved dyeability (Fig. 13). Developments in physical characteristics include decreasing the fibre's intensity so as to facilitate the rupture and removal of objectable 'fuzz balls' (pilling-resistant fibre) and anti-static finishing through the application of the hydrophilic finish which creates capillarity in the interfibre spaces (Brunnschweiler & Hearle, 1993). As for improvements in dyeing properties, modified polyester has been introduced that contains ionic sites to facilitate ionic dye attachment as well as the use of a copolymer that lowers the compact structure of polyester (Moncriff, 1970). To increase the aesthetic quality of textured yarns, high refractive index inorganic particles have been incorporated into fibres and silk-like polyester fibre have been developed (Brunnschweiler & Hearle, 1993). However, although these modifications enhanced the lustre of polyester, softness in handle was lacking. During the 1970's and 1980's, the 'touch' of polyester fibre was enhanced; alkali deweighting treatments were used to make the fibre more delicate and a wrinkle finish imparted it to an appearance similar to that of silk. In addition, there have been many other activities in fibre development, such as polymer modification, fibre blending, surface treatment, the mixture of various fibre cross sections, special spinneret design and fine denier spinning for polyester and silk-like fibre developments (Brunnschweiler & Hearle, 1993).

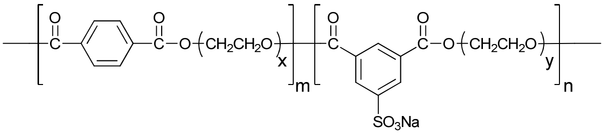


Fig. 13. Modified polyester dyeable with cationic dyes.

3.1.2 Properties of polyester fibres

Physical properties

Polyester fibres are very hydrophobic, therefore, they absorb only a very small amount of water and there is no significant change in their tensile properties when they are wetted. The moisture regain of polyester fibre is approximately 0.4% at 65% relative humidity and 20°C (Moncriff, 1970). Polyester materials dry quickly because of their very low water absorption.

The tensile properties of polyester fibres vary with temperature; at 180°C, the fibre retains approximately half the tenacity it possesses at room temperature and its extensibility increases (Nunn, 1979). Medium-tenacity yarns shrink by approximately 6% in boiling water but only by 3% in hot air at the same temperature; similar differences are found at higher temperatures. Polyester fibres will, however, take a permanent-set when distorted at high temperature (Moncriff, 1970)

Polyester fibres exhibit high initial moduli of elasticity, high resistance to blending deformations and good recovery from them, negligible creep under the low extensions to which the fibres are most commonly subjected in use and high resistance to abrasion [65].

Polyester can be exposed to sun light for 600 hours and the fibre strength will still be around 60-70% of its original strength (Moncriff, 1970).

Chemical properties

Polyester fibres show outstanding resistance to damage by most common chemicals under ordinary conditions of exposure and a wide range of substances have little or no effect on their strength.

Their resistance to oxidizing and reducing agents is excellent and, as a consequence, bleaching treatments using sodium chlorite, sodium hypochlorite or hydrogen peroxide may be employed. Concentrated formic acid, acetic and oxalic acids produce strength losses of 15%, 6% and 8%, respectively, after treatment at 80°C for 72 hours, but dilute solutions of mineral acids are resisted, even at 100°C.

Polyester fibres can be treated with dilute alkalis at temperatures up to 100°C and can withstand the strongly alkaline conditions used in vat-dyeing and or in mercerizing. However, solutions of caustic alkalis do, in fact, attack and hydrolyze the polymer, but at temperatures up to the boil, such attack is confined to the surface of the fibre; this particular characteristic has been utilized in the production of silk-like polyester.

Polyester polymers display the typical reactions of ester and can be hydrolyzed in the presence of dilute alkali or acid or by water alone. No serious change can be expected to be observable in the textile-processing properties of fibres and yarns dyed for one to two hours at 130°C, so long as the pH of the bath has been maintained close to 7. However, in an acidic bath of pH substantially less than 4 or in an alkaline bath, more rapid attack will occur Above pH 8, high-temperature dyebaths can induce serious degradation of polyester fibres if treatment is prolonged (Nunn, 1979).

3.2 Acetate fibres

Cellulose acetates are esters of cellulose in which a large fraction or even all the hydroxyl groups have been esterified using acetic anhydride. The two major types of cellulose acetate have about 55 and 62% of combined acetic acid. These values correspond to cellulose with degree of substitution of 2.48 and 3.00, respectively. The latter is called cellulose triacetate, and the former is called cellulose diacetate (Fig. 14) (Broadbent, 2001).

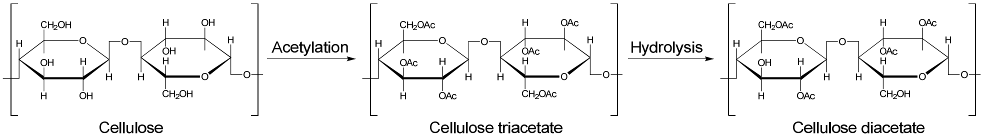


Fig. 14. Chemical structures of acetate fibres

Acetate fibres belong to the class of man-made cellulosic fibres and are manufactured by treating cellulose in the form of pure wood pulp or, less frequently, cotton linters, with a mixture of glacial acetic acid and acetic anhydride at low temperature in the presence of an activation catalyst such as sulphuric acid, perchloric acid, zinc chloride or similar salts (Rouette, 2000). Cooling prevents an increase in temperature of the mixture that will promote excessive hydrolysis of the cellulose. This initial product is cellulose triacetate (primary cellulose acetate) and cellulose diacetate (secondary cellulose acetate) is obtained directly from the triacetate by partial hydrolysis (Broadbent, 2001).

Cellulose diacetate, once widely known by its producer's company name, Celanese, can be written and drawn in a similar manner to cellulose, except that between 77-80% of the hydroxyl groups have been acetylated by reaction with acetic acid, to give cellulose acetate esters (Trotman, 1984).

3.2.1 Historical background

Acetate was the first hydrophobic man-made fibre, and when it appeared on the market, knowledge about the mechanism of dyeing and of molecular structure of fibres was limited. Because acetylation makes the fibre hydrophobic, resistant to swelling, and endows it with a greater electronegative surface charge in water, there is no response to direct dyes. The absence of basic groups affords no sites of attachment for acid dyes, but the yarn does show some substantivity for basic dyes. In the early days, limited ranges of water-soluble dyes, selected from a variety of sources by trial and error, were placed on the market. In many cases both their fatness and exhaustion left much to be desired (Trotman, 1984)

Cellulose di- or triacetates have no ionic groups. They are quite hydrophobic fibres. When introduced in the 1920s, cellulose diacetate was initially difficult to dye satisfactorily with existing ionic dyes. Fine dispersion of simple, non-ionic azo and anthraquinone compounds, of limited water solubility, however, efficiently dyed this fibre. These so-called disperse dyes are slightly soluble in water and are extracted from the aqueous solution by the solid fibre in which the dyes are quite soluble (Broadbent, 2001).

3.2.2 Properties of acetate fibres

Physical properties

These fibres in no way resemble fibres of cellulose. Both cellulose diacetate and triacetate are relatively hydrophobic and thermoplastic. The standard regains of cellulose di – and triacetate are 5.0 and 2.5%, respectively. They hardly swell in water(Broadbent, 2001).

Cellulose diacetate is thermoplastic in the hot dyebath and care should be taken to ensure the goods are not subjected to stretching. They are approximately 40% weaker wet than dry, and their extensibility is increased by about 40% when wet. They are permanently glazed at temperatures above approximately 175°C, soften at 205°C and melt at approximately 230°C. The low temperature of softening may be of advantage for embossed finishing (Trotman, 1984).

The mechanical properties of triacetate fibres are close to those of the secondary acetate but they do not lose a great deal of strength when wet. It gives fabrics with a firm crisp handle, less soft than that of the diacetate (Broadbent, 2001)..

Chemical properties

Both cellulose acetates are resistant to dilute solutions of acids but are sensitive to alkaline solution, which cause hydrolysis of the acetate ester to hydroxyl groups, especially at higher temperatures. The triacetate is more hydrophobic and more compact and crystalline than the diacetate and has better resistance to alkaline solutions and to solvents (Broadbent, 2001).

4. Disperse dyeing

For dyeing polyester fibres, in practical terms only disperse dyes are suitable. Through their hydrophobic properties, these dyes are capable of penetrating into the similarly hydrophobic polyester fibre. This class of dyes has only extremely poor solubility in water (Rouette, 2000); for this reason, dispersing agent is added to the dyebath to maintain dispersion stability, especially in the case of high temperature dyeings (Burkinshaw, 1995).

4.1 Basic principle

The inclusion of dispersing agent in the dyebath is a crucial factor in the application of disperse dyes. Once such a compound is added to water, its dual character results in the formation of micells above critical, but low, concentration. The hydrophobic tails of the dispersing agent molecules are inside the micelle which, as a consequence, is able to solubilise the disperse dye molecules, so conferring a higher apparent solubility on the dye. The dye transfer to the fibre from the micelles. As micelles empty their dye, they re-from and dissolve more dye from the solid particles (Ingamells, 1993)

Much of the evidence that is available on the subject suggests that in dyed polyester fibres the disperse dyes are present chiefly in the monomolecular state [Schroeder & Boyd, 1957; Hoffman et al, 1968]. At the end of the dyeing process, the dye that has been absorbed by the fibre is in a state of dynamic equilibrium with the dye that remains in the bath, and the fraction of the latter that is in aqueous solution must be present in the same state of aggregation as the dye in the fibre. It is reasonable to infer that the transfer of the dye to the fibre takes place from a monomolecular aqueous solution, the concentration of which is maintained during the first phase of the dyeing process by the progressive dissolution of solid dye from the particles in dispersion in the bath. In the presence of dispersing agents the following equilibrium situation is set up (Fig. 15) (Johnson, 1989).

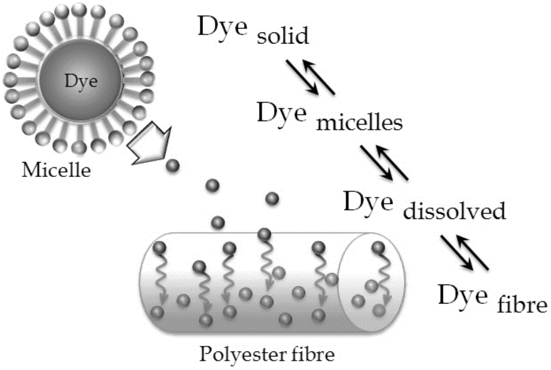


Fig. 15. Disperse dyeing mechanism

The four stages of the process mechanism are as follows (Murray & Mortimer, 1971):

a. Some of the dyes dissolve in the water of the dyebath.
b. Molecules of dye are transferred from solution to the surface of the fibre.
c. The solution in the dyebath is replenished by the dissolution of more solid material from the dispersion.
d. The adsorbed dye diffuses monomolecularly into the fibre.

The process of transfer from the aqueous solution to the fibre is comparable with the extraction of a solute from one solvent by a second, immiscible solvent and similar laws of partition are applicable. Distribution coefficients that are related to the solubilities of the dyes in the aqueous and fibre phases can be determined for different processing temperatures, although they may be affected by the simultaneous equilibrium between the aqueous and solid phases of the dye. The rates of the first and second stages of the process mechanism are governed by these solubilities.

It was established that the disperse dyeing system was truly reversible and that the results conformed to a rectilinear isotherm. Typical results show linear relationship in distribution of dye between polyester and water. It is well established that dyeing with disperse dyes is the transfer of dye molecules from a molecular dispersion into the fibre and because of the linearity of the isotherms obtained, the amount of dye adsorbed $[D]_{ad}$ relative to the concentration in the bath $[D]_s$ can be expressed by a partition coefficient K (A. Johnson, 1989), i.e.

$$\frac{[D]_{ad}}{[D]_s} = K \tag{1}$$

As more dye is introduced into the system a point will be reached at which the amount of dye in the dyebath at equilibrium exceeds the solubility of dye. In the ideal case further additions of dye will produce no further change in the concentration of dye in solution, and hence no change in the concentration of dye on the fibre. At this point, therefore, if the abscissa denotes total dye in the bath rather than dye in solution, then the isotherm will become horizontal (A. Johnson, 1989).

Dye molecules that have been adsorbed on the fibre surface diffuse into the interior of the fibre by a relatively simple mechanism, which appears to obey Fick's equation (Patterson & Sheldon, 1959). That is to say, the rate of diffusion of dye through unit area (transverse to the direction of diffusion) at any point in the fibre is directly proportional to the concentration gradient of the dye at that point. As would be expected, the amount of dye taken up by polyester fibres from a bath of constant concentration is found to be proportional to the square root of the dyeing time, until a saturation value is approached. Very similar results are observed during the earlier stages of the process in dyebaths of normal composition and concentrations, such as are employed in commercial 'exhaust-dyeing' processes. It is found that the rate of dyeing is quite independent of the concentration of the dyebath, practically up to the point at which equilibrium is established (Waters, 1950). For dyeings carried out at a constant temperature, a plot of the instantaneous fractional 'dye uptake' (C_t/C_∞) against time of dyeing gives a steeply-rising asymptotic curve, which appears to fit a law based on the hyperbola or, possibly, on the hyperbolic tangent (Cigarra & Puente, 1967).

An important difference between the dyeing behaviour of polyester fibres and that of other fibres such as nylon and secondary acetate, which also accept disperse dyes, is in their rates of dyeing. Polyester fibres dye very slowly at temperatures much below 100°C (Waters, 1950). Disperse dyes can be applied to cellulose secondary acetate readily over approximately 1 hour at 80°C. Higher temperatures are avoided as otherwise acetate groups on the cellulosic fibre can be hydrolysed to hydroxyl groups, which can spoil the surface of the fibres and reduce their substantivity towards the disperse dyes. Cellulose triacetate is more difficult to penetrate with disperse dyes because of its more compact molecular structure, but it can be dyed at the boil. Nylon fibres can be dyed under conditions similar to those used for cellulose acetate fibres. In case of acrylic fibres, the presence of anionic groups such as $-SO_3H$ and $-COOH$ permit only pale shades to be obtained under normal conditions with disperse dyes (Ingamells, 1993).

4.2 The effects of variations in disperse dyeing

Several factors affect the dyeing of polyester fibre with disperse dye such as crystal form of the dye, dispersing agents, particle size of the dye, pH of the dyebath, temperature of dyeing and heat setting, and fibre fineness.

Crystal form of the disperse dyes

The possible different crystal forms (e.g. α, β, γ, δ and ε) of disperse dyes have been suggested to influence the saturation values achieved on polyester, due to differences in the vapour pressure and solubility of the different forms of dye in both water and fibre (Biedermann, 1971, 1972).

Dispersing agent

Disperse dyes are sparingly soluble in water and often crystalline with varying particle size. These characteristics are inadequate for dispersing the dyes in water and cause unlevel dyeing. In order to achieve the required particle size and distribution (Heimanns, 1981), the disperse dye is milled, usually in the presence of a dispersing agent (Derbyshire et al, 1972). Generally, the dispersing agents are anionic, ligninsulphonates or polycondensates of arylsulphonic acids with formaldehyde which facilitate milling by preventing agglomeration of the dye particles.

Particle size in dispersion of the dyes

The aqueous solubility of disperse dye particles in a dispersion increases with decreasing particle size (Kenneth & Skelly, 1973). Thus an increase in the severity of milling that accompanies a reduction in the particle size of the dye enhances the solubility and adsorption of disperse dye.

pH of dyebath

Generally, in the commercial dyeing of polyester fibres with disperse dyes, dyeing is carried out within the pH range 5.5 to 6.5. Strongly alkaline or acidic conditions, such as higher than pH 9 and lower than pH 4, induce hydrolysis of the fibre as well as decomposition of azo disperse dyes (Nunn, 1979). In the case of high temperature dyeing, this degradation of polyester fibre and dye is accelerated.

Substantivity of disperse dyes

The substantivity of disperse dyes towards polyester fibres is one of the most critical factors in determining dyeing behaviour and there have been many studies carried out to evaluate the substantivity of disperse dyes towards hydrophobic fibres, including polyester, in order to select suitable dyes. These attempts include the ‘Solubility Parameter Concept’ (Ingamells, 1990) and ‘IOR (Inorganic/Organic) values’ (Kim et al, 2003).

Temperature

The adsorption and diffusion of disperse dyes on polyester are greatly influenced by temperature as an increase in temperature increases the mobility of the polymer chains in the amorphous regions of the fibre. Polyester fibres dye very slowly at temperatures much below 100°C. At 85°C, the temperature normally used for the dyeing of secondary cellulose acetate, it was found that polyester fibre dyed at rates between 700 and 1000 times slower than those measured for the same dyes on secondary cellulose acetate and nylon (Nunn, 1979). When, however, sufficient time was allowed for the polyester fibre to come nearly to equilibrium with the dyebath, it was found that it had taken up approximately the same amount of dye as had secondary acetate and in most cases about twice as much as nylon (Waters, 1950). For the dye-hydrophobic fibre system, the affinity of the disperse dye decreases with increase in dyeing temperature while the saturation value of the dye in the fibre increases with increasing temperature (Bird et al, 1959; White, 1960).

Heat setting changes the morphology of the polyester fibres. When fabrics of polyester are heat set in air under conditions of free shrinkage, the dye exhaustion first decreases and then increase with increasing setting temperature. The minimum exhaustion occurs after seeing at around 160-190°C. If applied tension prevents fabric shrinkage during heat setting, the dye uptake/temperature profile is similar to that under conditions of free shrinkage, but with higher uptake values (A. D. Broadbent, 2001).

Fibre fineness

Much attention has been given recently to dyeing microfibres. In a broad sense, especially in Europe, the term microfiber means fine fibers of less than 1.0 denier. However, in South Korea and Japan, where fine-fibre technology is more advanced, fine fibres of 0.04 – 0.4 denier class are generally used in this filament area (Koh et al, 2006). A useful preliminary relationship between the percentages of dye on weight of goods (C_1, C_2) needed to achieve a particular depth of shade on polyester fibres of two different fineness (D_1, D_2) was suggested by Fothergill (Fothergill, 1944):

$$\frac{C_2}{C_1} = \sqrt{\frac{D_1}{D_2}} \tag{2}$$

According to this equation, it takes much more dye to dye the microfiber to the same apparent depth as the regular fibre. Therefore, such marked denier difference can affect dyers in a number of ways (Aspland, 1997).

4.3 Recent requirements in disperse dyeing technology

Environmental issues have been gaining importance in all aspects of industrial production (McCarthy, 1998), and various legislative requirements have emerged with increasing regularity to reduce the impact of dyeing processes on the environment. In response, the industry has been forced to become increasingly innovative in order to develop new products and practices that are more environmentally friendly than existing ones (Lewis, 1999). Therefore, innovation and developments in color chemistry and dyeing will allow the colorist to meet ever-increasing environmental restrictions, produce novel effects, and reduce processing costs (Leadbetter & Leaver, 1989).

The demand for environmentally friendly dyes with high wet fastness on polyester is increasing, and the so-called alkali-clearable disperse dyes suggest a promising new direction (Fig. 8). These alkali-clearable disperse dyes obviate the need for sodium hydrosulphite and significantly reduce the cost of effluent treatment (Koh & Greaves, 2001). Recently, these types of dye have become technically important for the coloration of polyester and its cellulosic blends. They perform well on international standard and commercial wash fastness test (such as ISO C06 C2S) (Choi, 1999).

To achieve acceptable levels of wet fastness after post-heat treatment, the development of modern disperse dyes must be directed towards satisfying a number of needs. Firstly, new dyes need to be tailored towards satisfying shorter, more easily reproducible and more economical dyeing processes. Secondly, with the increasing use of polyester and polyester blends in sports and leisurewear, there is a clear demand for dyes of higher wet fastness. Indeed this requirement has become even more important with the introduction of polyester microfibres, where higher depths of shade have to be dyed in order to obtain the same visual yield as with conventional polyester fibre. Finally, the development of new disperse dyes must take into account the effect that effluent from the dyeing process will have on the environment, and aim to minimize such pollution. These objectives are not mutually exclusive but interrelated; they must all be taken into account in any dye development program (Leadbetter & Leaver, 1989).

5. Main methods of disperse dyeing

Disperse dyes are the most important class of dye used in dyeing polyester fibres and provide a wide range of hues with good build-up and fastness properties adequate for most purposes. The rate of dyeing may be raised to the level of commercial acceptability, either by raising the working temperature to the region of 130°C, or by dyeing at the boil in the presence of an accelerating agent or 'carrier' (Waters, 1950). Disperse dyes can also be transferred to polyester fibres under dry conditions by impregnating the goods with a suitable dispersion, drying and then baking at temperatures in the range 190-220°C (Ingamells, 1993).

5.1 Carrier dyeing

The term 'carrier' is originated from the idea that the compound and the dye formed a complex which could 'carry' the dye into the fibre, thus causing more rapid dyeing. It is now known that the carrier is adsorbed by the fibre and operates by modifying the structure of the amorphous regions (A. Johnson, 1989).

A carrier is an organic compound, dissolved or emulsified in the dyebath. Carriers allow dyeing of even deep shades at the boil within a reasonable dyeing time. Common polyester dyeing carriers include butyl benzoate, methylnaphthalene, dichlorobenzene, diphenyl and *o*-phyenylphenol, the latter two being the most popular.

The actual mechanism by which a carrier accelerates dyeing has been widely debated and probably depends on the carrier used. The polyester fibres absorb the carrier and swell. This swelling can impede liquor flow in packages causing unlevelness. The overall effect seems to be a lowering of the polymer glass transition temperature, thus promoting polymer chain movements and creating free volume. This speeds up the diffusion of the dye into the fibre.

A typical carrier dyeing procedure involves running the goods in the bath 60°C and adding dilute dispersing agent, emulsified carrier and lastly the disperse dyes. The temperature is then gradually raised to the boil and dyeing continued at this temperature (A. D. Broadbent, 2001). The sorped carriers must be removed from the polyester after dyeing, usually by hot-air drying the goods from 150-180°C. Residual carriers can adversely affect lightfastness if left on the goods.

The benefits of carriers were overwhelming in the early days of polyester dyeing because polyester fabrics could be dyed in unpressurized becks with no more dyeing problems than with direct dyes. However, carrier dyeing has steadily declined since the development of suitable machines for dyeing polyester under pressure at temperature around 130°C. Carriers are still used in some garment and small commission dyehouses where high temperature pressurized dyeing machines are not available (A. D. Broadbent, 2001).

5.2 High temperature dyeing

High temperature dyeing is the most widespread method of batch coloration. The temperatures (ca. 130°C) require pressurized equipment and impart increased diffusion of the dyestuff (and therefore increased rate of dyeing) by reducing cohesion between polymer chains and increasing the kinetic energy of the dye molecules. A typical exhaust dyeing application sequence for polyester is shown in Fig. 16, showing the three main phases of the process including the heating or adsorption phase, the high temperature or diffusion phase, and the clearing phase.

5.2.1 Adsorption phase

The heating or adsorption phase is the most critical in determining the levelness of the dyed fibre and it is essential therefore that the heating rate is appropriate to allow controlled adsorption of the dye. Although in the dyeing of polyester, levelling can occur through migration at top dyeing temperature, in rapid dyeing cycles the time at top temperature is minimal and it is even more critical to ensure dye is applied in a uniform manner during the adsorption phase.

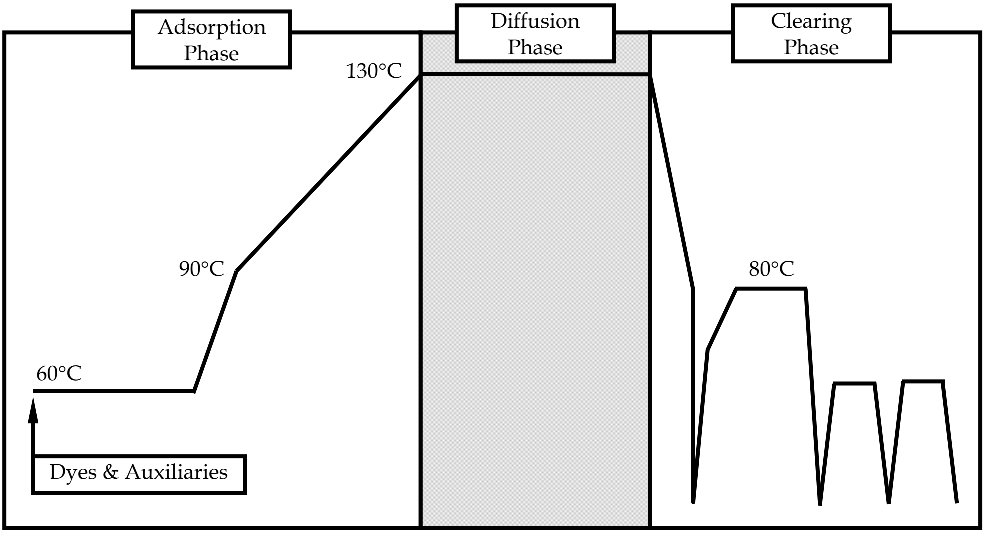


Fig. 16. Phases of exhaust dyeing of polyester.

The adsorption behaviour is strongly influenced by a number of factors, the most important of which are concentration of dye, temperature gradient, fibre type and auxiliary system.
The rate of exhaustion of a disperse dye by polyester is controlled by the rate at which the temperature is raised. At some temperature between 80°C and 120°C the dyeing rate for that dye reaches a maximum. The temperature range over which the dyeing rate is at this maximum is known as the 'critical dyeing temperature' (CDT). Slow-diffusing high-energy dyes have a high CDT, whereas more rapidly-diffusing dyes have a lower CDT. Specific values of CDT depend on the rate of temperature rise, dye concentration, liquor flow rate, liquor ratio and the substrate to be dyed. Rapid-dyeing procedures depend on adding the disperse dyes at a temperature just below the CDT and then raising the temperature slowly in the vicinity of the CDT to ensure that the exhaustion rate that just permits level dyeing is not exceeded. The temperature is then raised from just above the CDT to the top dyeing temperature at the maximum rate.

5.2.2 Diffusion phase

The dyeing of polyester is often described as a diffusion-controlled process. This is because of the diffusion phases shown in Fig. 16, including convective transfer through the liquor adsorption and molecular diffusion into the fibre, is the rate-determining step (Dawson & Todd, 1979). Where the time needed for the adsorption phase is largely influenced by the machine conditions, in the diffusion phase the time required at top temperature is directly related to the diffusion characteristics of individual dyes and dyeing depth, but generally, the standard time is 10-20 minutes for dyeing up to pale shades, 20-30 minutes for medium shades and 30-35 minutes for deep shades.

In the high temperature phase of the dyeing process, another important property of dyes is migration, or their tendency to level out. This phenomenon can be very important, particularly if dyes have been adsorbed in a non-uniform manner, perhaps due to inadequate liquor circulation or too rapid a heating rate. While the migration properties of disperse dyes may become a key factor if dyes are applied unevenly during the adsorption phase, the key parameter in the diffusion phase is the diffusion rate of the disperse dye.

5.2.3 Clearing phase

Because disperse dyes have such limited solubility in water, some particulate disperse dye may still be occluded on fibre surfaces after the dyeing phase is complete (Aspland, 1997). If not removed, this surface contamination can undermine the brightness of shade as well as the wash, sublimation and crock fastness results. Commonly, the dyed polyester is cleared of surface-deposited dye as well as auxiliaries (e.g. carriers, surfactants) by means of treatment with detergent or reductive or oxidative treatments, in order to secure optimum fastness of the dyeing and also to improve the brightness of shade (Burkinshaw, 1995).

The usual treatment carried out, especially in heavy depth, is reduction- clearing, where the dyed fibre is treated in a strong reducing bath, usually made up of sodium dithionite and caustic soda. A treatment for 20 minutes at approximately 70-80°C, is often sufficient to clear the fibre surface, but the ease of removal varies from chromophore to chromophore and dye to dye. This treatment acts to destroy loose azo disperse dye through chemical reduction of the azo link (Fig. 17). Anthraquinone disperse dyes are not fully destroyed by such a treatment but a degree of removal of surface dye is achieved through temporary solubilisation of the disperse dye to the alkali-leuco form. (Aspland, 1997).

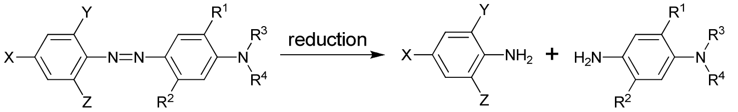


Fig. 17. Chemical reaction during reduction clearing

Research indicates that the polyester dyer will typically reduction-clear in the range of 30-50% of production shades and sometimes an even higher proportion in blend dyeing. Minimizing the need for reduction-clearing can lead to substantial productivity improvements and water and chemical savings as well as a reduction on the effluent load and should be a key objective in implementation of a rapid dyeing approach for polyester.

In the cases of pale and medium-depth dyeings or for those dyes which cannot withstand reduction-clearing, the dye fibre can be given an alkaline scour (Waring & Hallas, 1990); residues of anthraquinone dyes which may remain after reduction-clearing, may be removed using an oxidative treatment (Nunn, 1979).

5.3 Thermosol process

Thermosol dyeing process is important continuous process for dyeing polyester and polyester/cellulose fibre mixture with disperse dyes, which is used mainly for wovens and knitted materials (H. K. Rouette, 2000).

A dispersion of the disperse dye is padded onto the polyester fabric. The material is then dried using a hot flue air dryer or by infrared radiation, the latter usually giving much less migration of the dye. Final drying of the padded material takes place using heated cylinders and the dry fabric is then heated in air, or by contact with a hot metal surface, to a temperature in the range of 190-220°C for 1-2min. In hot air, as the fabric approaches the maximum temperature, the disperse dyes begin to sublime and the polyester fibres absorb their vapours (A. D. Broadbent, 2001).

Dyes of lower molar mass tend to sublime more readily, but they also suffer from low fastness and poor resistance to heat treatments. Dyes of higher molar mass have better fastness properties but are more difficult to apply. After thermofixation, scouring or even a reduction-clearing treatment is necessary to remove any dye remaining on the fibre surfaces (R. M Christie et al, 2000).

PET seatbelt webbing is typically dyed with disperse dyes using thermosol dyeing processes in which the webbing is dipped continuously into a dye solution and passed through a hot chamber (ca. 220°C) for approximately 2–3 min. The dyestuffs can penetrate the molecular chains of the fibres during their exposure to the hot chamber. This method has some advantages that could avoid a batchwise process (a conventional dyeing method), which is regarded as time-consuming and tedious, and would speed up the dyeing process.

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11

Pre-treatment of Textiles Prior to Dyeing

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1. Introduction

Cotton is the leading fibre in Textile Industry. Cotton is still the "King" of fibers because most of the world's apparel is made of Cotton. Apart from its fairly good strength, it is considered to provide comfort due to good moisture absorption and wicking properties[1]. It is estimated that approx. 20 million tons of Cotton is processed worldwide yearly. Unlike man made cellulosic fibers such as Rayon and Lyocell, Cotton must be properly prepared for Dyeing, printing and finishing.

1.1 Typical pre-treatment of cotton involves[2]

- Singeing
- Desizing (Conventional and Enzyme Processes)
- Scouring (Conventional and Enzyme Processes)
- Bleaching
- Neutralization
- Peroxide removal
- Bio-polishing
- Mercerizing
- Optical Brightening

1.2 Objectives of pre-treatment[2]

- Good desizing effect
- Removal of seed husks
- Removal of foreign substances from the fibers
- Lowest possible fiber damage
- High degree of Whiteness
- Good Physical/Technological ratings
- High color yield
- Levelness of the effects
- High and even Hydrophilicity / Rewettability

2. Water consumption in textile industry

Amount of water consumed depends to a large extent (refer Table A[3]), on machine design and complexity of process (refer Table B, C[3]). Different machines have their own characteristic features that set lower limits to the amount of water required e.g. machines such as winch or hank dyeing machine work at material to liquor ratio of at least 1:10-15 while jigger works at 1:3.

Many detailed surveys reveal remarkably wide variations in quantities of water used, i.e. from 5 - 5000 lit/kg of fabric processed. Average consumption in the scouring and bleaching of cotton fabrics was found to be in the range of 10 - 80 lit/kg and 10-130 lit/kg respectively depending on the machine and process employed. In case of dyeing carried out in jigger, the consumption of water is 10 - 60 lit/kg, while that carried out in a winch, it is around 100 - 450 lit/kg.

In another survey carried out at wool processing mills the average consumption of water for various unit processes showed marked variation and the average consumption appeared to be higher than necessary for efficient scouring, milling and dyeing. In case of consumption of water by various types of washing machine, some information has been published. The cost determining factors in this case are water hardness, level control, spray devices, water pressure and washing temperature.

Purpose	**Percent water Use**	
	Cotton textile	**Synthetic textile**
Steam generation	5.3	8.2
Cooling water	6.4	-
Demineralized or RO water for specific purpose	7.8	30.2
Process water	72.3	28.3
Sanitary use	7.6	4.9
Miscellaneous and fire fighting	0.6	28.0

Table A. Water usage in Textile Mills (%)

Process	**Percent water consumed**
Bleaching	38%
Dyeing	16%
Printing	8%
Boiler	14%
Other uses	24%

Table B. Total Water Consumed during Wet Processing

Process	Requirements in litres/ kg of product
Sizing	0.5-8.2
De-sizing	2.5-21
Scouring	20-45
Bleaching	2.5-25
Mercerizing	17-32
Dyeing	10-300
Printing	8-16

Table C. Water requirements for Cotton Textile Wet Finishing Operations

3. Future implications[4]

The Textile Industry is aware of the decrease in water sources and is developing new technology and new chemical alternatives, but the challenge will lay in converting the technology in current textile facilities into the new technology that uses less water. Another challenge will lie in changing the mindset of the current generations in the textile industry to use new chemical alternatives instead of the chemicals they have used in the past decades. This will be a slow process, but one that will need to happen in order for the textile industry to maintain current production and grow in the future.

3.1 Global trends

The textile companies are forced to reduce their consumption of water and energy. Due to

- The rising global consumption of resources like water and energy and the drastically increasing costs,
- Impact of the processes on the world climate,
- More stringent environmental obligations for water and air,
- More stringent regulations and limits

3.2 Present measures by the textile industry

- Reduction of heat energy consumption
- Reduction of fresh water consumption

3.3 New processes-breakthrough techniques

- Reduction of chemicals
- Replacement of chemicals by less harmful chemicals
- More advanced measurement and control techniques- Need for novel economical, environmentally friendly and gentle processes
- Designing machines that use solvents /media other than water for processing

4. Desizing

Conventional desizing of textile: Cold solutions of dilute sulphuric or hydrochloric acids are used to hydrolyze the starch; however, this has the disadvantage of affecting the cellulose fiber in Cotton fabrics. Alternative eco-friendly desizing agents are available in the market in the form of enzymes. Complete removal of starch-containing size without fiber damage is best obtained by using enzymatic desizing agents. Rossari offers wide range of desizing enzymes.

PAD BATCH

Rexsize LHT New Liquid	2.0-5.0 g/L
Common salt	1.0-5.0 g/L
Kleenox PSF Liquid	2.0-5.0 g/L
Proton WDE Liquid	1.0-3.0 g/L

pH: 6.5-8.0

Pad at 80-85°C, Batch at RT for 6-12 hours, Pick up: 80-100 %

CONTINUOUS - PAD STEAM

Rexsize LHT New Liquid	3.0-5.0 g/L
Common salt	1.0-5.0 g/L
Kleenox PSF Liquid	2.0-5.0 g/L
Proton WDE Liquid	1.0-3.0 g/L

pH: 6.5-8.0,Pad at 80-85°C Steam at 90-110°C for 1-2 mins, Pick up: 80-100 %

5. Scouring[5]

Scouring of cotton textiles is an essential treatment in textile wet processing in order to obtain a sufficiently hydrophilic fabric. During scouring, waxes and other hydrophobic materials are removed from the cotton fibers. In nature these non-cellulosic materials create a physical hydrophobic barrier to protect the fiber from the environment throughout its development. In aqueous textile processing the waxes and pectins impede wetting and wicking, subsequently obstructing aqueous treatments. Conventionally, scouring is done in a hot aqueous solution of NaOH to remove hydrophobic components from the primary wall (e.g. pectin, protein and organic acids) and the cuticle (waxes and fats). However, alkaline scouring is a nonspecific process. The use of high concentrations of NaOH also requires neutralization of wastewater. Even though alkaline scouring is effective and the costs of NaOH are low, the scouring process is rather inefficient because it consumes large quantities of water and energy. It is clear that this process needs to be improved considerably to meet today's energy and environmental demands. In the last couple of years, a lot of research has been directed to replace this process with an enzymatic one.

As far as scouring and bleaching is concerned, in earlier times this was supposed to be a two bath process, but currently majority of process houses do a one bath scouring and bleaching process.

In the present time the above mentioned one stage scouring and bleaching process seems to be very ideal with respect to the age old processes that were used earlier. Although robust, this process has some drawbacks that give us scope of further developments:

- **Temperature of Pre- treatment:** As can be seen above, the main backbone of the process is the one step scouring and bleaching that imparts the desired properties to the cotton substrate. The temperature of treatment for this chemical is close to boil. If this temperature can be reduced, there will be considerable amount of time and energy saving

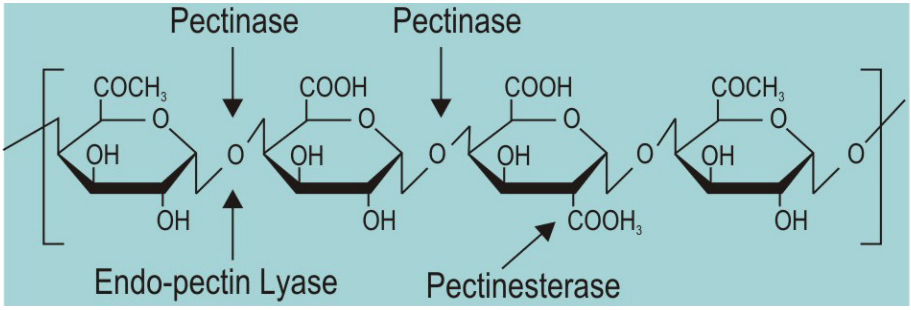
- **No. of Baths before dyeing:** There are total 5 baths that are used before the actual dyeing operation starts. Among 5, the last 3 baths are used basically because of the high pH value of the scouring treatment that requires intensive rinsing and neutralizing. This means that large amounts of water are also consumed. If somehow the scouring treatment can be carried towards neutral pH than we can save directly 3 baths of water. This will contribute significantly to water savings as well as reducing the load on ETP plant. For process houses that buy water in tanker, saving of three baths will be a boon.
- **Damage caused to the cotton substrate:** The aggressive scouring treatment conditions frequently damage the fibre. Due to complete removal of the outer pectin coating of the cotton fibre, the surface profile becomes rough. This affects considerably friction properties of yarn. This also leads to increase in the amount of fly generation. Also there is a considerable strength loss due to oxy-cellulose formation while carrying out peroxide bleaching in alkaline condition.
- **Time of Pre - treatment:** The total time currently required is 2 hrs and 50 min. If some alternative is available that will help to reduce this time than there will be an direct increase in the production and thus allow the organization to reap the benefits from increase in productivity without any increase in the cost of assets.
- **Increase in cost of auxiliaries:** Deployment of caustic and peroxide in the scouring treatment makes the use of peroxide remover and acetic acid mandatory. This further increases the cost of the process.

5.1 'Bio-scouring', the new way

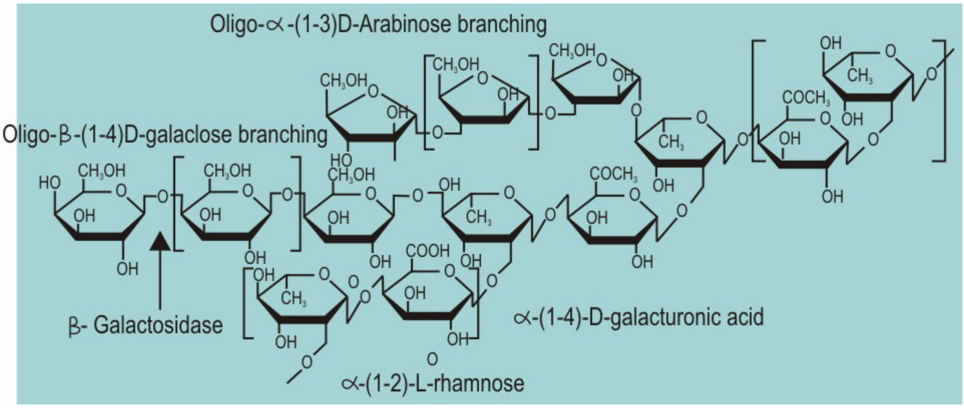
The aforementioned disadvantages of scouring with sodium hydroxide has motivated the textile industry to introduce more enhanced biological agents, which would be as effective in removing non-cellulose substances but would not have any damaging effects on cotton and would be less energy and water consuming. As we all know the outer protective coating of the cotton fibre is made up of pectin. The primary aim of any scouring process is to break this outer pectin layer. Once this is broken the cellulose polymers present inside the cotton fibrils are exposed. These have high affinity for water due to abundance of hydroxyl group, thus making the cotton fibre hydrophilic. If there is a way to break this pectin through some other route then the desired scouring effect can be achieved easily.

Pectins, chemically are high molecular weight, negatively charged, acidic, complex branched heteropolysaccharides primarily containing an alpha- (1,4) polygalacturonic acid backbone which can be randomly acetylated and methylated. Contrary to the proteins, lipids and nucleic acids, pectic substances do not have a defined molecular weight. Three different kinds of pectins have been isolated from cotton:

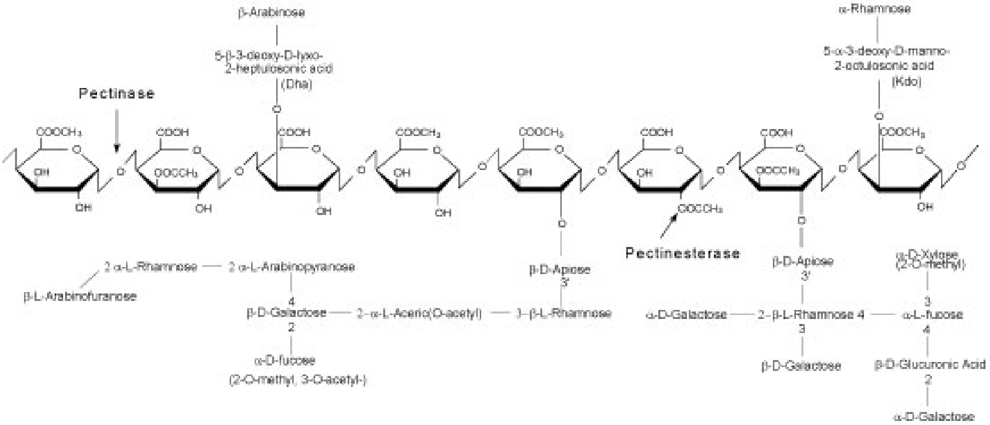
1. Homogalacturonans: These are composed of simple alpha-(1,4) polygalacturonic acid backbone. Some modifications of Homogalacturonans backbone with beta-D- Xylose branching at C3, or apiofuranose substitutions in the backbone with beta-D-Apiosyl-(1,3')-beta-D-Apiose branching are also found. A typical structure of homogalacturonans can be represented as follows:



2. Rhamnogalacturonans I. - This contains alternating alpha-(1-4) galacturonosyl and alpha-(1-2) rhamnosyl residues, with primarily oligo alpha-(1-3) arabinose and oligo beta-(1-4) galactose branching. Atypical structure of it can be represented as follows:



3. Rhamnogalacturonans II. - It is composed of simple alpha-(1,4) polygalacturonic acid backbone with complex branching with composed of up to 11 different monosaccharide types. A typical structure of it can be represented as follows.



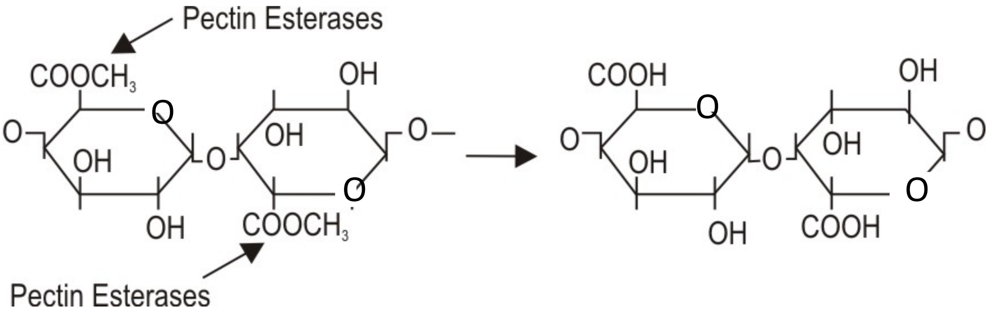
To break this outer pectin layer of cotton fibre, Pectinase enzymes can be used. In general it can be said that the pectinases or pectinolytic enzymes catalyze the random hydrolysis 1, 4-alpha-D-galactosiduronic linkages in pectin substances. These enzymes are further classified based on the specificity of their reaction sites. Four main types of enzymes are used to break down pectin substances namely protopectinases, pectin esterases, polygalacturonases and pectin lyases. All these three different types have different roles to play in pectin degradation.

Protopectinases: These catalyze the solubilisation of insoluble protopectin and give rise to highly polymerized soluble pectin.

$$\text{Protopectin (Insoluble)} + H_2O \xrightarrow{\text{Protopectinases}} \text{Pectin (Soluble)}$$

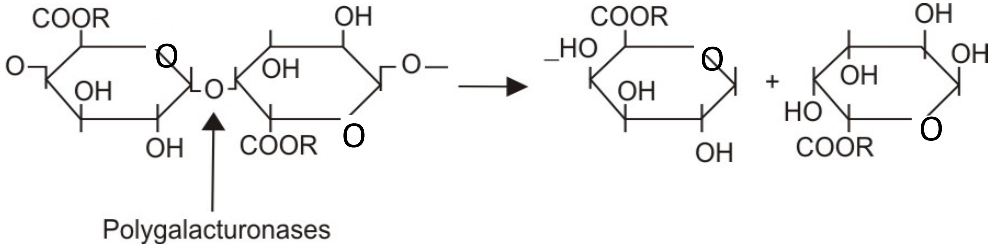
They are classified in to two types based on their reaction mechanism. A-type protopectinases and B- type protopectinases. A-type reacts with the inner site i.e. polygalacturonic acid of protopectin whereas B- type react on the outer side i.e. on the polysaccharides chain that may connect the polygalacturonic acid chain and cell wall constituents. A-types have molecular weight of about 30 KDa. B- types have molecular weight of about 45 KDa.

Pectin Esterases: These liberate pectin and methanol by de-esterifying the methyl ester linkages of pectin backbone.



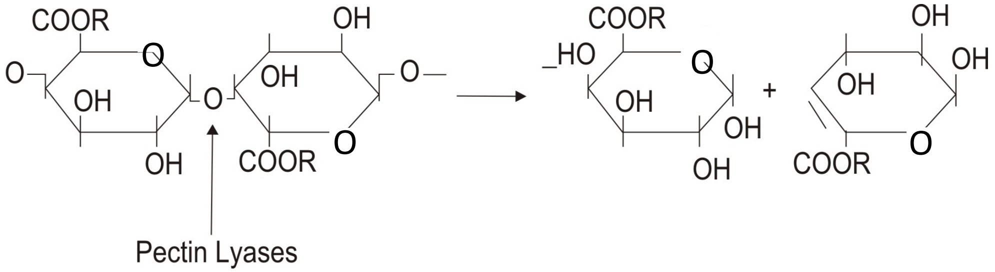
Their activity is highest on 65- 75% methylated pectin, since the enzyme is thought to act on methoxy group adjacent to free carboxyl group. Its action has very little effect on the molecular weight of the pectin. These are highly specific enzymes. Some of them attack only the reducing end while the others attack the non- reducing end. Molecular weights vary in the range of 35- 50 KDa. They are active in the pH range of 4-8. Optimal temperature range for maximum activity is 40- 50^{0}C.

Polygalacturonases: These enzymes directly reduce the molecular weight of the pectins. They catalyze the hydrolytic cleavage with the introduction of water across the oxygen bridge.

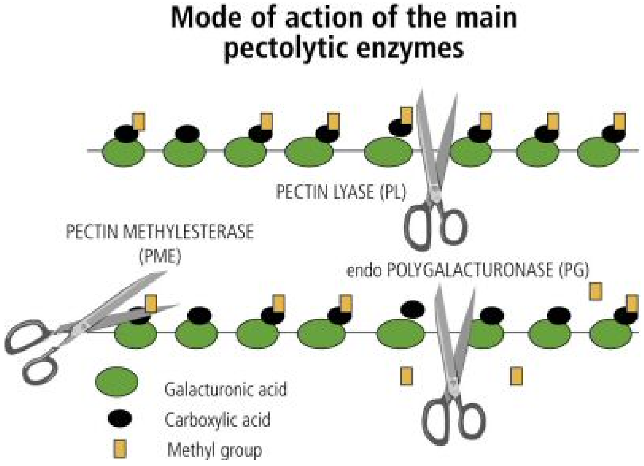


These are the most commonly used enzymes in the market. They are classified further as endo- galacturonases and exo- galacturonases. Endo types are found extensively in nature whereas exo-types occur less frequently. Polygalacturonases obtained from different sources vary widely with respect to their physiochemical and biological properties as well as their mode of action.

Pectin Lyases: They also contribute to the depolymerisation of pectin. These catalyse the trans- eliminative cleavage of the galacturonic acid polymer. The lyases break down the glycosidic linkages at C-4 and simultaneously eliminate H from C-5 position, producing an unsaturated product.



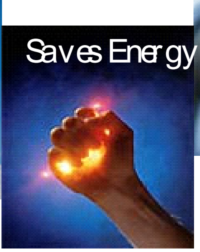
In a much simplified way, the action of the above mentioned Pectinase enzymes can be summarized pictorially in the figure given below:



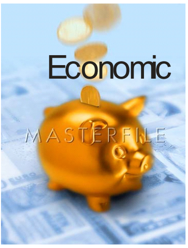
5.2 Rossari's Bio- scouring enzyme – 'Scourenz ABE Liquid '

From the above literature survey, it is very clear that the cotton can be bio- scoured using Pectinases enzyme. As we have seen there is a large pool of sources from which Pectinases enzyme can be obtained and also a huge number of combinations possible depending on the type of pectin degradation required. At Rossari Biotech Ltd, R & D department have developed a bio scouring enzyme named 'Scourenz ABE Liquid', that is successful in producing the desired scouring effects on cotton and its blends. It's a complex mixture of Protopectinases and Polygalacturonases that completes the bio scouring process in 30-45mins and gives a fabric with absorbency within 4-5 seconds. Lower treatment temperature of 55- 60°C and milder acidic conditions with a pH requirement of 5- 5.5 are the advantages that have proven to be a boon to our customers that are currently using this enzymes.

Environment Friendly



Saves Time



The process route that has to be used for carrying out bio scouring operation is:

Load the material
↓
Bio scouring at 55^{0}C for 30 min
↓
Raise temperature of same bath to 90^{0}C and hold for 10 min.
↓
Drain
↓
Start Dyeing

The actual bio-scouring process takes place at 55^{0}C. In this step the pectins are decomposed and emulsified. After bio-scouring, raising the temperature of the same bath to 90^{0}C helps in melting of waxes and oils. These released waxes are emulsified at high temperature and the bath is drained. This removes the entire impurities from the bath and the cotton substrate is ready for dyeing.

The enzymatic process of bio- scouring on bulk scale involves following stages:

- Transfer of enzyme molecules from aqueous phase to fibre surface
- Adsorption of enzyme molecule on to the substrate surface

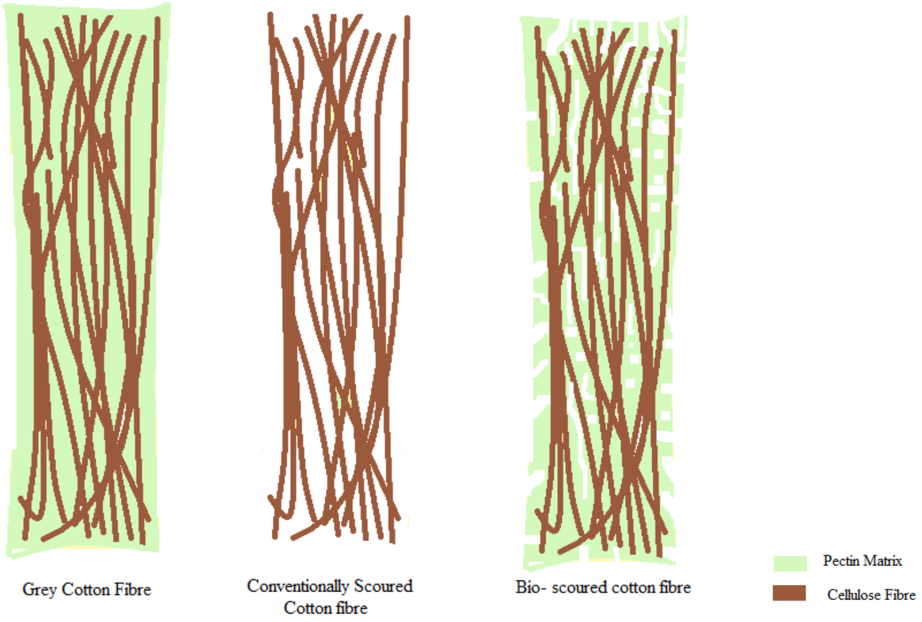
- Catalysis of surface hydrolytic reaction by the enzyme
- Transfer of hydrolytic reaction product to the aqueous phase. After breaking down and removing pectin, which binds, as a natural binder, non- cellulose substances within the fibre cellulose core, other non- cellulose substances can be removed from the cotton by using surfactants and by mechanical action.

Since at least two stages of the enzymatic reaction i.e. transport of enzyme molecules on the cotton substrate and transport of enzymatic reaction products from the cotton substrate in to the solution are controlled by diffusion, the overall rate of hydrolysis depends on the respective diffusion rates. This is the reason why, while carrying out bio- scouring high level of liquor exchange, agitation and turbulence is required. Mechanical agitation of the enzyme processing solution not only improves transport of bulky enzyme molecules toward the surface of the cellulose fabric and in to the interior of the cotton yarn but also helps in release of degraded pectin from the surface of the cotton in to the solution.

5.3 Structure of the bio- scoured fibre against conventionally scoured fibre

In conventional scouring the entire amount of pectin is removed from the cotton fibre. This pectin serves as a binding material for the cellulose fibrils. After its removal the coherence between the fibrils decreases due to which the strength of the structure goes down. Also it leads to harshness of yarn and increased hairiness on the surface.

While designing our bio- scouring enzyme we had the aim of removing the pectins to a level just enough that it facilitates the even absorbency of the yarn, but should not eliminate them completely from the surface. Presence of pectin leads to strength retention, lesser hairiness and smoother surface profile.



Advantages:

- **Water Saving**: In bio- scouring process only one bath is used before the actual dyeing starts, whereas in conventional process a minimum of 5 baths are used. This leads to a total 4 bath saving. Considering an MLR of 1:7, the total amount of water that will be saved is about 28 litres for every Kg. processed. For a unit doing a 30 Mt. of bleaching every day, the amount of water that will be saved is 840,000 Litres per day. On annual basis the amounts comes to be 306600,000 litres of water.
- **Temperature Saving**: The entire process takes place at a temperature of 55^{0}C as against 98^{0}C. The temperature difference is about 43^{0}C. The specific heat of water is 4.186 Joule/ gram K. It requires 4.186 joules of energy to heat 1 gm. of water by 1 Kelvin. Assuming an MLR of 1:7, for every Kg. of cotton, 7 litres of water is used during the bleaching process. In order to heat water from 55 degrees to 98 degrees the amount of heat energy required will be:

Amount of heat energy required per kg. of cotton
= (98- 55) x 1000 x 4.186 x 7= 1259998 Joules = 1260 KJ
1260 KJ is the amount of energy that will be saved for every Kg. of material processed. If calculated the impact of same on yearly basis for a production plant doing a bleaching of 30 Mt. On daily basis, the amount comes out to be
Amount of heat liberated per year for 30 Mt./ Day Plant
= 1260 x 30 x 1000 x 365 = 13797000000 KJ = 13797000 MJ
Thus on yearly basis a unit of daily production of 30 Mt. can save energy of the magnitude 1.38 x 10^7 MJ. If 1.38 x 10^8 MJ is extrapolated to various natural fuels available than we can save following quantity of fuel:

Fuel Source	Calorific Value (MJ/Kg.)	Fuel saved per year (6.41 x 10^6/ Calorific value)	Fuel saved per day
Coal (Anthracite)	27	510.63 Metric tonnes.	1400 kg
Coal (Lignite)	15	919.55 Metric tonnes	2519.8 kg.
Wood	15	919.55 Metric Tonnes	2519.8 kg.
Diesel	44.80	307.45 Metric Tonnes	842 Kg.
Kerosene	46.20	298.20 Metric Tonnes	817 Kg.

All the above mentioned figures are taken considering 100% performance of the concerned parameters involved. If taken in to account boiler efficiency, Combustion efficiency, Heat transfer losses, Steam Transportation losses than the figure will increase by 10 – 25%.

According to the United states Department of forestry, an average weight of a fully grown tree is about 680 Kg. Thus, by using Scourenz ABE Liquid, we would be indirectly contributing to plantation of 3.7 fully grown trees per day. Also, it will lead to reduction in contribution of global warming by any organization since we are inhibiting 1260 KJ of energy to enter in to our bio systems for every Kg. of cotton material bleached. Any organization will have its huge benefits in terms of carbon foot prints and help them to earn through carbon credits.

- **Time Saving:** The process of conventional scouring takes place about 2hrs 50 min. for completion. Whereas the bio-scouring process will not take more than 50 min. for completion. Thus for every batch dyed we are saving 2hrs per batch. A conventional dyeing process takes place in about 7 hours. Whereas using bio- scouring the same dyeing can be completed in 5 hours. In terms of percentage the time saving will be 29%. Thus any process house can raise its production by 29% approximately by using the bio-scouring process.

- **Smoother surface profile:** Presence of pectin in yarn helps to give a smoother profile. This binding agent prevents the hairiness of the cotton that gets generated due to abrasion with processing equipment's. Also pectin itself acts as a softener for the cotton. So the application of final softener can be reduced from 25- 40%. Smoother profile will also help in improving the loom running efficiency by 4% at least.
- **Lesser Weight loss:** Weight loss in bio- scouring process is not more than 1.5%. In conventional process the weight loss is close to 4%. The total saving in the weight loss can be close to 2.5%.In this era, where the cotton prices have shown a steady inflation, this will be a considerable advantage to the process owner.
- **Environmental benefits:** Reduced effluent treatment cost, as avoiding caustic soda, which in turn reduces TDS. During conventional scouring if we consider TDS to be 100% the Scourenz ABE Liquid process has only 20-40% TDS.
- **Lesser cost of Auxiliaries:** In a conventional scouring recipe the chemicals used and their respective cost are:

Summary of benefits:

Gain Type	Saving Parameter	Amount
Tangible and direct measurable gain	Energy Cost	1.51 Rs./ kg.
	Weight Loss	Less by 2.5% (4.0 Rs./Kg.)
	Softener cost	-15% (20 paise/ Kg.)
	Chemical Cost	75 paise/ Kg.
	Water saving	28 litres/ Kg.
Intangible gain leading to benefits	Loom performance	Improved by 4% (Direct increase in profit by 3%)
	Time saving	2 hours. (If utilised will give 29% higher profits)

6. Bleaching[6]

Traditional bleaches for cleaning clothes are hypochlorite and persalts. The proportions used differ widely, depending on the local environmental legislations. Over the last few years major changes have occurred in the bleach compounds used in the detergent formulations all over the world, as the chlorine – containing bleach compounds, which were popular for their low temperature application have been withdrawn for the market and their usage has become limited. This is due to the formation of highly toxic chlorinated organic by products (AOX) during the bleaching process as well as effluents discharged there from. Moreover, the legal regulations have stipulated very low limiting values for AOX in the textile effluent. Nowadays textile industries are obliged to bleach without using chlorine-containing compounds.

Maximum Levels for the indirect discharge of effluent	
Pollutant	Limits
AOX	0.5 ppm

Bleaching using Sodium hypochlorite in batch method, the fabric is treated using 1-3 g/L available chlorine at alkaline pH of 11-11.5 at room temperature for nearly two hrs. Disadvantages of Hypochlorite bleaching are a) all protein impurities must be completely removed before bleaching otherwise the fabric may turns yellowish. b) Residual chlorine must be removed otherwise fabric may be damaged.

As compared to other bleaching agents, bleaching the material with peroxide has following advantages:

1. It is a universal bleaching agent and can be used for bleaching cotton, wool, silk, jute.
2. Weight loss is less as compared to hypochlorite bleaching
3. Superior fastness can be achieved
4. Better absorbency
5. Lesser chemical degradation of cotton
6. Lesser tendency of after yellowing

6.1 Bleaching chemistry

Since hydrogen peroxide contains an atom of loosely combined oxygen, it has powerful oxidising properties. Due to this it has a bleaching action on textile substrate. In a neutral aqueous solution, hydrogen peroxide is ionised in to perhydroxyl and hydrogen ions.

$$H_2O_2 \rightarrow HOO^- + H^+$$

This perhydroxyl ion is supposed to be the active bleaching agent. But the bleaching effect is dependent greatly on the pH of the solution. In acidic or neutral pH, perhydroxyl and hydrogen ions are found in solution. These hydrogen ions have a tendering effect on cellulose due to its acidic nature. It is found that in acidic or neutral pH tendering effect of H^+ ions is more than the bleaching effect of the HOO^- ions. This tendering will in turn impart yellowness to the cotton substrate. So it is not recommended to carry out bleaching in acidic conditions.

On the other hand, in alkaline condition following equilibrium exists:

$$H_2O_2 + OH^- \rightarrow HOO^- + H_2O$$

Here we can see that along with perhydroxyl ion and water molecules are in equilibrium. Due to this in alkaline pH we get more bleaching effect and less tendering of cotton. This is the reason why bleaching is carried out in alkaline pH. But it is observed that in alkaline medium although the damage to cotton fibre is less, the stability of peroxide itself is also very less. In absence of stabiliser, in alkaline medium at temperatures as high as 100- 110^{0}C, the entire peroxide will get decomposed in less than 10 min. The presence of water hardness and the iron contamination in commercial processes further enhances the action of peroxide decomposition. If the bleaching is continued in such a way, that not only the bleaching efficiency will be hampered but also the uniformity of bleaching will not be good. Such material when taken for further dyeing will lead to problems like lesser depth, patchy dyeing etc. So it becomes mandatory to use a stabilising agent in bleaching baths to get good bleaching performance.

Conventionally Sodium Silicate was used as a stabiliser for peroxide bleaching. It stabilizes the peroxide solutions considerably even at pH of 10. It takes about 54min. for peroxide to decompose to extent of 50% in presence of silicate. The stabilising affect can be explained as follows:

$$Na_2SiO_3 + Ca^{+2} \rightarrow Ca\ (Sio^3)_2 + Na^+$$

$$Na_2SiO_3 + Mg^{+2} \rightarrow Mg\ (Sio^3)_2 + Na^+$$

This way the water hardness is removed from the solution. But this advantage is accompanied by a disadvantage that the calcium and magnesium silicate formed are sparingly soluble in water and get deposited on the surface of bleaching equipment leading to abrasion of fabrics, difficulty in washing off. Due to this silicates have been replaced by new generation stabilizing agent. One of these category includes magnesium based compounds like magnesium hydroxide, Magnesium – EDTA (Ethylene Diamine tetra acetic acid), copolymer of styrol- maleic acid with magnesium haloids, magnesium silicates etc. Other group of stabilising agents include polyorganosiloxanes such as poly-methyl and poly-ethyl siloxanes which along with stabilising effect have an added benefit of reducing the abrasion resistance when used for bleaching of yarn or sewing threads.

The world is facing a crisis of energy consumption, and the situation is worsening day by day. Correct practices for energy, consumption has become essential in everywhere of life, from industrial as consumer practices. The textile industry as a whole has taken some measures in this direction by combination of several step processes into one step process, the less use of water in processing to reduce the expense of energy in drying and chemical processing at lower temperatures.

The entire bleaching process takes place near about 3 hours for a full white process and about 2 hours for a RFD process.

6.2 Drawback of the conventional bleaching process

A very interesting phenomenon comes in to picture when we analyse the conventional bleaching process. Till now, it is very clearly understood that with increase in temperature the stability of peroxide decreases rapidly in alkaline medium. The bleaching temperature that is used conventionally is around 100^{0}C. At this temperature the peroxide is highly unstable. So in order to stabilise the peroxide we are adding an external stabiliser. These two facts are contradictory to each other:

1. Destabilization of peroxide by selection of a higher bleaching temperature
2. Addition of external stabiliser in order to stabilise the peroxide.
3. This makes us think as to why not lower the temperature of bleaching to a level that without decreasing the scouring efficiency we can achieve same bleaching efficiency at that obtained in conventional high temperature process.
4. On this idea, Rossari, which has always believed in innovating ways to make the process more eco- friendly and cost effective, has brought a new molecule to revolutionize the bleaching process used in textile industry. We are launching this molecule in the name of ‘Koolwhite 2020’ in the commercial market.

6.3 Need for research

Bleaching at low temperatures (ambient temperature to 30°C to 80°C)

Catalytic bleaching

- Use of catalysts in order to
  - lower the bleaching temperature (65- 80 °C; no steamer)
  - shorten the bleaching time (5-10 min)
  - decrease the damage of the fabric (DP value > 2000)
  - reduce the chemical consumption with lower pH range (3 g H_2O_2/l, pH 10)

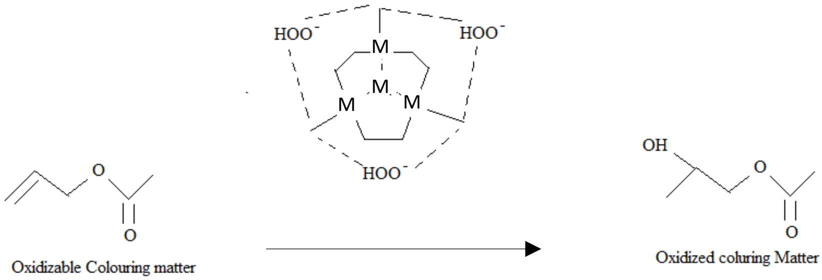
6.4 KOOLWHITE 2020 Liquid - Instant whiteness guaranteed at low temperature

In the coming times chemical processes in everyday's life has to be environmentally safe, cost effective and sparing energy. While designing this molecule we had the target of lowering the bleaching temperature without reducing the bleaching performance. As the bleaching temperature decreases, the activity of traditional bleaching agent like hydrogen peroxide is reduced. To maintain the bleaching efficiency, effective catalysts are required.

Several transition metal complexes with different ligands are reported to be promising low temperature peroxide bleach catalysts. In an intensive research carried out at our R&D centre, it has been found that transition metal derived complexes and related ligand systems are effective catalyst for oxidation of colouring matter by hydrogen peroxide at lower temperatures.

Similar kind of complexes in combination with peroxide have been reported to exhibit remarkable catalytic activity, in presence of suitable buffers, for stereo- selective epoxidation of olefins, oxidation of alkanes and alcohols at ambient temperature. For the first time these have been deployed commercially on a bulk scale in textile as a bleaching catalyst. Using this catalyst the bleaching can be carried out at temperatures as low as 80^{0}C.

At this low temperature, in alkaline medium the release of perhydroxyl ions is slower as compared to 100^{0}C. The metal- ligand system complexes these released perhydroxyl ions and prevent its decomposition in to water and oxygen. This further increases the stability of the perhydroxyl ions in the alkaline solution. When this 'Metal- Ligand- Perhydroxyl ion' complex comes in contact with an oxidizable colouring matter impurity on the textile substrate, the perhydroxyl ion is released. This released ion oxidizes the colouring matter and thus produces a bleaching effect. This can be pictorially represented as follows:



The major advantage of the molecule is that due to its stable intermediate structure it is relatively inert to cotton material and leads to lesser oxy-cellulose formation.

For carrying out bleaching on various cotton substrates a typical bleaching recipe using Koolwhite 2020 liquid can be stated as follows:

100% Cotton Woven:

Chemicals	RFD	Full white
Kleenox Knitz Liquid	1.5 g/L	1.5 g/L
Koolcat Liquid	0.1 %	0.1%
Koolwhite 2020 liquid	0.8%	1%
Caustic	1.2 g/L	2 g/L
Peroxide	2.5 g/L	7 g/L

100 % Cotton Yarn

Kleenox Knitz Liq	0.2%
Kleerix PER Liq	0.3%

MLR 1:10, Rotate at 60°C for 10 min.
In the same bath
add↓

Kleenox Knitz Liq	1.0%
Hydrogen Peroxide (50%)	7.0%
Caustic flakes	- To Adjust pH of 12
Koolwhite 2020 Liq	1%
Rosba NBS 200 Liq	0.5%

MLR- 1:10, Treat at 80°C for 30 min.

100 % Cotton Hosiery

Kleenox Knitz Liq	1.2%
Koolcat Liq	0.1%
Hydrogen Peroxide (50%)	7.0%
Caustic flakes	- To Adjust pH of 12
Koolwhite 2020 Liq	1%
Rosba NBS 200 Liq	0.5%

MLR- 1:10, Treat at 80°C for 30 min.

Terry towel

Kleenox LF Conc Liq	1.0% o.w.f.
Kool CAT Liq.	0.1% o.w.f
Hydrogen peroxide (50%)	7.0% o.wf.
Caustic soda flakes	2.0 % (To adjust pH at 12.0)
Kool white 2020 Liq	0.5% o.w.f.
Rosba NBS 200 Liq	0.4% o.w.f.

Bath Mat

Zywet Cab 125 Liq	0.6%
Kleerix PE 500 Liq	0.8%
Greendye Eco New Liq	1.0%
Hydrogen peroxide (50%)	3.0%
Caustic soda flakes	0.8 % (To adjust pH at 12.0)
Kool white 2020 liq.	0.7-1.0%

At 70°C for 30 mins

Continous Bleaching range recipe

Kleenox Knits Liquid	10 g/L
Hydrogen peroxide (50%)	10 g/L
Caustic soda flakes	10 g/L (To adjust pH at 12.0)
Koolwhite 2020 liquid	10 g/L

6.5 Bulk trial results

Today Kool'white 2020 is not merely a concept or a theoretical hypothesis but a well-established commercial bleaching catalyst that is giving benefits to our customer in terms of cost, time, and money saving and helping them to evolve as a green technologies user in international market. It has increased their market credibility and buyers prefer ability considering the fact that the ultimate consumer has become more conscious about the type of product it's using and its consecutive environmental impact.

Advantages of the process

Environmentally friendly

The specific heat of water is 4.186 Joule/ gram K. It requires 4.186 joules of energy to heat 1 gm. of water by 1 Kelvin. Assuming an MLR of 1:7, for every Kg. of cotton, 7 litres of water is used during the bleaching process. In order to heat water from 80 degrees to 100 degrees the amount of heat energy required will be:

Amount of heat energy required per kg. of cotton

= (100- 80) x 1000 x 4.186 x 7= 586040 Joules = 586 KJ

586 KJ is the amount of energy that will be saved for every Kg. of material processed. If calculated the impact of same on yearly basis for a production plant doing a bleaching of 30 Mt. On daily basis, the amount comes out to be

Amount of heat liberated per year for 30 Mt./ Day Plant

= 586 x 30 x 1000 x 365= 6416700000 KJ = 6416700 MJ

Thus on yearly basis a unit of daily production of 30 Mt. can save energy of the magnitude 6.41 x 10^6 MJ. If 6.41 x 10^6 MJ is extrapolated to various natural fuels available than we can save following quantity of fuel:

Fuel Source	Calorific Value (MJ/Kg.)	Fuel saved per year (6.41 x 10^6/ Calorific value)	Fuel saved per day
Coal (Anthracite)	27	237.5 Metric tonnes.	651 kg
Coal (Lignite)	15	427.7 Metric tonnes	1172 kg.
Wood	15	427.7 Metric Tonnes	1172 kg.
Diesel	44.80	143 Metric Tonnes	392Kg.
Kerosene	46.20	138.7 Metric Tonnes	380 Kg.

All the above mentioned figures are taken considering 100% performance of the concerned parameters involved. If taken in to account boiler efficiency, Combustion efficiency, Heat transfer losses, Steam Transportation losses than the figure will increase by 10 – 25%.

According to the United states Department of forestry, an average weight of a fully grown tree is about 680 Kg. Thus, by using Koolwhite 2020 Liquid as the bleaching catalyst we would be indirectly contributing to plantation of 1.5 trees per day. Also, it will lead to reduction in contribution of global warming by any organization since we are inhibiting 586 KJ of energy to enter in to our bio systems for every Kg. of cotton material bleached. Any organization will have its huge benefits in terms of carbon foot prints and help them to earn through carbon credits.

Strength retention

The intermediate manganese- perhydroxyl ion complex formed is a more stable complex as compared to perhydroxyl ions itself. Due to this the oxidation reaction becomes more site specific and there is a higher degree of decolourization and lesser degree of fibre damage. Fabric or yarn bleached using Koolwhite 2020 shows a lesser oxy-cellulose formations compared to conventional bleaching process.

Bleaching Process	CSP readings			RKM readings		
	Grieg	**RFD**	**Full white**	**Grieg**	**RFD**	**Full white**
Current Std.	2466	2453	2374	22.4	22.2	21.3
Koolwhite 2020	2466	2621	2412	22.4	22.6	22.1

The yarn bleached using Koolwhite 2020 process shows a lesser cuprammonium fluidity and higher degree of polymerization. This clearly demonstrates that Koolwhite 2020 process causes lesser damage to the fibre as compared to conventional bleaching at 100^{0}C. To confirm this CSP and RKM readings were taken for the same yarn and the results clearly justified the analogy.

The yarn bleached using Koolwhite 2020 is found to give better loom efficiency. In general the weaving performance is found to increase by 3-5 %.

Weight loss

The cuprammonium fluidity and the degree of polymerization data suggests that there has been lesser fibre degradation. Fibre degradation generally leads to formation of oligomers of lesser molecular weight. Due to their smaller size and partial hydrophilic nature, they tend to get easily suspended in water. Presence of emulsifying and wetting agents further enhance this action. This contributes to the weight loss of the fibre. Since in Koolwhite 2020 process there is a lesser extent of oligomer formation, the overall weight loss in the yarn or fabric is observed to be less. In general it has been seen that the weight loss is less by 2-5% on the weight of material.

Smoother surface profile

Koolwhite 2020 process leads to lesser oxy-cellulose formation. In bleaching process, it is observed that oxy-cellulose formation is higher on the surface as compared to the core of fibre. This is because of higher degree of abrasion and continuous contact with fresh bleaching solution. On the other hand Koolwhite 2020's reaction mechanism inhibits any damage to the yarn even after the ever changing fresh bleaching liquor on the surface of the yarn. Due to this the yarn profile is much smoother. This has an direct impact on the amount of finish to be used on the yarn. The customer using Koolwhite 2020 process can reduce the finish in the final bath from 15- 40%.

Time saving

Between the conventional bleaching temperature and Koolwhite 2020 bleaching temperature there is a difference of at least 25^{0}C. Also with tighter government regulations, hot drain has been banned. So even if the bleaching is taking place at higher temperature, it needs to be cooled down to 80^{0}C and then drained. With Koolwhite 2020 the bleaching temperature is itself at 80^{0}C. So, as compared to conventional process, we get an overall temperature difference of 50^{0}C including heating and cooling cycle. If we consider average rate of heating and cooling around 1.75^{0}C/ minute, the total time saving comes out to be 29 minutes. Just by adopting the catalyst and without changing any other parameter we can get a time saving of 30 min. minimum. A contribution of 30 min. for a 3.5 hr of cycle is 14%. This directly means that there is a scope of increasing the production by 14% if Koolwhite 2020 process is adopted.

Summary of benefits

Gain Type	Saving Parameter	Amount
Tangible and direct measurable gain	Energy Cost	70 paisa/ kg.
	Weight Loss	Less by 2% (3.2 Rs/Kg)
	Softener cost	-15% (20 paisa/ Kg.)
Intangible gain leading to benefits	Loom performance	Improved by 4% (Direct increase in profit by 3%)
	Time saving	30 min. (If utilised will give 10% higher profits)

Thus the use of Koolwhite 2020 can lead to overall cost reduction by at least 4.10 Rs/Kg. In present competitive market where every penny counts, this is a significant amount of saving.

Eco friendly textiles consume less energy and resources. Using eco-friendly fabrics and sustainable printing processes, alleviates the need for cost prohibitive energy and water consumption.

7. Advantages to the subsequent dyeing and finishing process

- In most cases a better colour yield
- Noticeably brighter shades
- Savings in dyeing costs possible
- Similar or even better wash, water- and rubbing-fastness properties
- Good hand feel
- Lower lint

Rossari Biotech Ltd has introduced environment friendly products:

- Greenacid New Liquid when used in processing sequence instead of acetic acid will contribute to reduction in BOD, COD.
- Greenacid ANV Liquid: an environment friendly solution for effluent treatment plants.

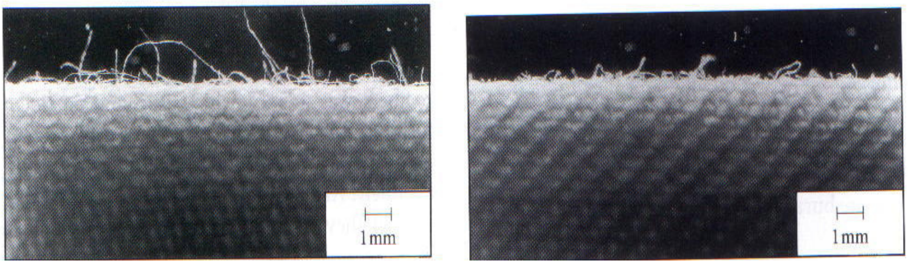
Features:

- Based on Organic acid, does not contain mineral acid
- Ultra low BOD and COD
- Toxicologically and environment friendly
- pH of neutralised fabric remains steady
- Also possess property of core alkali neutralization
- Good decalcifying property
- Possess good antimicrobial properties

Parameters	Greenacid ANV liquid
COD mg/l (mgO_2/mg)	0.90
BOD mg/l At 27°C 5 days (mgO_2/mg)	0.45

8. Bipolishing

Cotton and other natural fibres based on cellulose can be improved by an enzymatic treatment known as Bio Polishing.



Before Bio- polishing

After Bio- polishing

Lyocell fibres display a higher tendency to fibrillation compared with other cellulosic fibres because they have a higher degree of crystallinity on the fibre length (90% for Lyocell, in contrast with 60-70% for viscose fibres). In order to remove the primary fibrillation, in washing, whitening or dyeing, it is necessary to apply enzymatic treatment with the use of special cellulasic enzymes. Enzymatic treatment, doubled by a controlled mechanical action, lead to a complete and of long duration defibrillation. Bio polishing after dyeing results in colour loss, so it is preferred before dyeing.

9. Concluding remarks in general

- In textile focus should be on
  - Processes, environment and products
  - Products with enhanced functionality are important to survive the competition
- New Processing concepts have to be adapted in order to be able to produce short batches
- New processes offer the opportunity to fulfil the needs of the customers
- Reducing environmental impact will help textiles processors save resources
- Reduces water and energy use versus conventional high-temperature processes.

10. Conclusion

Adequate steps must be taken by the textile industries for the optimum utilization of energy and water resources. The textile industry is expected to play an ever-more-progressive role in developing environmentally friendly technologies and processes. Training the employees and creating awareness among them regarding the importance of water and energy conservation is also essential. There is a lot of potential for savings. By saving on the energy and water resources, textile industries can not only save on the costs, but can also help to slow down the climate change.

The textile industry is aware of the decrease in water sources and they are developing new technology and new chemical alternatives, but the challenge will lay in converting the technology in current textile facilities into the new technology that uses less water. Another challenge lays in changing the mindset of the current generations in the textile industry to use the new chemical alternatives instead of the chemicals they have used in the past decades. This will be a slow process, but one that will need to happen in order for the textile industry to maintain current production and grow in the future.

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12

Polyamide 6.6 Modified by DBD Plasma Treatment for Anionic Dyeing Processes

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1. Introduction

Plasmatic double barrier discharge (DBD) obtained in air at atmospheric conditions is widely used, among other non-thermal plasmatic alternatives, to modify chemical and physical properties of different textile polymers (Morent et al., 2007).

The impacts of DBD on environmental aspects of textile processing rise to get high attention due to important reduction of costs in dyeing by savings in processing times, products, human resources, water and energy (Carneiro et al., 2001). All fibers, from natural to synthetics, can be submitted to several irradiation methods with diverse and significant meaning in different areas of textile processing (Sparavigna, 2001).

The effects on surface are reported for cellulosic fibers (Carneiro et al., 2005; Souto et al., 1996), wool (Rakowski, 1992), polyester (Oktem et al., 2000, Leurox et al., 2009), polyamide 6.6 (Papas et al., 2006; Oliveira et al., 2009), polyamide 6 (Dumitrasku & Borcia, 2006), polytetrafluoroethylene (Liu et al., 2004), polyethylene (Oosterom et al., 2006), polypropylene (Yaman et al., 2009) and meta aramid (Chen et al., 2008), being roughness, microporosity and creation of polarity by oxidation mechanisms the main modifications induced by several types of irradiation techniques.

Acid dyes are the most common in use for polyamide dyeing, but some problems are very well known, as difficulties to manage uniformity and fastness. The necessary pH to achieve a good exhaustion of dye in the fiber must be carefully controlled and sometimes is excessively low.

Reactive dyes are very important for the dyeing of cellulosic and protein fibers, but in polyamide the results are not equivalent due to paler colors obtained (Soleimani et al., 2006). Reactive dyes for cellulose are similar to acid dyes in their chromophoric structure, but they possess reactive groups able to react chemically with the fiber in the presence of alkali. Only few of these dyes have been developed for polyamide application with ability to react with amino groups in fiber structure without the need of alkaline fixation. Stanalan (Dystar) and Eriofast (Ciba) are well known dyes for this purpose.

Reactive dyes for cotton fibers, Procion (Dystar), Kayacelon (Nippon Kayaku), and Drimarene (Clariant) were tested for polyamide dyeing at boiling temperature and different pH showing distinct results. At pH 4, the most convenient result was obtained due to a high protonation of nucleophilic amino groups, contributing to electrostatic attraction between anionic dye and positively charged fiber (Soleimani et al., 2006).

In order to achieve better dyeing results in polyamide fibers some trials are reported in the bibliography using new techniques for structural changes, being irradiation by means of lasers and plasmas presented as promising solution.

Low temperature plasmas via several gases such as oxygen, tetrafluormethane and ammonia were used for modification of fibers i.e. wool and polyamide 6. Dyeing of modified fibers was performed with several natural dyes and the dyeing rate of the plasma-treated wool was considerably increased (Wakida et al., 1998).

Polyamide 6 was treated with tetrafluoromethane low temperature plasma and then dyed with commercially available acid and disperse dyes. Acid dyeing results show that this type of plasma treatment slows down the rate of exhaustion due to an increase in hydrophobic groups at the surface originated by the type of gas used, without reduction of the amount of dye absorption at equilibrium.

The dyeing properties of disperse dyes on plasma-treated polyamide fabrics markedly increase comparing with untreated fabric by increasing hydrophobic attraction between disperse dye and the fiber (Yip et al., 2002).

Polyamide 6.6 fabric was dyed with a disperse-reactive dyestuff and a covalent bonding with the fiber was proved to occur if supercritical carbon dioxide is used (Liao et al., 2000).

Polyamide 6 materials irradiated with 193 nm ArF excimer laser developed micro-sized ripple-like structures on the surface, able to increase surface area and light diffuse reflection. Laser treatment is proved to be responsible by breaking the long chain molecules of polyamide resulting in an increase of amine end groups' content. Results revealed that dyeing properties of reactive dyes tested on polyamide fabrics improve after this treatment, in what concerns both kinetics and equilibrium phases (Yip et al., 2004).

In the present work, polyamide 6.6 fabrics were treated with different dosages of an atmospheric double barrier discharge obtained in a semi industrial prototype equivalent to an industrial machine installed in a Portuguese textile plant [Pat. PCT/PT 2004/ 000008(2004)]. The structural and chemical modifications of fabrics were further analyzed in terms of X-Ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) techniques. Moreover, the tinctorial behavior (color strength, exhaustion) of the polyamide fabric dyed with different dye classes, namely reactive dyes for wool, reactive dyes for cotton, acid and direct dyes, was studied as well as washing and rubbing fastnesses.

2. Experimental part

2.1 Materials

2.1.1 Fabric and dyes

A 100% polyamide 6.6 plain weave fabric (105 g.m^{-2}) was used as dyeing substrate. The samples were pre-washed with a solution of 1% non-ionic detergent at 30ºC for 30 minutes and then rinsed with water for another 15 minutes, before DBD treatment in order to minimize the contamination.

The dyes used were the following:

Reactive dyes for cotton - Levafix Red Brilliant E3BA (C.I. Reactive Red 147), Levafix Yellow CA (C.I. Reactive Yellow 26), Remazol Yellow Golden RNL (C.I. Reactive Yellow 27), Procion Crimson H-EXL (C.I. Reactive Red 231), Procion Yellow H-EXL (C.I. Reactive Yellow 138:1) and Remazol Blue Navy RGB (C.I. Reactive Blue 203).

Reactive dyes for wool - Realan Blue EHF, Realan Red EHF, Realan Yellow EHF and Lanasol Blue 3G (C.I. Reactive Blue 69).

Direct dyes - Sirius Orange 3GDL (C.I. Direct Orange 57), Sirius Scarlet KCF, Sirius Violet RL (C.I. Direct Violet 47) and Sirius Blue KCFN.

Acid dyes - Telon Blue MGWL, Telon Red A2FR and Rot M-6BW.
All of them were kindly supplied by Dystar ®.

2.2 Plasma treatment

2.2.1 DBD plasma machine

A double barrier discharge was produced in a semi-industrial machine (Softal/University of Minho) functioning with air at normal temperature and pressure, using a system of ceramic electrode and counter electrode with 50 cm effective width, and producing the discharge at high voltage and low frequency.

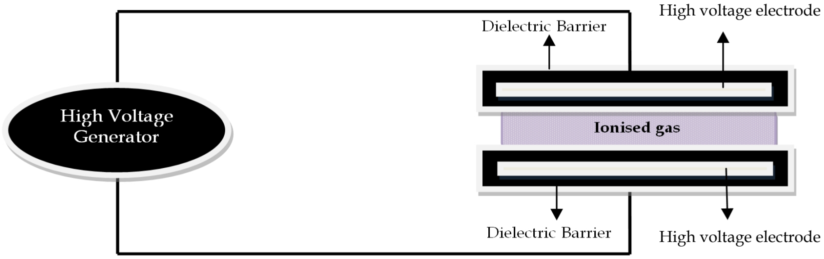

Fig. 1. DBD plasma machine diagram.

2.2.2 Plasma dosage

The power of discharge, velocity, number of passages of the fabric between electrodes were variable corresponding to calculated discharge dosages from 400 to 3600 W.min.m^{-2} (Table 1). The dosage was calculated according to the following equation (Eq.1):

$$Dosage = \frac{W \times P}{V \times L} \quad (1)$$

Equation 1. Plasma dosage determination, where W = power (Watts); P = number of passages; V = velocity (m.min^{-1}) and L = width of treatment (0.5m).

Power (W)	**Velocity (m.min^{-1})**	**Number of passages**	**Dosage (W.min.m^{-2})**
500	2.5	1	400
1000	2.5	1	800
1000	2.5	2	1600
1500	2.5	1	1200
1500	2.5	2	2400
1500	2.5	3	3600

Table 1. Experimental parameters of DBD plasma and dosage applied.

2.3 Characterization of DBD treated fabrics and structural analysis

2.3.1 Water drop absorption test

In order to evaluate the wettability of the untreated and of the plasmatically modified polyamide woven fabrics, a water-drop test was applied by measuring the time for its complete absorption into the material.

This test is performed in order to check the efficiency of the plasmatic treatment in function of the experimented dosages.

2.3.2 Contact angle measurement

Dataphysics equipment using OCA software with video system for the capturing of images in static and dynamic modes was used for the measurement of contact angles of the water drops in polyamide 6.6 fabrics.

2.3.3 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy analysis provides information about changes in chemical composition (elemental analysis) and chemical state (wave separation method) of atom types on the fiber surface. The VG Scientific ESCALAB 200A equipment was used to obtain a more detailed and complete analysis.

2.3.4 Scanning electron microscopy

Morphological modifications in samples taken from the polyamide 6.6 fabric were analysed with high resolution environmental scanning electronic microscope Schottky FEI Quanta 400FEG / EDAX Genesis X4M. The sample was mounted in aluminum specimen stubs and coated with a layer of gold.

2.3.5 Atomic force microscopy

The morphological and topographical characteristics of the polyamide surface before and after DBD plasma treatment were investigated, in a multimode SPM microscope controlled by a Nanoscope III - from Digital Instruments, equipped with an ultra light cantilever with 125 µm long by 30 µm large. The tips were silicon NHC type, with a resonance frequency from 280 to 365 kHz.

2.4 Dyeing methods

The dyeing properties were investigated using a dye-bath exhaustion process. The schemes of dyeing processes are shown in figure 2. Various dyeing tests were performed with differents parameters such as temperature, dye concentration (% w/w) and pH, in order to optimise dyeing method and conditions are presented in Table 2. Dyeings were carried out in a laboratorial "Ibelus" machine equipped with infra-red heating and the SIMCORT software was used for continuously assess dye exhaustion from the bath. The samples (each 5.0 g) were dyed with a liquor ratio of 40:1, using stainless steel dyepots with 200 cm^3 capacity each.

Process	Temperature (°C)	Dye concentration (%)	pH
1	100	0.05; 0.1; 1; 2 and 5	4.5 – 5.5
2	100	1	3; 4; 5; 6; 7 and 10
3	90	1	4.5 – 5.5
4	80	1	4.5 – 5.5
5	70	1	4.5 – 5.5
6	60	1	4.5 – 5.5
7	50	1	4.5 – 5.5

Table 2. Parameters used in the dyeing process.

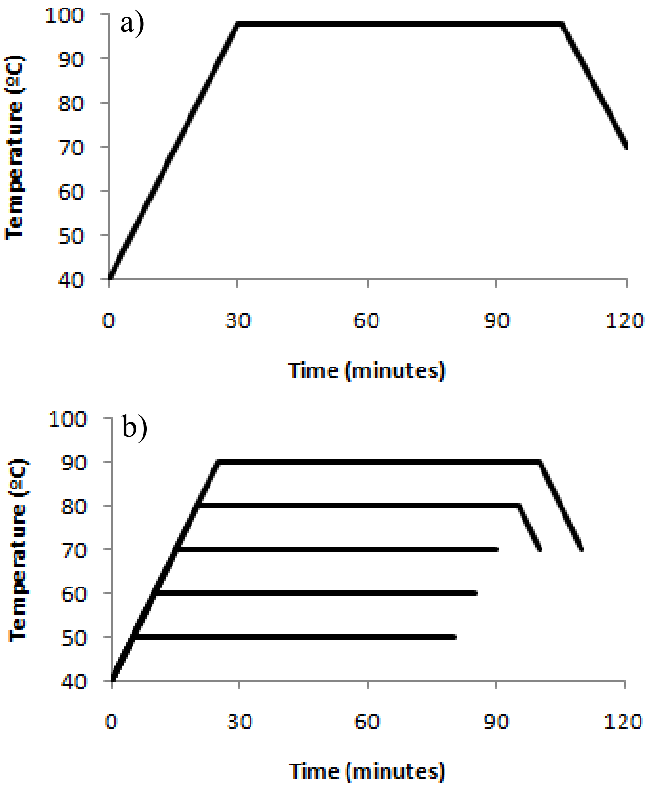

Fig. 2. Dyeing conditions used for (a) Processes 1 and 2 (b) Processes 3 – 7, according with Table 2

2.5 Whiteness and color strength

The whiteness (Berger formulae) of the polyamide fabric after DBD treatment and color intensities of the dyed fabrics were measured by using a Datacolor Spectraflash SF 600 Plus CT spectrophotometer for D65 illuminant, over the range of 390-700 nm.

The average of three reflectance measurements, taken at different positions on the dyed fabric, was adopted. The relative color strength (K/S values) was then established according to the Kubelka-Munk equation, where K and S stand for the light absorption and scattering, respectively:

$$\frac{K}{S} = \frac{(1-\mathrm{R})^2}{2\mathrm{R}} \,. \qquad (2)$$

2.6 Washing and rubbing fastnesses

The washing fastness was evaluated in accordance with stipulated in standard ISO 105 C06, method A1S, at temperature of 40ºC. The rubbing fastness was evaluated according to standard ISO 105 X12:2001.

2.7 Fluorescence microscopy

The level of dye penetration into fibers was visualised by fluorescence microscopy on polyamide transversal cuts. The fibers were embedded into an epoxy resin and transversal cuts of the fibers with 15 mm were prepared using a microtome (Microtome Leitz). Fibers' cross sections were analyzed by a fluorescence microscope LEICA DM 5000B at 40x magnification.

3. Results and discussion

3.1 Optimal plasma dosage

The color depth of dyed polyamide 6.6 was increased by using a reactive dye for wool dyeing (Lanasol Blue 3G), a reactive dye for cotton dyeing (Remazol Yellow Golden RNL) and a direct dye (Sirius Scarlet KCF), when different dosages of plasmatic discharge are used varying power of discharge and number of passages (Figure 3). The K/S values in polyamide samples depend on plasma conditions, being more intense for higher dosages. This criterion was used to choose optimal plasma dosage.

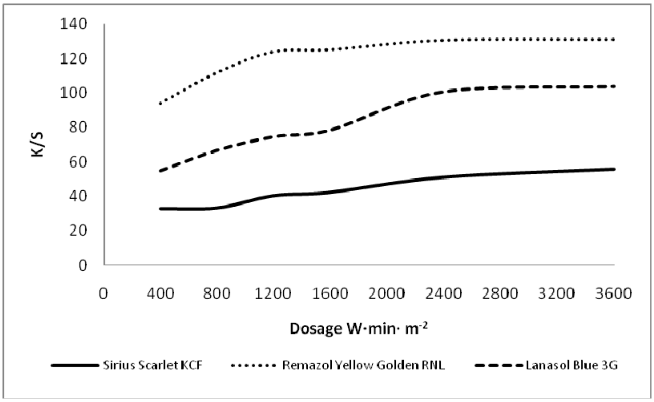

Fig. 3. K/S values of dyed samples of polyamide 6.6 pre-treated with different discharge dosages

A significant difference in the quantity of residual dye is noticed (Figure 4) by comparing colors of the baths obtained after dyeing process of the samples submitted to different dosages.

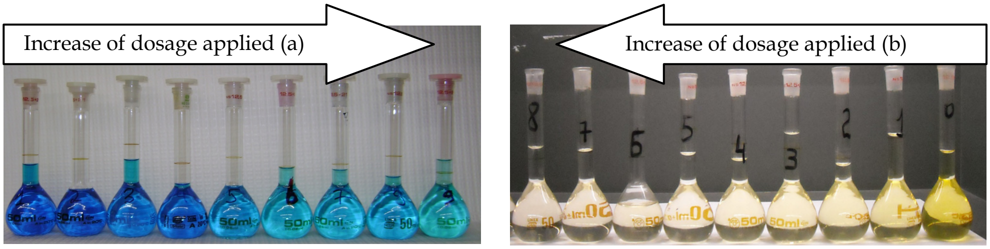

Fig. 4. Final dyeing baths corresponding to samples with increasing dosages of plasmatic discharge – a) Reactive Lanasol Blue and b) Reactive Remazol Yellow Golden.

According to the results obtained, the dosage of 2400 W.min.m^{-2} is enough to obtain maximum values of K/S and minimum quantity of dye in residual bath for the three dyes, with the following working parameters in DBD machine: power of discharge -1500 W; speed - 2,5 m.min^{-1}; n° of passages – 2. This dosage was further applied to all polyamide samples submitted to dyeing.

3.2 Characterization of DBD treated fabrics and structural analysis

3.2.1 Time of water drop absorption

Table 3 shows the difference between the wettability of the untreated and the plasmatically modified polyamide woven fabrics by measuring the time for complete water absorption into the material.

Tests	**Polyamide untreated**	**Polyamide with DBD treatment**
	Time (s)	
01	286.2	56.7
02	293.4	49.5
03	287.5	51.3
04	323.5	50.4
05	323.6	53.6
Mean Values	302.8	52.3
Standard Deviation	19.0	2.9
CV(%)	6.3	5.5

Table 3. Wettability results

3.2.2 Contact angle measurement

The hydrophilicity of the polyamide fabric is highly improved by the plasmatic treatment in accordance with the results published by several authors for different synthetic and natural fibers, mentioning modifications in accessible polar groups at the surface and creation of microporosity (Pappas et al., 2006, Oliveira et al., 2009, Yip et al., 2002).

This surface modification might transform the synthetic fiber from hydrophobic to hydrophilic which is key point for the absorption of aqueous dye solutions.

The static and dynamic contact angle evaluation of a water droplet in the textile polyamide fabric is shown in figures 5, 6 and 7, corresponding to a mean value of five measurements.

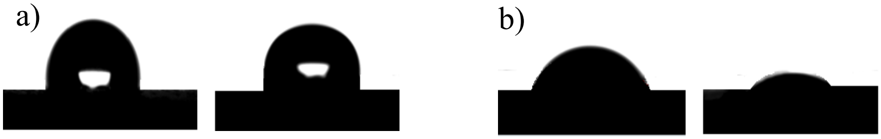

Fig. 5. Contact of water drop in the sample without (a) and with DBD plasma treatment (b) (time =0 s and after 30 s).

After DBD treatment, the wettability of the polyamide fabric considerably increases. This result may be attributed to the incorporation of polar groups onto the fabric surface.

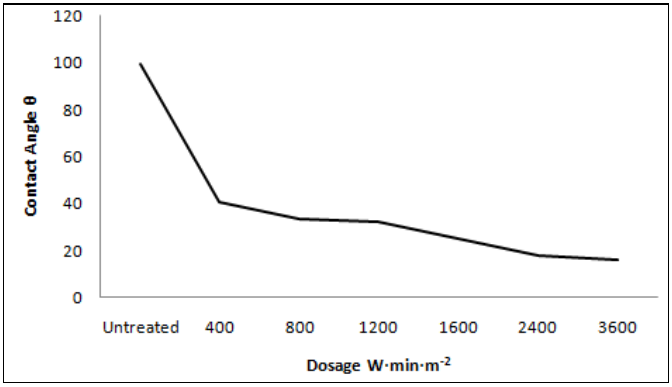

Fig. 6. Static contact angle measurement of a water drop for the samples: untreated and with different plasma dosages.

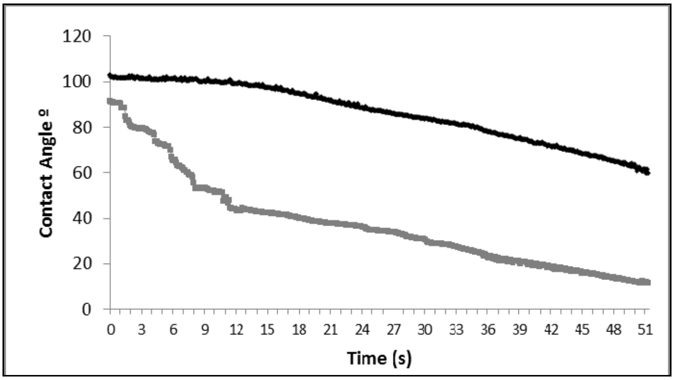

Fig. 7. Dynamic contact angle measurement of a water drop in the sample without treatment (a) and treated with dosage 2400 W.min.m^{-2} (b).

3.2.3 X-ray photoelectron spectroscopy

The XPS analysis shows that the oxygen and nitrogen content level was increased after DBD treatment. This indicates a substantial incorporation of these atoms onto the fabric surface. Chemical states of atoms, represented by relative peak areas, can be obtained by wave separation method. The carbon component can be divided into peaks (280.5 to 294.0 eV), assigned as CH_2, CH_2CO, CH_2NH and NHCO (Pappas et al., 2002). It can be observed that the relative peak areas of sub-components change significantly after DBD treatment.

Results reveal that the element C1s decreases while both N1s and O1s increase. DBD treatment can be responsible for the breaking of the long chain molecules of polyamide 6.6, causing an increase of carboxyl and amine end groups. The table 4 shows the elementary composition and the atomic ratio before and after plasma treatment.

Sample	Atomic composition (%)			Atomic ratio	
	C	O	N	C/N	C/O
Untreated	74.67	17.75	7.58	9.85	4.21
DBD Treated	70.25	19.83	9.92	7.08	3.54

Table 4. XPS results in samples with and without DBD treatment

The figure 8 shows the increase of O_{1s} and N_{1s} atoms and consequently decrease of C_{1s} when DBD treatment is applied, which corresponds to an enhancement of hydrophilicity of fabrics due to an increase of polar groups in the surface of polyamide fabrics.

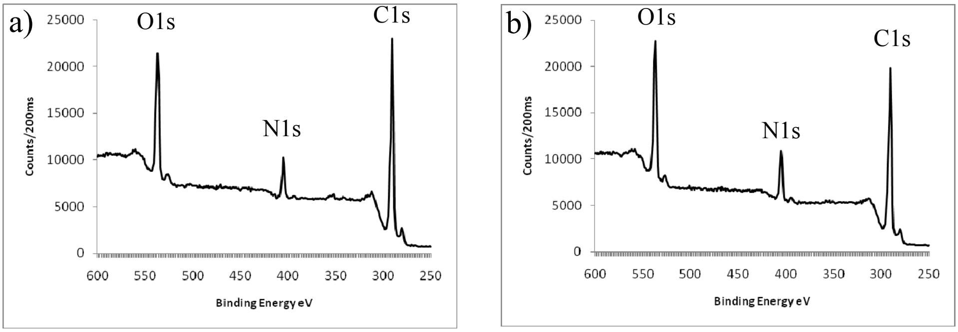

Fig. 8. XPS analysis of polyamide fabric a) without treatment and b) with DBD treatment.

3.2.4 Scanning electron microscopy

The surface modification by DBD plasma on polyamide fabrics was detected by the scanning electron micrographs (Figure 9). Compared to untreated polyamide 6.6, the DBD plasma treated polyamide 6.6 presents small patches on the surface responsible for an increase of surface area.

The comparison of the images obtained with and without DBD plasma treatment, shows a somewhat different surface morphology.

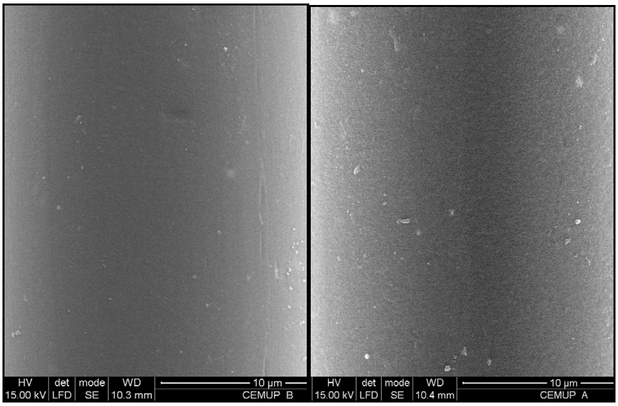

Fig. 9. Increase of roughness after DBD treatment (right) in SEM micrographic

3.2.5 Atomic force microscopy

The increase in roughness can be better understood when AFM images are compared (Figure 10). The following results were obtained for Ra (arithmetic average roughness), Rq (root mean squared roughness) and Rmax (Table 5), regarding untreated and plasma treated samples.

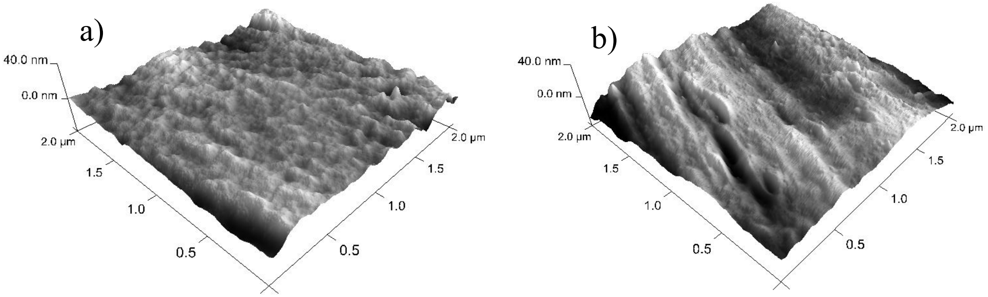

Fig. 10. AFM increase of roughness after DBD treatment (b)

Samples	Ra (nm)	Rq (nm)	Rmax (nm)
Untreated	2.36	3.21	29.2
Treated	6.50	7.99	48.0

Table 5. AFM results for samples with and without treatment

The surface of the sample without treatment is relatively smooth while the treated polyamide has rougher surfaces.

The AFM analysis shows that the Ra, Rq and Rmax roughness increases with the DBD plasma treatment and the modification of the shape of surface features is quite evident. The applications of these results illustrate, for example, the increasing of wettability (as showed by contact angle measurements) and consequently polyamide dyeability properties.

3.3 Berger whiteness

The figure 11 shows the results obtained for Berger whiteness when different plasma dosages were applied to the polyamide fabric.

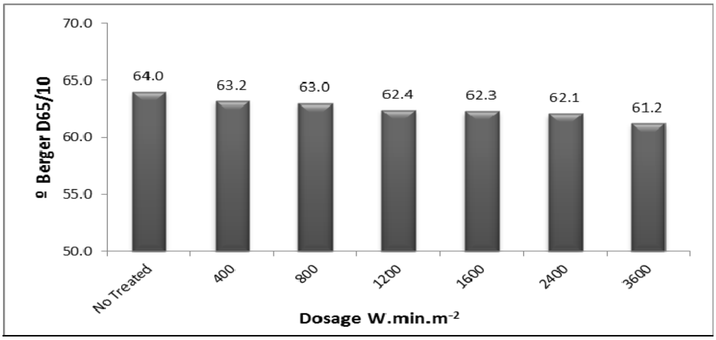

Fig. 11. Whiteness degree – Illuminant D65/observer 10º

Whiteness of polyamide fabric slightly decreases (2.8 degrees for a dosage of 3600 W.min.m^{-2}) for higher dosages, although without noticeable effect in product characteristics.

3.4 Dyeing properties

Results show the effect of the plasma discharge on dyeing behavior of polyamide 6.6 with direct dyes, reactive dyes for cotton and wool and acid dyes.

The surface modification of the polyamide fiber after DBD plasma treatment permits very intense and fast colors with dye exhaustion almost reaching 100% in every case.

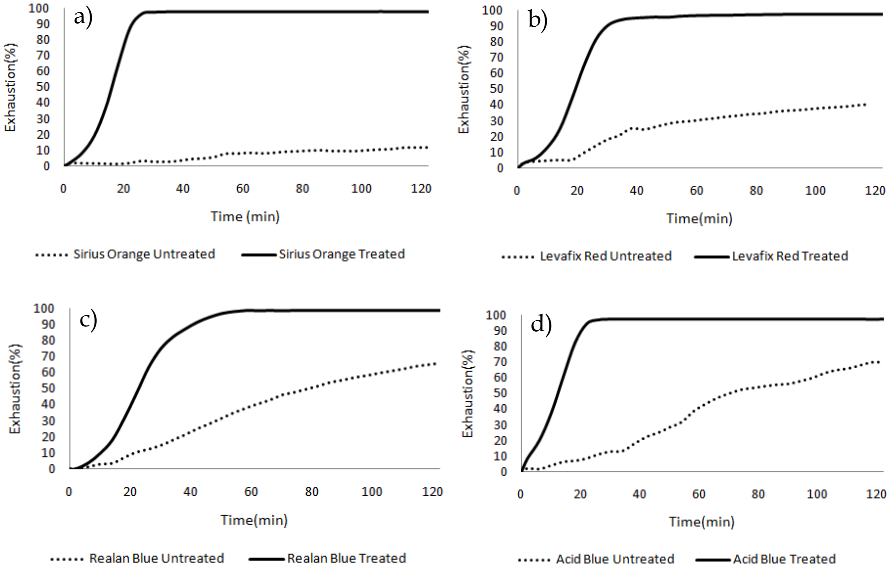

Fig. 12. Exhaustion results for a) direct dye, b) reactive dye for cotton, c) reactive dye for wool and d) acid dye in polyamide 6.6 samples with and without DBD treatment (dyeing conditions: 100ºC and 1% dye concentration).

The complete bath exhaustion was obtained in very short time during dyeing processes with remarkable positive difference when a plasmatic treatment is made on polyamide fabrics (Figure 12). Forty minutes are enough to exhaust dye from dyebath which is a very attractive behavior regarding industrial application.

The direct and acid dyes are anionic and water soluble and the increase of fiber hydrophilicity with plasmatic treatment is favorable to dye adsorption, essential to promote coulombic dye fixation to protonated amine groups of the polyamide.

Reactive dyes are also water soluble and anionic, apart being able to form covalent bonding with reactive groups in the fiber, namely the amine groups of polyamide. The same factors promoting adsorption and diffusion of dye in the fiber for the acid dyes are present for reactive dyes, explaining complete exhaustion of dye in the fiber after forty minutes of dyeing.

The table 6 shows the comparative results of K/S with reactive dyes, direct dyes and acid dyes in polyamide 6.6 with and without plasma (DBD) treatment. The results demonstrate that in dyeings carried with these anionic dyes, the color strength (K/S) is considerably higher for the fabric with DBD treatment, quantified by means of the percentage gain of the treated sample when compared to the non treated one.

Dye Class	**Commercial Name**	**Without Treatment (K/S)**	**With Treatment (K/S)**	**DBD gain (%)**
Reactive for Cotton	Remazol Golden Yellow RNL	84.4	88.9	5.4
	Procion Crimson H-EXL	15.6	24.9	60.0
	Levafix Yellow CA	43.1	102.6	137.8
Reactive for Wool	Realan Red EHF	36.1	48.6	34.7
	Realan Yellow EHF	54.8	60.9	11.1
	Realan Blue EHF	49.9	86.8	73.9
Direct	Sirius Scarlet KCF	111.6	185.5	137.8
	Sirius Violet RL	100.8	138.7	16.8
	Sirius Orange 3GDL	68.4	199.3	45.8
Acid	Telon Blue MGWL	51.5	66.1	28.3
	Telon Red A2FR	80.7	95.9	18.9
	Telon Rot M-6BW	131.2	149.3	13.8

Table 6. K/S values for dyeings of polyamide 6.6 fabric with and without DBD treatment

The gain in color yield obtained with DBD treatment is effective for all the dyes, although results are quite variable for the different colors of each commercial dye.

3.4.1 The influence of temperature in dyeing processes

The figure 13 shows the influence of the temperature in polyamide dyeing process with the following dyes: Levafix Brilliant Red E-BA (reactive dye for cotton), Sirius Orange 3GDL (direct dye,) Realan Blue EHF (reactive dye for wool) and Telon Blue M-GLW (acid dye). Comparisons were made between the samples with and without plasmatic treatment.

The increase in temperature of all dyeing processes (Figure 13) leads to an increase of the color yield (K/S values) of the polyamide dyed samples. Nevertheless, it is evident that dye absorption mechanism is quite influenced by plasmatic treatment.

In fact, a linear behavior of K/S with temperature is much more present when the fiber is plasma discharged, demonstrating that structural transitions are not the main driving force for dye penetration in polyamide.

Meanwhile it is quite clear that the untreated fiber is highly dependent on temperature to achieve high K/S values, being noticeable that structural changes may occur at temperature around 90ºC.

Therefore, the reduction in energy demand can be considerable in the dyeing process when plasmatic pre treatment is made compromising the same color yield (K/S) at much lower temperatures.

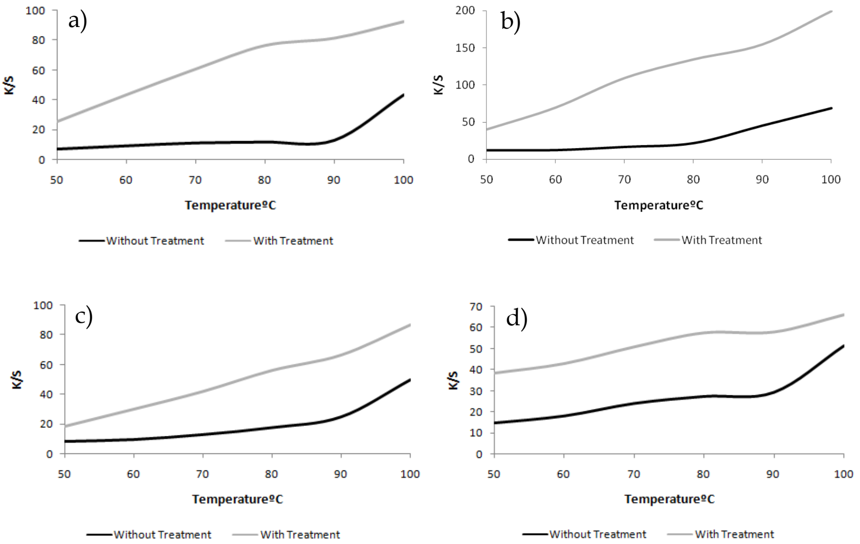

Fig. 13. K/S values of reactive dye for cotton (a), direct dye (b), reactive dye for wool (c) and acid dye (d) in polyamide 6.6 with different temperatures (dye concentration: 1% dye weight/fiber weight).

3.4.2 The influence of dye concentration in dyeing processes

The figure 14 a, b, c and d shows the influence of the dye concentration in the polyamide dyeing.

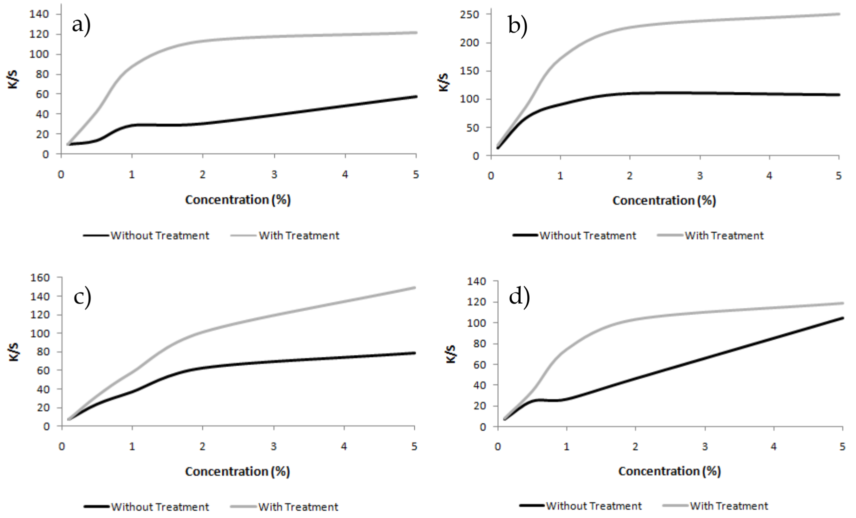

Fig. 14. K/S values of reactive dye for cotton (a), direct dye (b), reactive dye for wool (c) and acid dye (d) in polyamide 6.6 with different dye concentrations (dyeing temperature: 100ºC).

Since polyamide has only a small number of amine end-groups, saturation is easily got and it is difficult to achieve darker colors by dyeing with anionic dyes (Yip et al., 2002; Perkins, 1996).

Figure 14 shows a considerable increase of color yield with the increase of dye concentration being that the total amount of dye in the fiber is always higher after DBD treatment.

Darker colors in the fabric of polyamide 6.6 can be achieved when the plasmatic treatment is applied, with less dye concentration, meaning that is now possible to dye polyamide materials in darker colors by adopting a much more economic process.

The form of the curves concerning polyamide dyeing with the reactive dye for cotton, direct dye and acid dye shows a much higher but limited saturation in plasma treated fabric, whenever the behavior of the reactive dye for wool demonstrates the formation of higher level of linkage groups in the plasmatically treated polyamide.

3.4.3 The influence of pH in dyeing processes

The figure 15 a, b, c and d shows the influence of the pH in the polyamide dyeing process, comparing results between the samples with and without plasmatic treatment.

When acid is added to dye bath, the polyamide fiber develops an overall positive charge (-NH_3^+). Thus, in acidic conditions the polyamide fiber becomes positively charged and strongly attracts the negative groups of the anionic dyes. At pH 3 all the studied dyes give similar dyeing yield, either plasma treated or not treated polyamide. However, at pH 3 the polyamide 6.6 fabrics can be degraded, which is very inconvenient for the final quality of dyed materials (Burkinshaw, 1995).

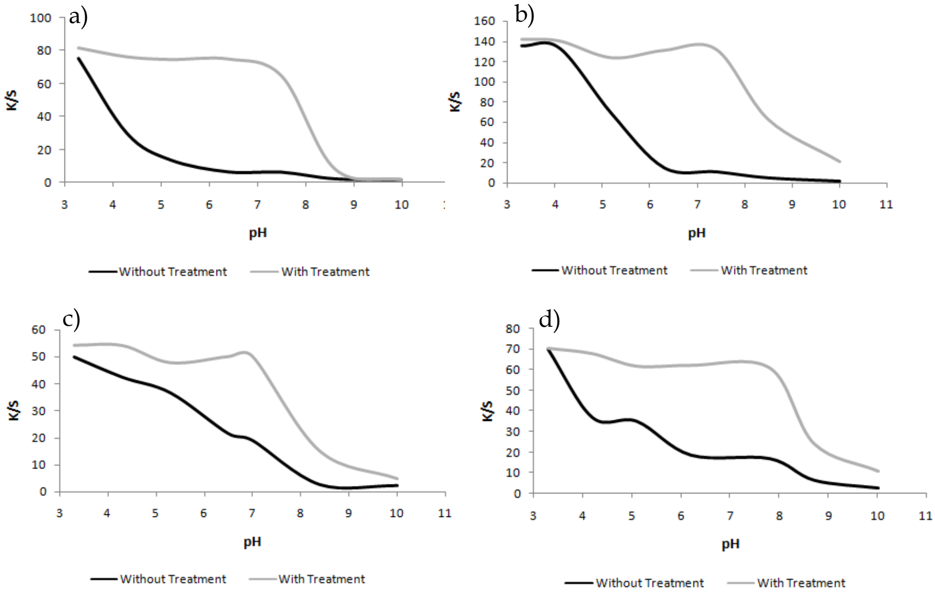

Fig. 15. K/S values of reactive dye for cotton (a), direct dye (b), reactive dye for wool (c) and acid dye (d) in polyamide 6.6 with different dyebath pH (dyeing conditions: 100ºC and 1% dye concentration).

When pH of the dye bath is increased, the color yield reduces considerably in the samples without DBD treatment. On the other hand, if samples are treated with plasma and dyed, a type of “buffer systems” can be observed for all the dyeings, propitiating a very important stabilization during the dyeing process in case of pH variations.

Dyeing results are pH independent in the interval 3 to 7, which gives strong indications about the huge influence of plasmatic discharge in chemical composition of fiber surface.

3.5 Washing and rubbing fastnesses

Table 7 shows the results of washing fastness for reactive (wool, cotton) and acid dyes in dyeing of polyamide 6.6.

The results of washing fastness at 40 °C are very good confirming the level of dye diffusion and fixation into the fiber. The surface modification of the polyamide fiber after DBD plasma treatment permits to obtain very fast colors, with the best result for washing fastness.

The results of rubbing fastness in dyed fabrics with and without treatment are very good. The value 5 in the gray scale was obtained for all the samples.

Dyes	**Sample**	**AC**	**CO**	**PA**	**PES**	**PAC**	**WO**	**Color Change**
Procion Yellow H-EXL	UT*	4/5	4	5	5	5	4/5	4
	T**	5	4/5	5	5	5	5	4/5
Remazol Blue Navy RGB	UT*	5	5	5	5	5	5	5
	T**	5	5	5	5	5	5	4/5
Levafix Red EBA	UT*	4/5	3	4/5	5	5	5	4
	T**	4/5	3/4	4/5	5	5	5	4
Sirius Orange 3GDL	UT*	5	4/5	5	5	5	5	4
	T**	5	4	5	5	5	5	3
Sirius Blue KCFN	UT*	5	4/5	5	5	5	5	5
	T**	5	4/5	5	5	5	5	4/5
Telon Blue M-GLW	UT*	5	5	5	5	5	5	4/5
	T**	5	5	5	5	5	5	4/5
Realan Blue EHF	UT*	5	4/5	5	5	5	5	4
	T**	5	5	5	5	5	5	4

*UT – Sample Untreated ** T - Sample with treatment

Table 7. Washing fastness of reactive and acid dyeing with previous DBD treatment by Norm ISO 105C06/A1S

3.6 Fluorescence microscopy

Figure 16 shows the results obtained from fluorescence microscopy analysis in the case of polyamide dyed with reactive dyes for cotton (Levafix Red – EBA). The dye shows a perypherical distribution in the sample without treatment (c), while in the case of the plasma treated sample the dye presents a deeper diffusion into the core of the fiber (d).

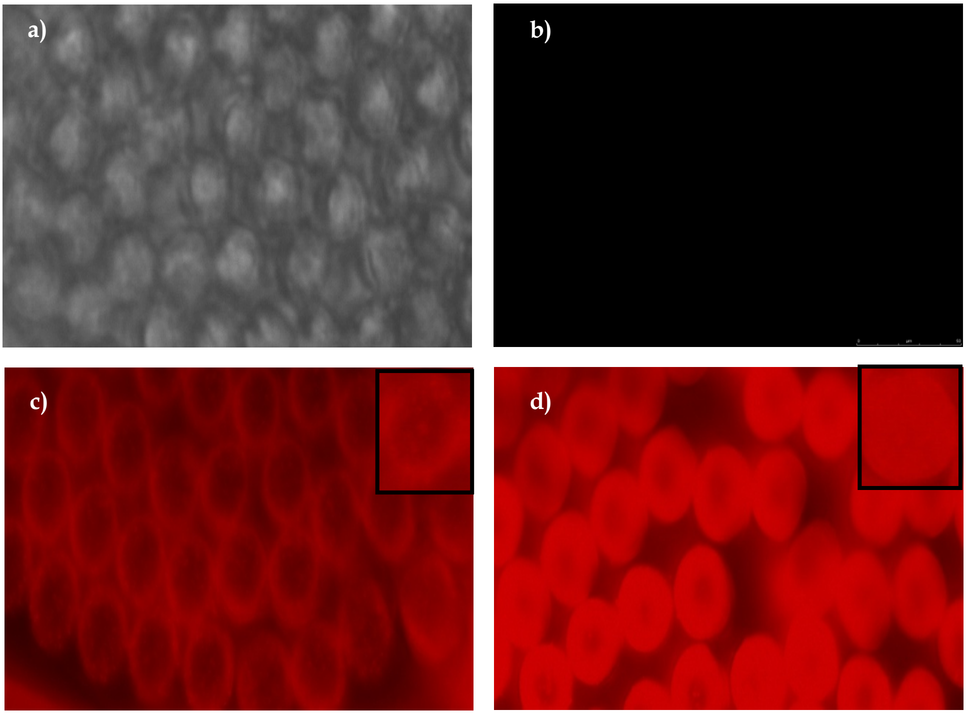

Fig. 16. Fluorescence microscopy (Levafix Red EBA dye): a) polyamide control in bright field b) polyamide control in fluorescence field c) untreated polyamide after dyeing and d) polyamide treated after dyeing.

These results are very promising, because after the plasma treatment the dye is able to penetrate into the fiber so giving high guaranty of good fastness results.

3.7 Dyeing process optimization

The dyeing process of polyamide 6.6 is usually performed at boiling temperature and the time required for this process is around 120 minutes (Figure 2a). However, after DBD plasma treatment (2400 W.min.m^{-2}) a new process will be checked with lower temperature and time than those generally used in the polyamide dyeing. This process will start at 40ºC, the temperature is raised until 70°C with a gradient of 1ºC/min and remains in this temperature during 60 minutes.

The maximum values of exhaustion for samples with and without treatment (traditional process 100ºC) and for the samples dyed by optimized dyeing process at 70ºC are shown in table 8.

In this optimized dyeing process, the temperature and dyeing time were reduced of 30°C and 25% respectively. The best results are obtained when DBD treatment was applied. The reduction of bath exhaustion, when compared the process (b) at 100ºC with process (c) at 70ºC were: 0.5% for the direct dye Sirius 3GDL, 2.6% for the acid dye Telon MGLW, 3.8% for Levafix Red EBA and 4.1% for Red dye Levafix EBA. This way, it is possible to dye polyamide 6.6, treated with DBD, at 70ºC with an excellent bath exhaustion.

Dyes	Exhaustion (%)		
	Without treatment (100ºC) - **a**	With Treatment (100ºC) – **b**	With Treatment Optimized (70º) - **c**
Direct Orange 3GDL	11.7	97.9	97.4
Acid Telon MGlW	70.0	97.4	94.8
Reactive Remazol Red RB	18.9	92.0	88.2
Reactive Levafix Red EBA	48.1	97.2	93.1

Table 8. Comparison of the maximum exhaustion for different dyeing processes.

The figure 17 shows the bath exhaustion behavior of the reactive dye Levafix Red, for the samples prepared with DBD discharge (b, c) and dyed at 100ºC and 70ºC respectively, compared with the untreated sample conventionally dyed at 100ºC (a). A smoothest curve and excellent bath exhaustion of 93% are observed for the optimized process performed at 70ºC.

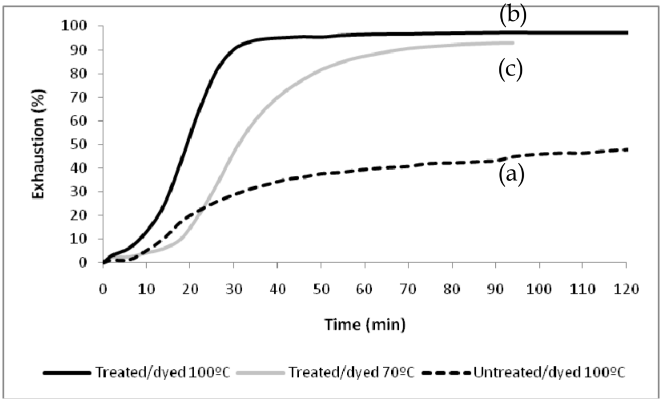

Fig. 17. Exhaustion curves of polyamide dyeing with Levafix Red EBA dye for samples with and without treatment dyed at 100ºC (b, a) and with treatment dyed at 70ºC (c).

3.7.1 Washing and rubbing fastnesses

Table 9 shows the results of washing fastness for direct, acid and reactive dyes for the optimized dyeing of polyamide 6.6. The results of washing fastness are very good, confirming the level of dye fixation and diffusion into the fiber, despite of this process had been performed at 70ºC.

Dyes	Sample	AC	CO	PA	PES	PAC	WO	Color Change
Direct Orange 3GDL	Treated	5	4	5	5	5	4	4
Acid Telon MGlW	Treated	5	4/5	5	5	5	4/5	4/5
Reactive Remazol Red RB	Treated	5	4/5	5	5	5	5	5
Reactive Levafix Red EBA	Treated	5	4/5	5	5	5	5	4

Table 9. Washing fastness of reactive and acid dyeing with previous DBD treatment (norm ISO 105C06/A1S)

The optimized process performed at lower temperature and time than conventional dyeing of untreated polyamide did not change the washing fastness results.

The results of rubbing fastness in dyed fabrics with and without treatment are very good. The value of 4/5 or 5 in the gray scale was obtained for all the samples.

3.8 Cost of DBD plasma treatment

The DBD treatment used the following parameters: power - 1500 W, number of passage - 2, velocity - 2.5 $m.min^{-1}$.

The cost to treat one kilogram of polyamide 6.6 fabric (weight : 105 $g.m^{-2}$) is calculated according to table 10.

Dosage ($kW.min.m^{-2}$)	$kW.h.m^{-2}$	Price kW.h (€)	Cost per m^2 (€)	Cost per kg (€)
2.400	**0.040**	**0.094***	**0.0038**	**0.036**

Table 10. Cost of DBD plasma treatment (* mean value of kW.h - Portugal 2010).

Despite the cost of the treatment DBD is around 0.036 €.kg^{-1}, several benefits are achieved such as: reduction of 30ºC in the temperature of dyeing with an excellent bath exhaustion; reduction of dyeing time of around 25%; reduction of the quantities of dyeing auxiliaries and the possibility to get more intense colors.

4. Conclusion

A relatively low plasma dosage (DBD), around 2400 $W.min.m^{-2}$, can be used to modify the surface of polyamide textile materials, leading to enhanced hydrophilicity and dyeability. Due to these modifications, dyeing of polyamide 6.6 fiber is now possible using nonconventional dyes for this fiber, such as direct and reactive dyes for cotton and wool.

The results suggest that the change in exhaustion and dyeing yield in different dyeing conditions closely correspond with the roughness´s creation and the changes in chemical oxidative properties induced by DBD treatment in polyamide fabrics. These results reflect directly on dyeing ability of the fiber providing more terminal groups to make dye bonding.

The application of anionic dyes in discharged polyamide 6.6 shows extensive improvement of dye exhaustion from baths easily achieving 100% in shorter dyeing times. The kinetics of dyeing in every case is quicker, but leveled results are obtained.

It should be noted that deeper dyeing is a great advantage for all anionic dyes since darker shades are obtainable using less amount of dyestuffs. Using plasmatic treatment in polyamide substrates it is possible to obtain decisive energetic gains by dyeing at lower temperatures, to have quite pH independent processes similar to a buffer effect and to reduce dyes and auxiliaries with deeper colors and less pollutant charges.

The DBD plasma treatment has an high industrial potential, because it is an environmental friendly dry process. Including a plasma treatment in the processing of the substrate, dyeing properties obtained by using anionic dyes are improved, namely yield, dyebath exhaustion, washing and rubbing fastness, providing a cheap, clean and high quality option for the dyeing of polyamide materials.

Another important possibility is to achieve different and wider gamut of colors in polyamide fibers provided by direct and reactive dyes, with lower energetic and processing time costs and very important environmental gains, meaning excellent opportunities to add value to new textile products.

5. Acknowledgments

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13

Surface and Bulk Modification of Synthetic Textiles to Improve Dyeability

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1. Introduction

Synthetic fibers, mainly polyethylene terephthalate (PET), polyamide (PA), polyacrylonitrile (PAN) and polypropylene (PP), are the most widely used polymers in the textile industry. These fibers surpass the production of natural fibers with a market share of 54.4%. The advantages of these fibers are their high modulus and strength, stiffness, stretch or elasticity, wrinkle and abrasion resistances, relatively low cost, convenient processing, tailorable performance and easy recycling. The downside to synthetic fibers use are reduced wearing comfort, build-up of electrostatic charge, the tendency to pill, difficulties in finishing, poor soil release properties and low dyeability. These disadvantages are largely associated with their hydrophobic nature. To render their surfaces hydrophilic, various physical, chemical and bulk modification methods are employed to mimic the advantageous properties of their natural counterparts. This review is focused on the application of recent methods for the modification of synthetic textiles using physical methods (corona discharge, plasma, laser, electron beam and neutron irradiations), chemical methods (ozone-gas treatment, supercritical carbon dioxide technique, vapor deposition, surface grafting, enzymatic modification, sol-gel technique, layer-by-layer deposition of nano-materials, micro-encapsulation method and treatment with different reagents) and bulk modification methods by blending polymers with different compounds in extrusion to absorb different colorants.

Nowadays, the bulk and surface functionalization of synthetic fibers for various applications is considered as one of the best methods for modern textile finishing processes (Tomasino, 1992). This last stage of textile processing has employed new routes to demonstrate the great potential of nano-science and technology for this industry (Lewin, 2007). Combination of physical technologies and nano-science enhances the durability of textile materials against washing, ultraviolet radiation, friction, abrasion, tension and fading (Kirk–Othmer, 1998). European methods for application of new functional finishing materials must meet high ethical demands for environmental-friendly processing (Fourne, 1999). For this purpose the process of textile finishing is optimized by different researchers in new findings (Elices & Llorca, 2002). Application of inorganic and organic nano-particles have enhanced synthetic fibers attributes, such as softness, durability, breathability, water repellency, fire retardancy and antimicrobial properties (Franz, 2003; McIntyre, 2005; Xanthos, 2005). This review article gives an application overview of various physical and chemical methods of inorganic and organic structured material as potential modifying agents of textiles with emphasis on dyeability enhancements.

The composition of synthetic fibers includes polypropylene (PP), polyethylene terephthalate (PET), polyamides (PA) or polyacrylonitrile (PAN). Synthetic fibers already hold a 54% market share in the fiber market. Of this market share, PET alone accounts for almost 50% of all fiber materials in 2008 (Gubitz & Cavaco-Paulo, 2008). Polypropylene, a major component for the nonwovens market accounts for 10% of the market share of both natural and synthetic fibers worldwide (INDA, 2008 and Aizenshtein, 2008). It is apparent that synthetic polymers have unique properties, such as high uniformity, mechanical strength and resistance to chemicals or abrasion. However, high hydrophobicity, the build-up of static charges, poor breathability, and resistant to finishing are undesirable properties of synthetic materials (Gubitz & Cavaco-Paulo, 2008).

Synthetic textile fibers typically undergo a variety of pre-treatments before dyeing and printing is feasible. Compared to their cotton counterparts, fabrics made from synthetic fibers undergo mild scouring before dyeing. Nonetheless, these treatments still create undesirable process conditions which can result in increased waste production, unpleasant working conditions and higher energy consumption. Therefore reducing pollution in textile production is becoming of utmost importance for manufacturers worldwide. In coming years, the textile industry must implement sustainable technologies and develop environmentally safer methods for textiles processing to remain competitive (Agrawal et. al., 2008).

1.1 Fiber-forming synthetic polymers

Fibers comprising at least 85% by weight of a substituted aromatic (or aliphatic) carboxylic acid ester are termed polyesters. The most important representative of this category is polyethylene terephthalate or PET (BISFA, 2009). PET is a hydrophobic fiber with maximum moisture regain of only 1% at 100% relative humidity. Until the development of disperse dyes, dyeing of polyester was difficult. Disperse dyes with very low water solubility can sublime into PET fibers by heat through Thermosol and/or thermofixation processes. It can be applied with heat, pressure or via carriers by an exhaust process (Cavaco-Paulo & Gubitz, 2003). Alkali treatment can be used to etch the PET surface to increase the hydrophilicity of the fiber resulting in better dyeability. However, the rate of hydrolysis is very low without a catalyst and surface-limited (BISFA, 2009).

In generic terms, aliphatic polyamides (PA) are called nylons and aromatic PAs are called aramids. The first important PA was Nylon 66 as produced by the reaction of adipic acid and hexamethylene diamine monomer (Cavaco-Paulo & Gubitz, 2003). Several structural modifications with differing temperature capabilities have become commercially available, including Nylon 46, 610, 612, 6, 11, and so on. Polyamides have applications in many areas, the most important being in the production of fiber-based materials (BISFA, 2009). Nylons are dyeable with disperse dyes or with acid dyes under mild acidic conditions. Aqueous acids (below pH 3) as well as bases cause the rupture of the polymer backbone. In the case of acid dyeing, dye molecules only attach to available amino end groups, thus shade depth is determined by the ratio of negatively charged groups of the dye molecule to positively charged end groups in the fiber.

2. Classification of methods used for synthetic textiles modification

Synthetic fibers have relatively high levels of orientation and crystallinity that impart the desired properties. These same characteristics contribute to their structural resistance to coloration by dye compounds and finishing with various materials necessitating enhancement of the fiber surface for improved dye receptivity. In this sense, a large body exists to improve fiber dyeability via physical methods (corona discharge, plasma, laser, electron beam and neutron irradiation functionalizations), chemical methods (enzymatic modification grafting of different monomers, utilization of supercritical carbon dioxide as the solvent carrier for disperse dyes, sol-gel technique, layer-by-layer deposition and treatment with different reagents) and bulk modification methods using various additives during fiber processing. In last decade, traditional methods that consume high amounts of energy and water are under pressure for replacement due to high manufacturing costs and negative environmental impact. In addition, some processing negates the bulk properties of fibers, require harsh process conditions, and produce undesirable side effects and /or waste disposal problems. Recent methods address these challenges and deficiencies of traditional techniques and will be discussed in this chapter (Textor et al., 2003).

2.1 Physical methods

Traditional transformation of a hydrophobic polymer such as poly(dimethylsiloxane) (PDMS) to a hydrophilic state has been achieved via techniques such as corona and plasma treatments (Ferguson et al., 1993; Owen, 2005). Corona, plasma, irradiation, and laser technologies are ideal for textile surface modifications due to the energy-efficient dry-state processing, continuous on-line applicability, and minimal precursor quantity requirements. In addition, surface modification does not ingress to the bulk fiber's mechanical properties although physical alterations are generally realized on the fiber's outermost surface layer. Depending on the treatment duration, the changes can propagate several microns below the surface. X-ray photoelectron spectroscopy (XPS) analysis on oxygen plasma treated samples demonstrated a rapid substitution of carbon atoms by oxygen atoms, which led to the formation of hydrophilic surfaces (Hillborg & et al., 2000). This treatment will propagate several hundred nanometers below the surface with irreversible chemical changes at the near-surface region (Hillborg & Gedde UW, 1999; Hillborg & et al., 2000; Owen & Smith, 1994). The various physical methods all have their merits with some processes, such as corona, more applicable to simple on-line installation. This section will highlight each technique with some examples on their resultant properties.

2.1.1 Corona discharge

Corona discharge is the breakdown of a gas between two electrodes. When the gas is anything but air, it is termed plasma modification to be discussed in the next section. The generation of the initial hydrophilic surface is the same in both modifications with just different outcomes based on the introduced gas stream. **Figure 1** (Borcia, 2006) depicts a typical schematic for dielectric discharge modification. When the high voltage or electric field is applied in a gas layer exposed to a polymer surface, the gas molecules, in this case air, breakdown to ions to conduct electricity. It is the bluish air glow from the electric source that is termed corona. This phenomenon starts with a few stray electrons colliding with other gas molecules. The collision rapidly generates several multiple electrons, positive ions, and excited molecules. The unstable excited molecules decompose to radicals, ions and photons, i.e. reactive species. When the gas is oxygen (or air), the reactive species are elemental oxygen (O•), ozone (O_3) and activated oxygen (O_2*). **Scheme 1** shows the general reactions of polyethylene terephthalate (PET) in the presence of either UV or corona as the mechanisms are believed to be the same. The terminal phenols and hydroxy phenolics are rapidly formed on the surface of corona-exposed PET between the reactive oxygen species and moisture in the air (Owens, 1975; Valk, Kehren, & Daamen, 1970; Zhang, Sun, & Wadsworth, 1998). Other polar moieties that are formed during corona treatment include carbonyls (-CO) and carboxyls (-COO). This change in surface polarity has been widely studied for increases in adhesion, wettability, printing, and as the subject of this chapter, dyeing. Several excellent reviews are referenced here that detail the specific and mechanisms of the treatment (Nitschke, 2008; Podhajny, 1987; Zhang, Sun, & Wadsworth, 1998}).

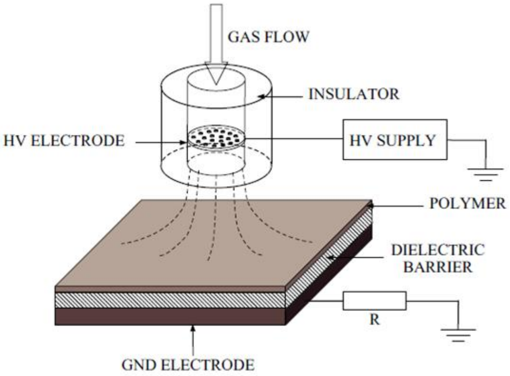
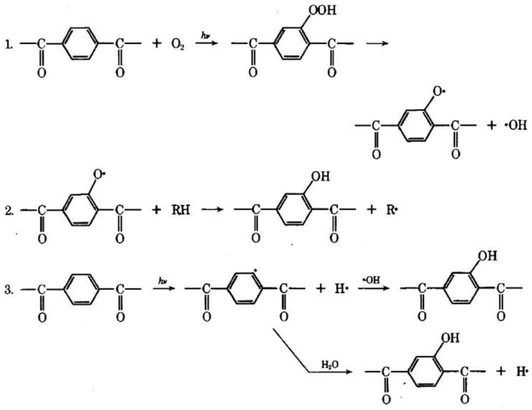


Fig. 1. Typical setup for corona discharge modification to a polymeric surface (Borcia, 2006).



Scheme 1. Phenolic hydroxy groups in PET after exposure to physical treatment such as corona or oxygen plasma (Owens, 1975).

A recent study evaluated not just how corona discharge affects conversion to hydrophilicity in terms of enhanced dyeability of synthetic fibers but also in how the fiber topography changes as a result of physical treatment ultimately influencing dyeability as well (Brzezinski et al., 2010). The study postulated that without fully understanding topography, specifically fiber roughness, correlating the varying results of the many conflicting studies of fiber dyeing with respect to corona treatment is too convoluted. To this extent, three synthetic fibers in separate woven mats were evaluated 1) polyester (PET), 2) polyamide (PA6) and 3) polypropylene (PP). The corona generator was unique in that its construction afforded a high degree and uniform surface modification to the fibers. This was by designing a multi-segmented electrode system where continuous low energy doses equated the larger required total energy dose for adequate surface modification. The process conditions previously determined for each fiber resulted in total activation energies E_j of 75.6 J/cm^2 for PET, E_j of 18.9 J/cm^2 for PA6, and E_j of 22.7 J/cm^2 for PP fabrics. **Figure 2** depicts the difference via atomic force microscopy (AFM) before and after modification for the PP fabric sample where clear disruption of the fiber surface is apparent. In addition to increased roughness, the change in free surface energy was approximately 10, 4, and 30 J/cm2 for PET, PA6, and PP respectively. Dyeability for the modified samples was assessed with two techniques; 1) exhaustion and 2) the preferred Thermosol continuous method. The results between unmodified and modified samples showed little difference in the dyeing attributes via the exhaustion methods, as measured by degree of dye exhaustion, ΔE or color difference, and dyeing fastness. This was attributed to the fact that corona discharge does not modify the entire fiber depth but rather only the first 200nm from the surface of the approximately 6500nm diameter fiber. Therefore in the dyeing techniques, such as exhaustion, where the entire fabric is immersed into the bath batch-wise, the dye pick-up rate is minimal. In contrast, dyeing methods that are applied only to the surface of the fiber, as in the case with the Thermosol method, surface hydrophilicity and roughness are far greater parameters to gauge the receptivity of the dye. In this case, the dye intensity for the corona-modified samples was significantly enhanced as measured by the color difference ΔE for the two dyes studied, C.I. Disperse Blue 73 and C.I. Disperse Red 54 (Brzezinski et al., 2010).

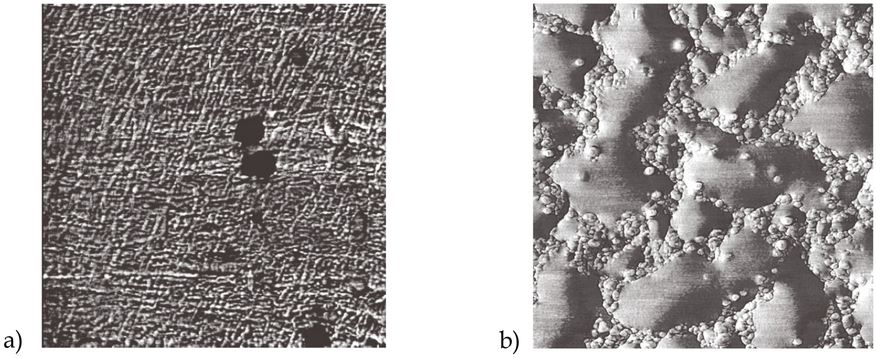


Fig. 2. AFM images of polypropylene woven fabric a) before and b) after corona discharge treatment (Brzezinski, Kaleta, Kowalczyk, Malinowska, & Gajdzicki, 2010).

2.1.2 Plasma functionalization

As mentioned, when the dielectric discharge occurs in environments besides air, the technology is referred to as plasma treatment; it has been studied at both vacuum and atmospheric pressures. The various gases employed include oxygen, nitrogen, argon, ammonia and reactive monomers. The hydrophilicity of poly(ethylene terephthalate) (PET) was greatly improved with the plasma method where the discharge barrier occurred in argon, nitrogen and air (Hsieh & Chen, 1985). The surface wettability enhancements were due to two reactions; 1) direct reaction (i.e. oxidation) of reactive gases (oxygen plasma) and 2) free radical formation and their subsequent reactions such as degradation and crosslinking (Hsieh & Chen, 1985). In this study, it was determined that a nitrogen atmosphere with a glow discharge of 30W provided the most durable and wettable surface finish for PET. The optimum power level of 30W was chosen from experiments in air at power levels ranging from 10-30W. **Figure 3** illustrates the differences of wettability at the optimum power level.

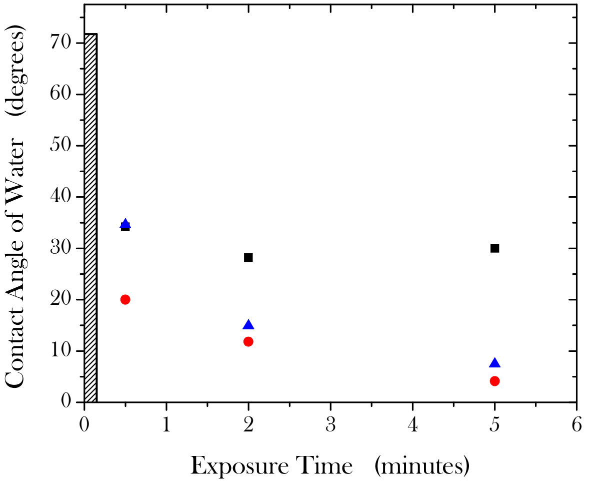


Fig. 3. Advancing water contact angles for PET modified as a function of plasma exposure time in air (■), argon (▲), and nitrogen (●). The bar at time zero is the contact angle for virgin PET. Replotted from data in (Hsieh & Chen, 1985).

Plasma treatment has also been performed on PET fiber prior to coating with a PDMS surfactant. In this case the efficacy of the surfactant was greatly enhanced with plasma activation at 1kW, 10 kHz, in the presence of air. It was determined by scanning electron microscopy that the plasma treated fibers were rougher allowing increased PDMS deposition via observation of a smoother coating, less moisture regain after coating with PDMS which is hydrophobic in nature, better drape recovery and more wrinkle resistance (Parvinzadeh & Ebrahimi, 2011).

2.1.3 Laser treatment

Laser induced surface modification of polymers provides a unique and powerful method for the surface modification without any changes in their bulk properties. The smooth surface of synthetic fibers can be modified by this technique to a regular, roll-like structure, which has a striking effect on adhesion of particles and coatings, wetting properties and optical appearance (Knittel & Schollmeyer, 1998; Watanabe & Takata, 1996; Ondogan et al., 2005; Shaohua et al., 2003).

Yip et al. applied a 193 nm argon fluoride excimer laser on polyamide (nylon 6) fabrics. Micrometer-sized ripple like structures were developed on the surface of irradiated fabric and chemical analysis indicates that carbonization has occurred. It is believed that the laser treatment breaks the long chain molecules of nylon, thus increasing the number of amine end-groups (Yip et al., 2002).

Kan stated that properties such as wettability and air permeability of polyester were positively affected by laser while fiber weight and diameter, tensile strength, yarn abrasion and bending were adversely affected (*.cf* **Figure 4**). In this study, laser irradiation was not found to affect the bulk properties of polymer due to its low penetration depth (Kan, 2008a; 2008b).

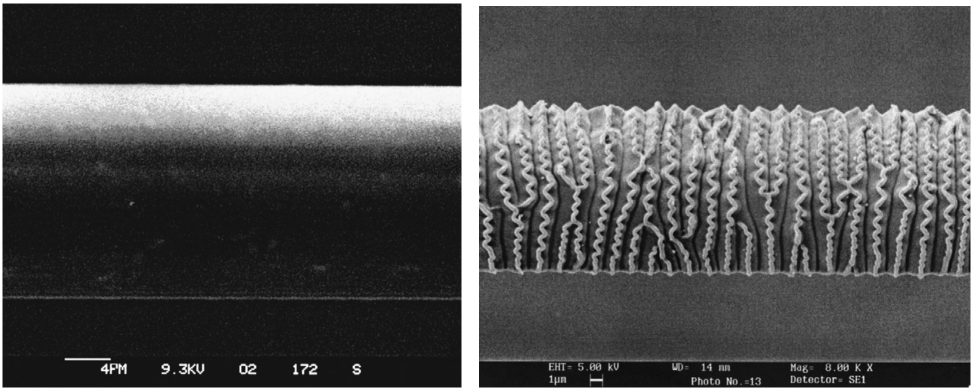


Fig. 4. Surface structure of polyester fiber before and after laser treatment
(Kan, 2008a)

2.1.4 Other physical methods

Exposing fibers to a stream of high-energy electrons is another method for surface modification. The dyeability of hydrophobic polypropylene fibers was enhanced by Kim and Bae using electron beam irradiation and sulfonic acid incorporation. The color strength of polypropylene fibers after irradiation was examined according to the dyeing conditions including the pH of the dye bath, absorbed doses, and the introduction of a functional group to the fiber substrate. The best dyeing result was obtained with cationic dyes at alkaline conditions (Kim & Bae, 2009; Alberti et al. 2005).

Neutron irradiation significantly changes the material properties by displacement of lattice atoms and the generation of helium and hydrogen by nuclear transmutation. Mallick et al. considered the shift in some of the Raman peak positions to a higher value with the development of micro-stresses due to neutron irradiation of synthetic fibers. The defects due to irradiation were confirmed by SEM micrographs of virgin and irradiated fibers (Mallick et al., 2005).

Critical temperature and pressure describes a fluid at temperatures and pressures higher than those at which the liquid and gaseous states of the given substance would have the same density. Prorokova et al. showed modification of the surface of PET fabrics by application of a water-repellent coating in supercritical carbon dioxide medium. It was believed that in treating PET fiber materials with a solution of low-molecular-weight poly(tetrafluoroethylene) in supercritical carbon dioxide, an ultrathin layer of fluoropolymer is formed on the surface. This layer gives the fabric a high degree of water repellency (Prorokova et al., 2009).

Another potentially attractive approach would take advantage of UV light's ability to transform chemistry of the polymer surface. Zhu and Kelley modified the surface of PET by deep UV (172 nm) irradiation. The main effects were increased conversion of the C=O moiety to carboxylic acid with negligible change to fiber topography. Other studies revealed that surface chemical composition, morphology, adhesion, thermomechanics, and stiffness/modulus of PET are strongly influenced by UV irradiation in the presence of bi-functional media (Zhua & Kelley, 2004; Gao et al., 2005).

2.2 Chemical methods

The methods discussed in the following sections include ozonolysis, supercritical carbon dioxide, chemical vapor deposition, "grafting to", enzymatic modification, sol-gel deposition, layer-by-layer, micro-surface modification by alkaline or acidic means, and macro-encapsulation of dye molecules. In many instances, the best performance is obtained from a combination of physical and chemical methods, especially for poly(propylene).

2.2.1 Ozone gas treatment

Hydrophilicity of synthetic polymer surfaces can be achieved with functionalization of peroxide molecules via exposure to ozone (O_3). An advantage of ozone treatment is the uniform coverage of the reactive molecules on 3-D structures. It is also well-known that ozone will treat not only the surface but diffuse through the polymer bulk (Fujimoto et al., 1993; Ko et al., 2001; Kulik, Ivanchenko, Kato, Sano, & Ikada, 1995). The process is often done in the gas phase but aqueous treatment has also been employed with good results (Gu, Wu, & Doan, 2009). In an early study by Fujimoto et al., the surface oxidation of polyurethane (PU) and polyethylene (PE) films were evaluated by both ozone and plasma treatment(Fujimoto et al., 1993). The process conditions for ozone treatment followed typical gas reactor set-up as illustrated in **Figure 5**. Of the process variables to control, gas mass flow rate, voltage and time are the most common to control ozone concentration. The formed polymeric peroxides on the surface and in the bulk were quantified by iodide (Frew, Jones, & Scholes, 1983), DPPH (Frew et al., 1983), and peroxidase spectrophotometric methods (Suzuki, Kishida, Iwata, & Ikada, 1986). Additional surface analysis to confirm reactivity of the ozone included wettability measurements, Fourier infrared spectroscopy in the attenuated reflectance mode (FTIR-ATR), and X-Ray Photoelectro Spectroscopy (XPS/ ESCA). Subsequent to oxidation was the graft polymerization of acrylamide which will be discussed in Section 2.2.4. The surface oxidation efficiency was evaluated based on water contact angle (*cf.* **Figure 6**) and peroxide concentration. Of interest is that the wettability of the plasma exposed films is much higher than the ozonated films but the peroxide concentration in the plasma treated polyurethane film (Power = 24W, exposure time = 20 seconds) is lower than its ozone counterpart (Voltage =100V, exposure time =20 minutes, O_2 flow = 50 L· hr^{-1}). It should also be noted the concentration of peroxide decreases with polymer rigidity and nonpolar constituents (C-F).

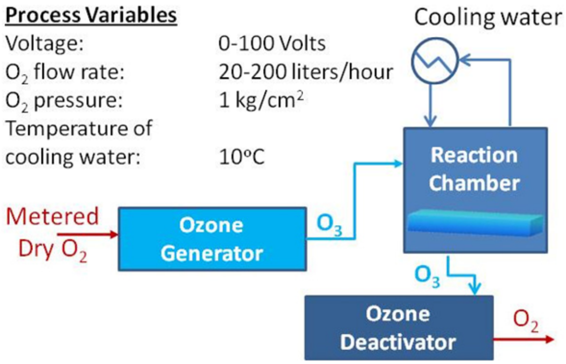


Fig. 5. Typical set-up for ozonolysis of substrates. Redrawn from (Fujimoto, Takebayashi, Inoue, & Ikada, 1993)

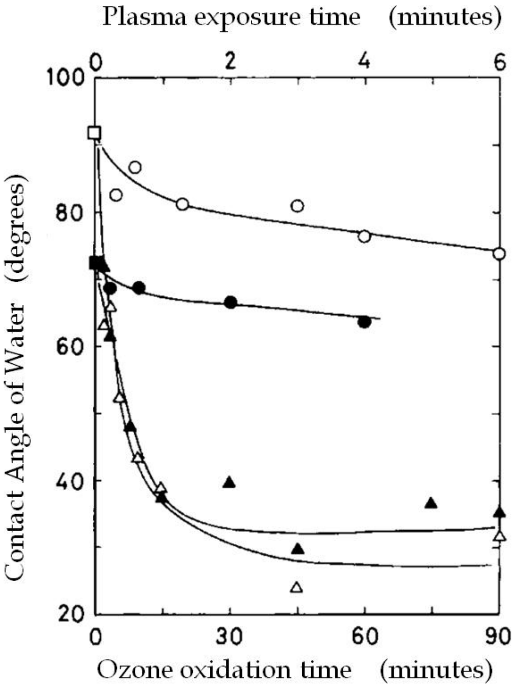


Fig. 6. Decrease in contact angle of PE and PU films by ozone oxidation and plasma exposure. Ozone (60V, 50 Lhr-1): (○) PE, (●) PU. Plasma (Ar, 24 W): (Δ) PE, (▲) PU. Virgin: (☐) PE, (■) PU. From (Fujimoto et al., 1993).

Ozone self-decomposes rapidly in water producing free radicals, a stronger oxidant than ozone itself (Hoigne & Bader, 1976). This property was utilized to produce hydrophilic and highly reactive high-density polyethylene (HDPE) films (Gu et al., 2009). The O_2 gas rate in this study was about twelve times higher with exit ozone concentrations ranging between 1-3.7 weight percent.

Figure 7 illustrates the difference of ozone treatment in the aqueous phase versus the gas phase. While initially there is no apparent difference in the media treatment, the peroxide generation (as measured by the iodometric method (Kokatnur & Jelling, 1941)) is greater and faster for ozonation in the aqueous phase. For all samples, it was demonstrated that the stability of the generated peroxides lasted at least 15 days with no change in concentration. The subsequent grafting of acrylamide on the aqueous ozone treated samples was successful but its performance in terms of surface energy was not contrasted to acrylamide graft polymerization on gas-phase ozone treated samples.

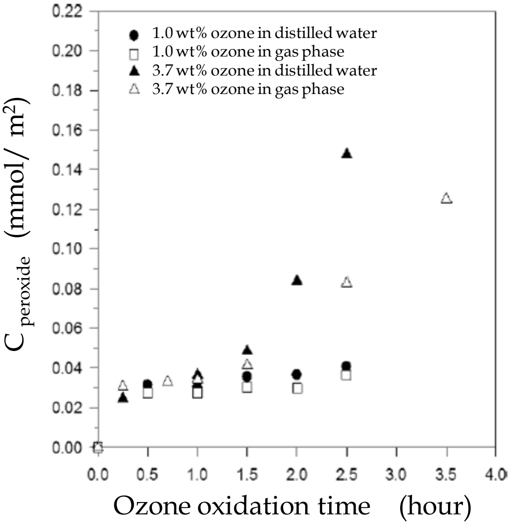


Fig. 7. Peroxides generated after different ozonation times in different media (Gu et al., 2009)

Specific to fabrics, chemical modification via gas-phase ozone treatment was performed on nylon 6 taffeta, polyester taffetas (Lee et al., 2006), cationic dyeable polyester (CDP) and poly(butylene terephthalate) fibers (Lee et al., 2006, 2007). The surface analysis via ESCA was very comparable to the plasma studies by others (Fujimoto et al., 1993), the reader is referred to previous methods for process conditions (Wakida et al., 2004). Notable is that the processing time was only 10 minutes with similar surface chemistries for operations at atmospheric pressure and 0.1 MPa. The ozone-modified fabrics were treated with Disperse Red 60 and Disperse Blue 56 dyes in batch immersion at 100°C for up to 120 hours. The authors found that the internal structure of the fibers increased in crystallinity (as measured by a density gradient column and X-ray diffraction), wettability and moisture uptake upon ozone treatment. These characteristics of the modified fibers were attributed to the increase in dye uptake rate, especially for polyester fibers. The equilibrium dye uptake increased for PBT fibers, polyester taffeta and nylon 6 taffeta but remained unchanged for CDP fibers.

2.2.2 Supercritical carbon dioxide technique

In recent years, waterless dyeing in supercritical carbon dioxide ($scCO_2$) fluid has been gaining much interest to textile chemists. This process is deemed an environmentally safe solvent as opposed to the traditional solvent of choice, water. Application of these techniques can result in reducing waste and cost for the entire dyeing process of synthetic textiles (Kikic & Vecchione, 2003).

The possible advantages of this process are

1. Plasticizing effect due to CO_2 on textiles decreasing the glass transition temperature.
2. Elimination of contaminated waste water streams.
3. Elimination of chemicals, such as leveling agents, pH regulations and dispersants, to solubilize disperse dyes in medium.
4. Controllable solubilities of disperse dyes via pressure.
5. Diffusion of dyes and penetration of voids within the fiber structure in the fluid is higher/ faster due to zero surface tension between air and $scCO_2$ carbon dioxide.
6. Generation of effluents due to dyeing or recycling of contaminated gas streams does not exist.
7. Energy consumption is low for heating up dyeing liquor.
8. For polyester, elimination of reduction clearing process, short dyeing times, and high diffusivities resulting in high extraction/ reaction rates.

Figure 8 shows the supercritical carbon dioxide apparatus which is usually used for dyeing of synthetic fibers. Fabric and dye are put in the container before starting the process. The apparatus is then sealed and heated to a pre-selected dyeing temperature and CO_2 is pumped simultaneously to the set pressure. The dyeing is carried out on textile depending on the type of fiber and then the pressure is slowly reduced to atmospheric at isothermal conditions (Li-qiu et al., 2005).

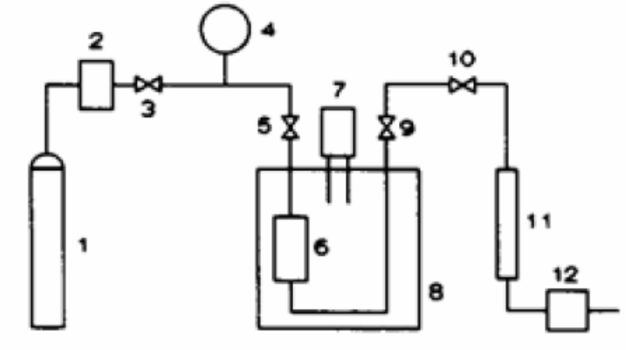


Fig. 8. The supercritical carbon dioxide apparatus used for dyeing of synthetic fibers 1. Liquid CO2, 2. Pump, 3,5,9. Pressure-control valves, 4. Manometer, 6.Autoclave, 7. Temperature sensor, 8. Dyepot, 10. Adjust valve (Li-qiu et al., 2005)

Bach et al. dyed PP fibers in $scCO_2$ with different disperse dyes. They showed that disperse azo dyes with a naphthalene moiety gave much deeper colors on PP versus benzo-azo or anthraquinone dyes. They stated that improvement in dyeability is due to the changes in the crystal network of PP by the treatment in CO_2 as contrasted with PP dyed in water or air (Bach, 1998).

FTIR and NMR results obtained from Nylon 6,6 fabric samples that underwent $scCO_2$ dyeing of with a disperse-reactive dye confirmed a covalent bond with the fibers. Wash and light fastness of the fabrics showed satisfactory results. Their results indicated that fabric immersed in $scCO_2$ does not undergo any fiber damage (Liao et al., 2000). Shim et al. studied sorption of disperse dyes in PET and PTT textiles in the presence of $scCO_2$. They found that the dyeing rate increased monotonically with pressure at isothermal conditions and increased with temperature isobaric conditions (Shim et al., 2003). Generally, this method plasticizes the polymeric fibrous chains enhancing dye diffusion rates and increasing the ease of solvent removal. Moreover, it replaces water in dyeing processes, overcoming the problem of wastewater treatment.

2.2.3 Textile surface functionalization by vapor deposition methods (VDM)

Sputter coating is a significant technique producing functional nanostructured fibers. These functionalized fibers are essential for realizing their applications in microelectronic elements, photonics devices, and medical implants (Wei et al., 2006). Wei et al. used magnetron sputter coatings to generate functional nanostructures on polymer fiber surfaces. Conducting aluminum (Al) film, piezoelectric aluminum nitride (AlN) film, and ceramic film of aluminum oxide (Al_2O_3) were deposited onto PET fibers at low temperature. These nanostructured fibers have great potential for applications ranging from conductive shields, packing, and protective materials to electronic sensors.

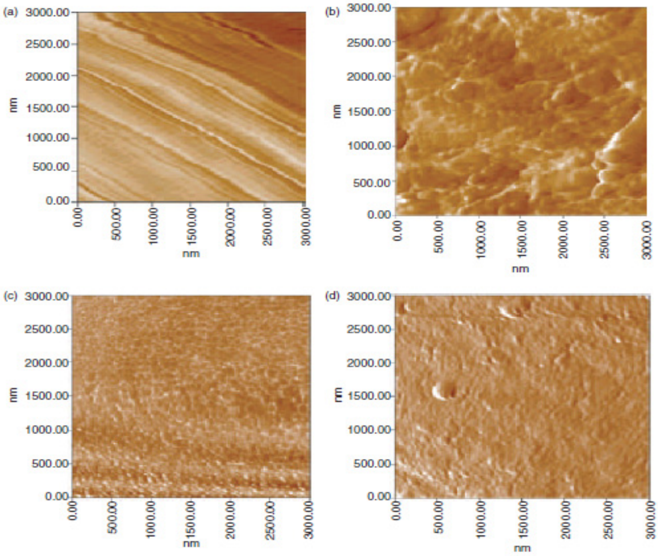


Fig. 9. Surface morphology of textile fiber: (a) original polypropylene fiber; (b) 20nm copper coated polypropylene fiber; (c) 50nm copper coated polypropylene fiber; and (d) 100nm copper coated polypropylene fiber (Wei et al., 2008).

Copper (Cu) nanocomposite textiles were prepared by magnetron sputter coating as discussed by other researchers. The surface conductivity of the textiles coated with Cu nanostructures showed a significant increase compared to the uncoated ones. The increased coating thickness improved electrical conductivity (.*cf* **Figure 9)**. The coated textiles also showed considerable improvement in UV and visible light shielding as examined by UV/Vis spectrometer (Wei et al., 2008).

2.2.4 Surface grafting

Covalent bonding of a molecule to most non-reactive synthetic surfaces such as polyolefins typically requires surface activation via one the physical methods described earlier. To this extent, graft peroxide-initiated polymerization of acrylamide (AAm) proceeded successfully on the ozonated surfaces described in Section 2.2.1. The SEMs in **Figure 10** clearly show the progression of the surface treatment to the final brush-like topography of AAm-grafted HDPE film (Gu et al., 2009). FTIR confirmed the presence of the amide groups with peak intensity at 1667 cm^{-1} increasing for the samples exposed longer to ozone treatment. Finally contact angle of the samples proceed from 74.92° for virgin HDPE to 38.55° for the AAm-grafted HDPE (*cf.* Inset of **Figure 10**). Grafting of AAm to the PU and PE films by Fujimoto et al. was favorable although the methodology was different (Fujimoto et al., 1993). In this case, thermal activation of the peroxide for AAm grafting occurred at lower temperature (60°C versus 85°c) for less time (3 hr versus 24 hr). The end result was still an outermost layer of polyacrylamide on the PU film as measured by FTIR, optical microscopy, and graft density determination by the ninhydrin method (150 $\mu g \cdot cm^{-1}$). It was also demonstrated, however, that the grafting efficiency was reduced when the procedure was performed on PE film. This is attributed to lower levels of peroxides incorporated to the more chemically-resistant PE film as compared to PU film (Gu et al., 2009). These two surface modifications are categorized as "*grafting from*" methods as the peroxide initiator was tethered to the fiber surface prior to the polymerization reaction. When polymer chains are absorbed (and then subsequently reacted) to a solid surface, the correct term is "*grafting to*". A thorough overview of this subject is provided by Minko (Minko, 2008).

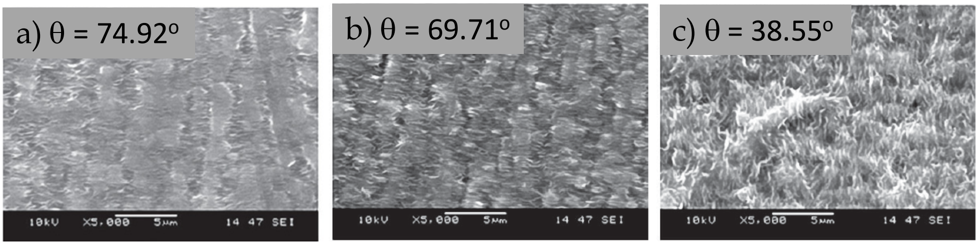


Fig. 10. SEM images of the morphology of the film surfaces (x 5000): a) Virgin HDPE film, b) HDPE film after ozonation in distilled water at 3.7 wt% for 1 hour, and c) AAm-grafted HDPE film ozonated in distilled water at 3.7wt% for 1 hour. Adapted from (Gu et al., 2009).

Polymerization processing parameters for the grafting of 4-vinyl pyridine to PET fiber was done to increase wettability and heavy-metal capture from aqueous media (Arslan, Yigitoglu, Sanli, & Unal, 2003). Similar to previous work (Hebeish, Shalaby, & Bayazeed, 1979; Shalaby, Allam, Abouzeid, & Bayzeed, 1976; Shalaby, Bayzeed, & Hebeish, 1978), benzoyl peroxide was used as the initiator. The researchers pre-swelled the fibers in dichloroethane to aid in the absorption of initiator and monomer prior to polymerization. They evaluated monomer concentration, initiator concentration, reaction temperature and time to determine the optimum grafting conditions for a maximum yield of 70%. The incorporation of 4-vinyl pyridine resulted in a 40% increase of water absorption at the maximum graft yield. The chemical initiator immersion technique for benzoyl peroxide and ammonium persulphate was implemented for grafting acrylic acid onto polylactide fibers. Both techniques for grafting were inefficient to produce significant improvement in dyeability. They do note that layer-by-layer deposition provided surprising results in that the alternative barrier layer impeded the diffusion of oxygen thus prevention of polymer (PLA) degradation fibers. Dyeability as observed by K/ S values was also the highest for the layer-by-layer modification technique.

Table 1 contrasts four chemical reaction schemes to modify PET surfaces without physical modification (Chen & McCarthy, 1998; Nissen, Stevens, Stuart, & Baker, 2001). PET modification by glycolysis was determined most effective as measured by percent concentration of hydroxyl groups. The quantity of hydroxyl groups was assessed by X-ray photoelectron spectroscopy (XPS), dynamic contact angle (DCA) and labeling reactions. The labeling reactions combined with DCA are key results to conclude the increase effectiveness of glycolysis over hydrolysis and reduction of PET surfaces for incorporating hydrophilicity. Although XPS is surface sensitive to the first 100 angstroms, it is also performed in vacuum. Functionalizing the surface with non-polar moieties (fluorine) insure that their preferred orientation state is at the non-polar interface (air then vacuum) versus buried beneath the polymer surface. One final chemical reaction to be discussed for PET modification is aminolysis (Nissen et al., 2001). This reaction forms amide groups through the reaction of polyester's carbonyl with a primary amine. This reaction was done in the early 1960’s to improve wettability, reduce static electricity and increase dyeability (Farrow, Ravens, & Ward, 1962; Kim & Ko, 1989). This reaction can be quite severe to the fibers with complete degradation as a result. To temper fiber degradation, long chain multifunctional amines such as tetraethylenepentamine (TTEPA) has been employed with favorable results (Nissen et al., 2001). While XPS showed no difference in % nitrogen content with reaction time, titration and DCA methods show an optimum wettability or amide content at 180 minutes. This indicated that the reaction was proceeding through the depth of the fiber which can also positively impact the diffusion of a dye throughout the fiber.

2.2.5 Enzyme surface modification of textiles

Processing with enzymes is one of the best environmental friendly applications of biotechnology in textile industry (Cavaco-Paulo & Gubitz, 2003; 2008; Agrawal et. al., 2008; Parvinzadeh et. al., 2009). Enzymes are biological catalysts that mediate virtually all of the biochemical reactions that constitute metabolism in living systems. They accelerate the rate of chemical reaction without themselves undergoing any permanent chemical change.

All known enzymes are proteins and consist of one or more polypeptide chains. The influence of many chemical and physical parameters such as salt concentration, temperature and pH on the rate of enzyme catalysis can be explained by their influence on protein structure. Some enzymes require small non-protein molecules, known as cofactors, in order to function as catalysts (Palmer & Bonner, 2007). Enzymes differ from chemical catalysts in at least two ways. Enzymes have far greater reaction specificity than chemically catalyzed reactions rarely forming by-products. In contrast to chemical catalysis, enzymes catalyze reactions under milder reaction conditions (temperatures way below 100°C), at atmospheric pressures and at neutral pHs (Cavaco-Paulo & Gubitz, 2003).

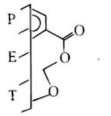
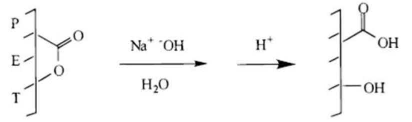
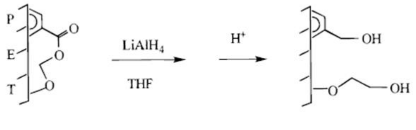
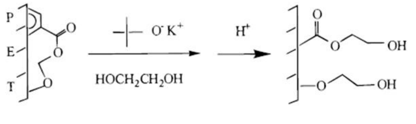
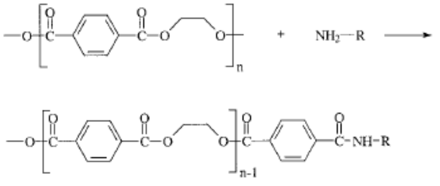
Reaction or molecule	**Contact Angle of Water**	**%C/ %O/ %N (XPS)**
 a) Virgin PET surface	$\theta_a = 77^{\circ}$ $\theta r = 55^{\circ}$	71.5/ 28.5
 b) Modification via Hydrolysis	$\theta_a = 62^{\circ}$ $\theta r = 16^{\circ}$	69.9/ 30.1
 c) Modification via Reduction	$\theta_a = 72^{\circ}$ $\theta r = 32^{\circ}$	70.7/ 29.3
 d) Modification via Glycolysis	$\theta_a = 63^{\circ}$ $\theta r = 25^{\circ}$	69.1/30.9
 e) Modification via Aminolysis	$\theta_a = 39.4^{\circ}$ @ 180 minutes	75.0/ 21.0/ 4.3 @ 180 minutes

Table 1. Chemical reactions to the surface of PET film or fiber with corresponding wettability (as measured by DCA) and XPS results; a)-d) adapted from (Chen & McCarthy, 1998) and e) from (Nissen et al., 2001).

In this section, we summarize how enzymes can be used to increase the hydrophilicity of selected synthetic polymers. Increase in hydrophilicity often leads to improved dyeability of the textile products. Enzymes are also used for the synthesis, surface functionalization and grafting of polymers that are used as textile fibers, however it is beyond the scope of this book chapter. We will discuss both the enzymes for hydrolysis of synthetic fibers as well as the test methods utilized for their characterization and performance.

2.2.5.1 Enzymatic hydrolysis of polyesters / PET

Enzymes are potential tools for PET hydrolysis (Vertommen et. al., 2005). As illustrated in Table 2, PET hydrolyzing enzymes belong to the hydrolase class (EC 3.1) such as cutinases, lipases and esterases (Vertommen et. al., 2005; Wang et. al., 2004; Battistel et al., 2001). PET was hydrolyzed by cutinases from organism *F. solani, F. oxysporum* and from *Pencillium citrinum*. Other PET-hydrolyzing enzymes are lipases, such as those from *Humicola sp., Candida sp., Pseudomonas sp.* and *Thermomyces lanuginosus* (Gubitz & Cavaco-Paulo, 2008). In addition to enzymatic hydrolysis, the simple adsorption of enzyme protein to the polymer can also increase the hydrophilicity of PET owing to the hydrophilicity of the protein. High crystallinity of PET polymers negatively affects the ability of the enzymes to hydrolyze which has already been shown for enzymes from *F. solani* and from *T. fusca* (Vertommen et. al., 2005; Cavaco-Paulo & Gubitz, 2008).

2.2.5.2 Enzymatic hydrolysis of polyacrylonitrile (PAN)

PAN (*.cf* **Figure 11**) is a collective name for all polymers that consist of at least 85% acrylonitrile monomer (BISFA, 2009). The homopolymer (100% acrylonitrile) is difficult to process and dye thus is only for industrial applications. The co-monomers in acrylic fibers are selected for fiber specific properties, such as dyeability with sodium methallyl sulfonate, sodium sulfophenyl methallyl ether, etc (Cavaco-Paulo & Gubitz, 2003).

Acrylic fibers comprising negative groups can be dyed with basic (cationic) dyes under carefully controlled conditions. Dyeing is usually performed in the presence of a retarder, which decreases the dyeing process rate for uniform shade reproduction. Finishing processes for PAN are limited since desirable properties can be more easily incorporated by copolymerization or by modification on the fiber level. For example, highly absorbent fibers are made by inclusion of a hydrophilic co-monomer which is subsequently removed by hydrolysis.

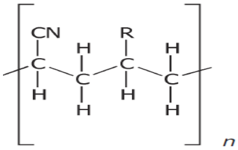


Fig. 11. Polyacrylonitrile 89-95% homopolymer, R = CN and up to 10% copolymer, R = vinyl acetate, COOH, SO_3H, OSO_3H etc

It has been shown that bacterial strains, such as *Micrococcus luteus,* can degrade PAN fibers. During this process, poly(acrylic acid) is released from PAN as confirmed by NMR analysis (Fischer-Colbrie et al., 2007). The release of poly(acrylic acid) from PAN, together with the formation of ammonia, was also shown for commercial nitrilases (Matama et. al., 2007). Several researchers converted the nitrile groups of PAN to the corresponding acids or amides by nitrilases or by an enzyme system comprising nitrile hydratase and amidase, respectively resulting in major increases in hydrophobicity (Tauber et. al., 2000; Fischer-Colbrie et al., 2007) (*.cf* **Table 2**). These changes in surface properties corresponded to an 80% increase in the surface oxygen-to-carbon (O/C) ratio attributed to enzymatic hydrolysis of the nitrile groups (Matama et. al., 2007). Commercial PAN-based materials usually contain around 7% vinyl acetate to reduce rigidity of the polymer. The vinyl acetate moieties in PAN can be hydrolyzed by cutinases and lipases, making this approach applicable to most commercially available PANs (Matama, et. al., 2006).

2.2.5.3 Enzymatic hydrolysis of polyamides (PA)

Enzymes such as proteases, amidases and cutinase can hydrolyse PA (*.cf* **Table 2**). A model substrate (adipic acid bishexyl-amide) has been developed for screening PA hydrolysis activity of given enzymes. It has been found that protease from *Beauveria sp.*, an amidase from *Nocardia sp.* and a cutinase from *F. solani pisi* can degrade the model substrate and correlated with PA hydrolysis activity (Heumann, et. al., 2006). For actual PA substrates; it has been demonstrated by Parvinzadeh et.al (2009) that protease treated Nylon 66 fabrics shows higher dye bath exhaustion with reactive and acid dyes. The intensity of major peaks in FTIR spectra of the protease treated samples is in favor of chemical changes of the polypeptide functional groups in the fabric. The results of color measurements showed that there is a direct co-relation between the concentrations of enzyme against the darker shade of the dyed fabric. In a separate study performed by the same researchers, it was confirmed that acid and disperse dyes showed higher exhaustion on the protease (Parvinzadeh, 2009) & lipase (Kiumarsi & Parvinzadeh, 2010) treated Nylon 6 samples.

Key Synthetic Fibers	**EC 3: Hydrolase class of enzymes**			**Key Analysis Methods**
	EC 3.1: enzyme acting on ester bond	EC 3.4: enzymes acting on peptide bond	EC 3.5: enzymes acting on carbon-nitrogen bonds, other than peptide bonds	
PET – Polyethylene terephthalate	Cutinase [1] Lipase [3] Serine esterase [4]	-	-	XPS, HPLC, NH_3 formation, dye-binding assay [1,3,4]
PAN – Polyacrylonitrile	Cutinase[a] [6]	-	Nitrile hydrolase [2]	XPS, NH_3 formation, dye-binding assay [2]
			Nitrilase [5]	XPS, FTIR, SEM, dye-binding assay [5]
PA – Polyamide	Cutinase [3]	Proteases [4, 9]	Amidase [7]	Release of oligomers, reactive dye-binding assay, hydrophilicity [3,7]
	Lipase [9]			FTIR, SEM, UV-vis spectrophotometer, thermal, dyeability, hydrophilicity [8-10].

[a] PAN co-polymer with 7% vinyl acetate, FTIR: Fourier-transform infrared spectroscopy, SEM: scanning electron microscopy, HPLC: High Performance Liquid Chromatography,
[1] = Vertommen et. al., 2005; [2] = Tauber et. al., 2000; [3] = Wang et. al., 2004; [4] = Battistel et al., 2001;
[5] = Fischer-Colbrie et. al., 2006; [6] = Matama, et. al., 2006 ; [7] = Heumann, et. al., 2006;
[8] = Parvinzadeh, 2009; [9] = Kiumarsi & Parvinzadeh, 2010; [10] = Parvinzadeh et. al., 2009

Table 2. Enzymatic modification of synthetic polymers

To conclude, in coming years, the textile industry will go towards sustainable technologies and developing environmentally safer methods for textiles processing. One way is the processing with enzymatic system, rather than conventional chemical methods. There are several ways to improve the dyeability of any synthetic fibers. However, enhancement of the hydrophilicity of synthetic polymers is a key requirement for better dyeability. Enzymes have proved to be environmental friendly tools for hydrolysis of synthetic polymers, specifically on the polymer surface, without compromises in polymer bulk properties. In general hydrolases class of enzymes (EC 3.1: cutinase, lipase, esterase, EC 3.4: protease and EC 3.5: nitrilase, nitril hydrolase, amidase etc) are used for improving hydrophilicity of synthetic fibers such as PET, PAN and PA respectively.

2.2.6 Modification of textile surfaces using sol-gel technique

A sol-gel technology is probably one of the most important developments in material science during the last decades. The sol-gel technique offers far reaching possibilities for creating new surface properties. Scientific literature demonstrates a wide array of functionalities that have been achieved by application of sol-gel coatings on textile surfaces. Its inorganic nature makes sol–gel layers very strong with nanometer-thick layers (Mahltig & Textor, 2008). Sol gel applications for textiles includes manipulation or changing

- Key textile properties e.g. stiffness, handle, absorbency, permeability etc.
- Surface properties e.g. hydrophobicity, hydrophilicity, abrasion resistance, photocatalytic activity, other barrier functions etc.
- Optical properties e.g. improving dyeability, photochromic effect, UV-absorption properties.
- Bio-active systems such as biocidal coatings, controlled release systems, immobilization of biological materials (enzyme, cells) etc.
- And other physical properties e.g. heat resistance, conductivity etc.

Sol-gel technology offers the possibility of tailoring surface properties to a certain extent, and combining different functionalities into a single material. The added advantage is that the application of sols can be carried out with techniques commonly used in the textile industry such as, a simple dip or padding process followed by a thermal treatment in a stenter frame.

2.2.6.1 The sol gel principle

The preparatory material or precursor used to produce the "sol" usually consists of inorganic metal salts or metal organic components, such as metal alkoxides (Mahltig & Textor, 2008; Chládovál, et. al., 2011). These precursors are subjected to a series of hydrolysis and polymerization reactions to create a colloidal suspension or "sol". This sol is deposited on the surface of materials, transferred into a gel and finally into a layer of oxide by heat treatment. In production and for research purposes, SiO_2 and TiO2 layers are deposited most often. Also, layers of many other compositions containing Al_2O_3, B_2O_3, ZrO_2, PbO and other oxides are often prepared. Next to the clearly inorganic layers, hybrid inorganic-organic layers have also been developed (production terms ORMOCER, ORMOSIL and NANOMER), which contain both chemical bonding of organic substances and functional groups next to silicon, titanium, zirconium and oxygen (Chládová, et. al., 2011).

2.2.6.2 Dyeing of textiles based materials

Currently, we are observing an intensive increase in the production of textiles made of synthetic polymers. Synthetic fibers have high mechanical properties and are extremely rigid apart from other properties such as having low porosity and lower swelling etc. These properties are directly related to low dyeability with the standard dyeing technology. Synthetic fibers normally have a high glass transition temperature which makes it impossible for the dye molecule to penetrate into the fibers, especially when using water (H_2O) as a solvent. In some cases, it is possible to use other solvents or other fiber-swelling compounds to reduce the glass transition temperature of fibers. **Table 3** illustrates some key examples of sol gel method applied on textile based materials to improve it dyeability.

Materials/ Fabric	Dye(s)	Technique / key results	Reference
Polyester /Viscose	Rhodamine B, Naphthol Blue Black, Metanil Yellow & Bismarck Brown R	Dyes immobilized modified silica sol to reduce dye leaching from the substrate.	(Nedelčev et. al., 2008)
Polyester (PET)	Disperse Blue 56	Sol was prepared by hydrolysis of tetraethoxysilane (TEOS) in presence of HNO_3 and H_2O, for deposition of porous SiO_2 film on polyester fabric.	(Barabi et. al., 2010)
Glass fibers	Total 12 dyes belongs to cationic dyes, disperse dyes & metal complex dyes	The sol is the blending of 3-trimethoxysilyl propyl methacrylate in isopropanol with supporting chemicals (water, HCl, benzoyl peroxide).	(Chládova, et. al., 2011)
Glass	pH sensitive dye methyl red (MR), tropaeolin (TO) and bromocresol green (BCG).	The sol–gel consisted of 50% tetraethoxysilane (TEOS) and 50% methyltriethoxysilane (MTEOS) (w/w).	(Ismail, et. al., 2011)
Titanosilicates	Azo dye Orange II	Functionalization of the titanosilicates with ethylenediamine groups was carried out via the sol gel process, using the hydrolytic route followed by dyeing.	(Marc¸al, L. et. al., 2011)

Table 3. Improving dyeability of various textile based materials using sol gel method.

In the surface treatment of polymer structures, it is necessary to use hybrid layers based on a mixture of inorganic and organic polymer compounds, which are connected at the end of the process to a single macromolecular network (.*cf* **Table 3**). The inorganic part is linked with chemical, mechanical and thermal stability. The application of sol gel technology for improving dyeability is still at relatively early stage of development. However, looking at the trends, it is expected that sol gel technology will play important role towards improving dyeability and bringing new functionality together.

2.2.7 Nano-modifications of textiles surfaces using layer-by-layer deposition methods

A variety of functional thin films can be produced using the layer-by-layer (LbL) assembly technique (Ariga, Hill, & Ji, 2007; Decher, 2003). LbL-based thin films are currently being evaluated for properties that include antimicrobial (Dvoracek, Sukhonosova, Benedik, & Grunlan, 2009; J. H. Fu, Ji, Yuan, & Shen, 2005; J. Fu, Ji, Fan, & Shen, 2006), anti-reflection (Hiller, Mendelsohn, & Rubner, 2002), electrical conductivity (Park, Ham, & Grunlan, 2011), anti-flammable (Carosio, Laufer, Alongi, Camino, & Grunlan, 2011; Li et al., 2010; Li, Mannen, Schulz, & Grunlan, 2011), gas barrier (Priolo, Gamboa, & Grunlan, 2010; Priolo, Gamboa, Holder, & Grunlan, 2010; Yang, Haile, Park, Malek, & Grunlan, 2011), and UV resistance (Dawidczyk, Walton, Jang, & Grunlan, 2008). These films, typically < 1μm thick, are created by alternately exposing a substrate to positively- and negatively-charged molecules, polymer electrolytes, or particles, as shown in **Figure 12**. Steps 1 – 4 are continuously repeated until the desired number of "bilayers" (or cationic-anionic pairs of layers) is achieved. **Figure 12b** provides an illustration of a film deposited with cationic and anionic polymers. Individual layers may be 1 – 100+ nm thick depending on chemistry, molecular weight, charge density, temperature, deposition time, counterion, and pH of species being deposited. The ability to control coating thickness down to the nm-level, easily insert variable thin layers without altering the process, avoid disturbing intrinsic mechanical behavior of the substrate, and process under ambient conditions are some of the key advantages of this deposition technique. In nonwovens, each thread can be individually coated with a uniform LbL nanocoating and still remain soft and flexible.

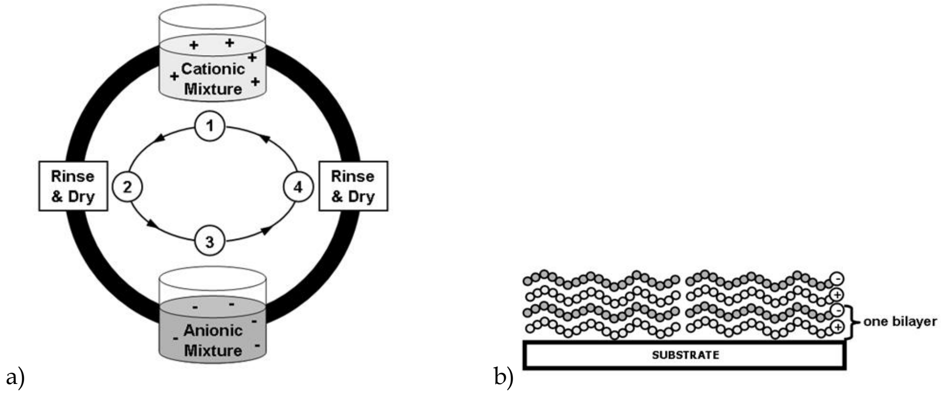


Fig. 12. a) Schematic of layer-by-layer deposition process used to prepare functional thin films and b) steps 1 – 4 are repeated until the desired number of bilayers are generated on a substrate. From (Jang & Grunlan, 2005)

Surface roughness of materials has been intensely studied over the last decade. When this aspect is coupled with low surface energy components, "rough" materials become superhydrophobic. Olephobicity also comes into play when the material becomes nanoporous, minimizing void volume between molecular substituents, preventing wetting of low surface tension liquids in addition to polar liquid (i.e. water) (Zenerino, Darmanin, de Givenchy, Amigoni, & Guittard, 2010). Designing superhydrophobic surfaces via the layer-by-layer assembly method have included covalently bonded interlayers (Amigoni, de Givenchy, Dufay, & Guittard, 2009), integrated organic and inorganic components, and induced micro-roughness from the underlying substrate to mimic the back of the Stenocara beetle where the hydrophilic/ superhydrophobic regions allow self-cleaning surfaces (Garrod et al., 2007; Zhai et al., 2006). Interesting alternating layers of the anionic and cationic mixtures have allowed for facile fabrication of the resultant surface chemistries. To further enhance the viability of the LbL technique for organic polymers, pH-amplified exponential growth LbL self-assembly was implemented for poly(ethylenimine) (PEI) and poly(acrylic acid) PAA as the polycation and polyanion respectively. This technique takes advantage of the synergistic effect of the pH-dependent tunable charge density and weak polyelectrolyte diffusivity. The end result is fast LbL layer formation in a limited number of deposition cycles. This research proved that only three bilayers were necessary to achieve a lotus-like superhydrophobic surface (.*cf* **Table 4**) (Sun, Shen, Wang, Fu, & Ji, 2010).

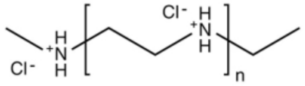
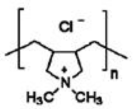
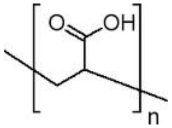
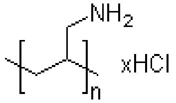
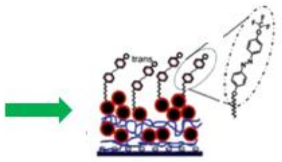
Property	**Polycation**	**Polyanion**
Super-Hydrophobicity From (Sun et al., 2010)	PEI  Polyethylenimine	PAA
Super-Hydrophilicity From (Grunlan, 2011)	PDDA  Poly(diallyldimethyl ammonium chloride)	PAA  Poly(acrylic acid)
Switchable –philic/ -phobic From (Lim et al., 2006)	PAH  poly(allylamine hydrochloride) Inorganic-Organic Hybrids to induce roughness with azofunctional moieties	SiO_2 

Table 4. Polyelectrolytes for LbL formulations with imparted functionality.

LbL deposition of polyelectrolytes can also be used to impart a hydrophilic surface to polyolefins. In the case of polyethylene, this would be useful for high performance fibers that might eventually be used for athletic clothing to wick away moisture as well as increase dye receptivity. With a contact angles (θ_{dH20}) around 70°, polyethylene (PE) surfaces could actually be called slightly hydrophilic. In reality, contact angles below 45° are typically needed for a surface to exhibit facile wetting by a water droplet or hydrophilic behavior. **Table 4** shows a matrix of polymer polyelectrolytes that are used for imparting various finishes to substrates via LbL deposition. Specifically implemented by the Grunlan laboratory to determine the possible hydrophilic coatings onto PE, 2.5 bilayers were needed to achieve a θ_{dH20} of 22° when using the system of poly(diallyldimethylammonium chloride) (PDDA-PAA) as compared to other systems comprising 6 or more bilayers. The elevated pH of PAA (pH = 5) created an increased negative charge density and thinner deposition relative to unmodified PAA (pH < 3). Additionally, stopping deposition at half bilayers, where PDDA was at the surface, proved much more hydrophilic than full bilayers due to its high charge density (Grunlan, 2011). They also noticed upon further evaluation, full bilayers of PDDA-PAA (pH = 5) had a contact angle of 11 degrees. This near super-hydrophilic value is much lower than the initial screening attributed to a more pristine PE film cleaning and controlled polyelectrolyte deposition. The half bilayer protocol, with PDDA at the film's surface, had contact angles that could no longer be measured (i.e., < 5 degrees), suggesting a superhydrophilic surface. This was shown to be reproducible and unchanging as the assembly was built from 2.5 to 6.5 bilayers.

Another unique utilization of LbL deposition was demonstrated by Cho and researchers (Lim, Han, Kwak, Jin, & Cho, 2006). They formed a nanoporous substrate with microscale roughness through alternating electrostatic deposition of poly(allylamine hydrochloride) (PAH) as the polycation and SiO$_2$ nanoparticles as the polyanion for a substrate with reversible wetting properties. The exposed SiO$_2$ layer was treated with 3-(aminopropyltrichlorosilane) providing reactive binding sites (-NH$_2$) for photo-switchable moieties (7-[(trifluoromethoxyphenylazo)phenoxy]pentanoic acid (CF$_3$AZO)). The CF$_3$AZO moieties in vis (440nm) light are in a hydrophobic *trans* orientation but orient to a *cis* state upon exposure to UV (365 nm) light. After the LbL-CF$_3$AZO fabrication, the surface measured contact angles up to 156^{0}, as dictated by the number of bilayers (.*cf* **Figure 13a**). In contrast, the contact angle of water for a CF$_3$AZO-functionalized flat film measured 76^{o} (θ_{dH2O}). The flat surface after exposure to UV light for 10 minutes, demonstrated a contact angle change of 5^{o}, whereas the LbL functionalized surface could switch between being superhydrophobic at 156^{0} to superhydrophilic at < 5^{o}, for nine bilayers. This reversibility was repeated up to 5 cycles with essentially zero hysteresis (see **Figure 13b**).

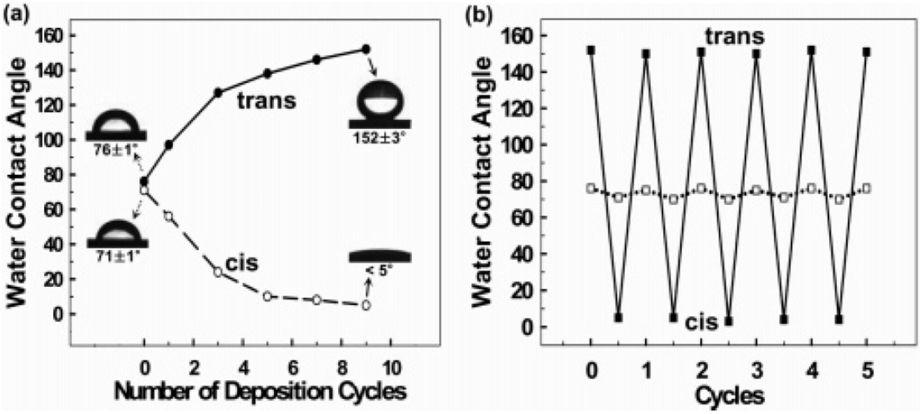


Fig. 13. a) the number of LbL bilayers necessary to induce super-hydrophobicity/ super hydrophilicity on CF$_3$AZO-LBL surfaces and b) corresponding reversibility for the nine bilayer surface after UV/Vis exposure. Adapted from (Lim et al., 2006).

To conclude, LbL deposition is a unique surface modifying technique that gives ultimate flexibility for the design of the surface. Challenges for this technique include cost-effective commercial implementation at high on-machine line speeds for continuous operations. Engineering creativity to meet this challenge holds promise for a facile surface treatment technology for textiles.

2.2.8 Micro-encapsulation method to enhance dyeing process

Microencapsulation is actually a micro-packaging process involving the production of microcapsules. These materials act as barrier walls of different solids or liquids as cores. The wall has the ability to protect the core from hazardous environments, i.e. oxidization, heat, acidity, alkalinity, moisture or evaporation. They are produced by depositing a thin polymer coating on small solid particles or liquid droplets, or on dispersions of solids in liquids. The core contents are released under controlled conditions to suit a specific purpose (Cheng et al., 2008).

The most commonly methods used for preparation of microencapsules are complex coacervation, polymer-polymer incompatibility, interfacial polymerization and in situ polymerization, spray drying, centrifugal extrusion, air suspension coating, pan coating and emulsion hardening method (Cheng et al., 2008). In dyeing of synthetic fibers, the major interest in microencapsulation is currently in the application of dyes as core and liposome as shell. Liposomes are artificially prepared vesicles made of lipid bilayer that can be filled with various materials. They comprise naturally-derived phospholipids with mixed lipid chains (*.cf* **Figure 14**).

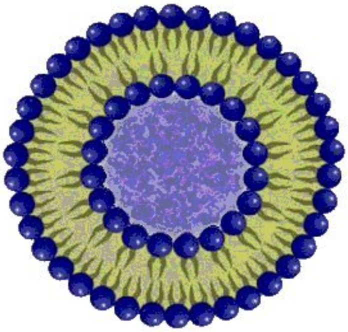


Fig. 14. Structure of liposome.

Gomez and Baptista studied microencapsulation of the dye in liposomes with lecithin from soy as an alternative to retarding and leveling agents. Liposomes were prepared with soy lecithin at different concentrations, containing the commercial acid dye C.I. Acid Blue 113. The effect on the dyeing rate of the microencapsulated dyes was compared with that from common retarding and leveling agents. The influence of surfactants on the stability of the liposomes and hence on the exhaustion curves of the dyeing was also evaluated. Interesting results obtained from exhaustion curves of anionic and non-ionic surfactants compared with commercial retarding and leveling agent (Gomez & Baptista, 2001).

Marti et al. used phosphatidylcholine liposomes instead of synthetic surfactants as dispersing agent for disperse dyeing. They calculated the turbidity ratio to assess the dispersion behavior of different liposome-dispersed dye preparations compared with commercial dye forms. Results indicated that liposomic preparations diminish the aggregation of dye molecules that normally occurs at high temperatures. They also found the potential efficacy of liposomes as natural surfactants which can be applied to disperse dye formulations to dye polyester fibers with good dye exhaustion and washing fastness. This environmentally friendly biological surfactant, phosphatidylcholine, duly structured as liposomes, can substitute high amounts of synthetic dispersing agents in disperse dye formulations (Marti et al., 2011).

Yan et al. suggested microencapsulated disperse dyes to dye PET in the absence of auxiliaries and without reduction clearing. They studied the dyeing behaviors and dyeing kinetic parameters of microencapsulated disperse dye on PET compared with those of commercial disperse dyes with auxiliary solubilization. Their results showed that the dyeing behaviors of disperse dye are influenced greatly by microencapsulation. The diffusion of disperse dyes from microcapsule onto fibers can be adjusted by the reactivity of shell materials and mass ratios of core to shell. The disparity of diffusion between two disperse dyes can be reduced by microencapsulation. In addition, the microencapsulation improves the utilization of disperse dyes due to no auxiliary solubilization (Yan et al., 2011).

2.2.9 Micro surface modification of textiles by aqueous solutions

Alkaline, acidic and solvents hydrolysis is another method to improve various physical and chemical properties of synthetic fibers (Shcherbina et al., 2008; Park et al., 2009; Veronovski et al., 2009; Barantsev et al., 2007; Konovalova & Rabaeva, 2007; Chapurina et al., 2005; Hou et al., 2009). Alkaline hydrolysis has been studied extensively to overcome some problems of low water absorption properties and softness as alkaline hydrolysis improves the water absorption properties and softness of the PET fiber to give it a character similar to that of natural fibers (Prorokova et al., 2009; Chu et al., 2005). The alkaline hydrolysis of PET fibers is usually carried out with an aqueous alkaline solution, such as sodium hydroxide. In the alkaline hydrolysis process, PET undergoes a nucleophilic substitution. Chain scission of PET occurs, resulting in a considerable weight loss and the formation of hydroxyl and carboxylate end groups, which improves the handling, moisture absorption and dyeability of the fabric with enhanced softness (Mikhailova et al., 2008; Prorokova & Vavilova, 2004; Sohn et al., 2007; Stakne et al., 2003, Akbarov et al., 2006; Pavlov et al., 2001).

The effects of pretreatment reagents on the hydrolysis and physical properties of PET fabrics were investigated under various alkaline hydrolysis treatment and pretreatment conditions by Kim and his colleagues. Solvents used for pretreatment included benzyl alcohol and 2-phenyl ethanol. Results indicated that fabric weight loss, crystallinity, the initial and maximum water absorption increased with increasing hydrolysis time (Kim et al., 2009).

Jain et al. reduced multi-filamentous polyacrylonitrile (PAN) fibers to amino groups using lithium aluminum hydride for immobilization of antibodies and detection of analyte. 24 h reduced fibers gave the most stable and reproducible results on immobilization of antibodies. Modified PAN fibers had a strong potential to be used as matrix for the detection of pathogenic bacteria and medical diagnostics (Jain et al., 2009). Another approach carried out by Cui and Yoon to modify the surface of PET film by treatment with ethoxylated hexylaminoanthraquinones synthesized by the reaction of 1-aminoanthraquinone with poly(ethylene glycol)s via hexamethylene spacer. The ethoxylated hexylaminoanthraquinones were adsorbed only onto the extreme surface of PET and water contact angle was decreased by the adsorption (Cui & Yoon, 2003).

A comprehensive collection of wet-chemical analyses of oxidized surfaces of poly(ethylene terephthalate) or polyolefin was presented by Knittel and Schollmeyer. Advanced oxidation of textile samples has been done using ozone and UV functionalization. They claimed that method presented uses inexpensive equipment and can be done quickly in a normal lab even as a process control (Knittel & Schollmeyer, 2008).

3. Bulk modification of synthetic textiles using nanomaterials

In recent years, synthetic polymer-nanometric filler composites have generated significant attention in diverse applications such as transportation vehicles, construction materials, electronics, sporting goods, packaging, household and textile industries (Sinha Ray & Okamoto, 2003; Leszczy´nska et al., 2007a). The aim is to enhance a wide range of properties including mechanical properties (modulus, stiffness and strength), barrier, flame retardancy, solvent and heat resistance, biodegradability, chemical and thermal stability as well as improvement in dyeability relative to a virgin polymer (Leszczy´nska et al., 2007b, Pesetskii et al., 2007). In order to obtain these specifications, fillers such as cellulose, clay, calcium carbonate, carbon, metal oxides and various forms of silica have been developed by different researchers. In this regard, the geometrical shape of the particles plays an important role in determining the properties of composites (Bhat et al., 2008; Njuguna et al., 2008; Ma et al., 2003).

Processing of such polymeric nanocomposites are more difficult compared to the corresponding pure polymers since such inorganic nanoparticles have strong tendencies to agglomerate. To overcome such difficulties, the sol-gel method, LbL deposition, in situ polymerization and melt processing are put into practice. The last method is still the most cost effective, simple, feasible and environmentally benign process for the mass production of polymeric nanocomposite (Burgentzle´ et al., 2004; Modestia et al., 2007).

Considerable efforts have been devoted to improve various physical, mechanical and barrier properties of PET through mixing it with nanoclays (Phang et al., 2004; Chang et al., 2004; Chang et al., 2005; Jawahar et al., 2005). The layered clays used are mica, fluoro-mica, hectorite, saponite, etc., but one of the most commercially interesting clay is bentonite belonging to a structural family known as the 2:1 phyllosilicates (Calcagno et al., 2007). It is well known that the clay minerals have also been used as adsorbent for removal of acid, reactive, disperse and basic dyes from aqueous solutions due to the fact that they are globally abundant and inexpensive (Xiao et al., 2005). Their inner layers comprise an octahedral sheet, which is situated between two tetrahedral sheets. The substitutions of Al3+ for Si4+ in the tetrahedral layer and Mg2+ or Zn2+ for Al3+ in the octahedral layers result in a net negative surface charge ion in water which cause the repulsion interaction with anionic dyes (Parvinzadeh & Eslami, 2011).

The dyeability of synthetic fibers depends on their physical and chemical structure. Dyeing process consist of three steps including the diffusion of dye through the aqueous dye bath on to the fiber, the adsorption of dye into the outer layer of the fiber and the diffusion of dye from the adsorbed surface into the fiber interior. It was shown by researchers that functional groups of PET and water molecules play a great role in this process. The terminal carboxylic and hydroxyl groups in PET chains interact with water molecules. This makes a swelled fiber resulting to increase the attraction of disperse dye by these functional groups of fiber (Kirk–Othmer, 1998).

The proportion of crystalline and amorphous regions of polymer is another factor influencing the dyeability. Researchers are concerned with the development and implementation of new techniques in order to fulfill improvement in dyeability of various polymers. Blending of polymeric fibers with nanoclays as inexpensive materials is still claimed as cost effective method to enhance dyeability (Geoghegan & Krausch, 2003). Up to now, only two research articles are focused on dyeing properties of polypropylene- and polyamide 6- layered clay incorporated nanocomposites prepared by melt compounding

(Razafimahefa et al., 2005; Toshniwal et al., 2007). Toshniwal et al. suggested that polypropylene fibers could be made dyeable with disperse dyes by addition of nanoclay particles in polymer matrix (Toshniwal et al., 2007). Another research work done by Razafimahefa and her colleagues showed that the introduction of the nanoclay improves the dyeing ability of nylon with disperse dyes. Nevertheless, because of the interactions between the anions in montmorillonite and the amino groups on the polyamide, the dyeing sites are occupied with the nanoclay. This led to inferior dyeing with acid or metal complex dyes than in the case of the unfilled polymer (Razafimahefa et al., 2005).

Our previous study on dyeability of PET/clay nanocomposites stated the following type of interactions between the disperse dye and clay surfaces:

- Hydrogen bonding between OH groups of modified clays and the NH_2 and CO groups of disperse dye molecules.
- Electrostatic bonding between the negatively charged oxygen atom of carbonyl groups in disperse dye molecule and positively charged nitrogen atom of quaternary ammonium salt in modified clays.
- Direct π interactions and van der Waals forces between methyl and ethyl groups of modified clays on one hand and methoxy group and benzene rings of disperse dye molecule on the other hand.

The second reason for improving disperse dye absorption of PET/clay nanocomposites could be the relatively large voids between clay platelets after modification with quaternary ammonium salts (Parvinzadeh et al., 2010a; Parvinzadeh et al., 2011). It was shown that the surface morphology of PET/clay nanocomposites has great influence on water contact angle of the resultant nanocomposite (*.cf* **Figure 15**).

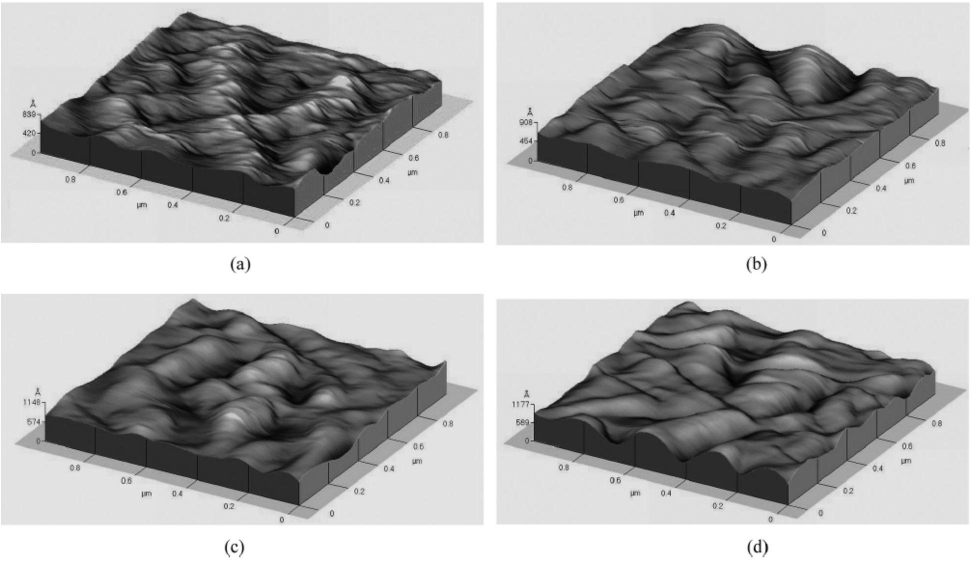

(a) (b) (c) (d)

Fig. 15. 3d topographic images of atomic force microscopy for various composites:
(a) Pure PET, (b) PET=15A, (c) PET=30B, (d) PET=Na^+
(Parvinzadeh et al., 2010a).

Another applicable nanofiller is silica nanoparticle which impacts high stiffness, tensile strength, modulus, toughening, crystallinity, viscosity, creep resistance, coefficient of friction, wear resistance, toughness and interfacial adhesion in various polymer nanocomposites (Xanthos, 2005, Parvinzadeh et al., 2010b). Recently, a research program to explain dyeability of PET/silica nanocomposite was done by Yang and Gu. They used *in situ* polymerization to prepare PET/SiO_2 nanocomposites. According to the results, the color strength of the dyeing increased with increasing SiO_2 content in polymer (Yang & Gu, 2007).

Over the last 20 years polymer chemistry has created a non-linear polymeric structure coined dendritic polymers. Their architecture arises from the introduction of a large number of branches with many functional end groups (Froehling, 2001).

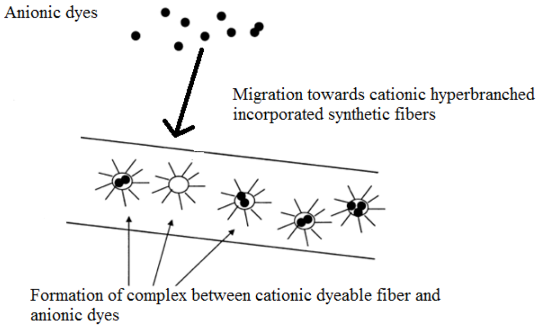


Fig. 16. Incorporation of hyperbranched polymers into the fiber structure (Froehling, 2001)

Two classes of these polymers are dendrimers with a perfectly branched uniform structure and hyperbranched polymers with non-uniform ones. It was already suggested by different authors that highly branched molecules should be able to act as a host for the encapsulation of guest molecules of dyes or a dendritic box. This structure can lead to industrial development of dyeable poly(propylene) fiber (Froehling, 2001) (*.cf* **Figure 16**). Other authors suggested that an improvement in dyeability of the polymeric- hyperbranched additive nanocomposites can be attributed to the decrease in glass transition temperature and the lower crystallinity of the polymers (Khatibzadeh et al., 2010).

4. Remarks and outlook

Various types of physical and chemical finishing methods have been described in this chapter. Most of them are developed to solve problems with synthetic fibers to expand their usefulness. Examples of such problems are their insufficient fabric softness, low absorbency of water, flammability, and pilling, low dyeability, slipping and static problems during production and usage. New finishing processes using physical and chemical methods can solve these problems and restrictions. Both the improved and the newly developed finishes based on nano-science are valuable tools that can project an enhanced image of the finish producers for the next textile industry revolution.

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14

Pretreatment of Proteinic and Synthetic Fibres Prior to Dyeing

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1. Proteinic fibres

1.1 Wool

1.1.1 Treatment with metal salts

The effect of absorption of some metal ions by wool such as copper, iron, aluminum, cobalt and nickel was thoroughly investigated. The pretreatment of wool with some di- carboxylic acids was studied to present their impact on the amount of metal uptake by wool on its dyeing properties(1-3). Wool fabric was treated with copper sulphate and ferric chloride solutions (1.5% o.w.f.) at 40° and 60° C for 30 min. The effect of starting pH value of the salt solution on the acquired uptake of copper and iron by wool is illustrated in Fig. 1.1. It can be noticed that the metal uptake increases linearly and strongly for both copper and iron in the range of pH value 3-6 and 1.5-3.5 respectively. Increasing the temperature from 40° to 60°C led to an increase in the amount of metal uptake but the rate was considered to be almost the same or slightly changed. The metal uptake by wool fibres could be enhanced by chemically modifying the fibre with chelating agents able to coordinate the metal ions. It was found that treatment of wool with tannic acid and EDTA has increased the metal uptake by wool and consequently increased the weight gain (4, 5). Wool was treated with some organic acids such as oxalic, maleic, succinic and adipic acids at 75°C for 90 min. There was a weight gain in wool accompanied to these di-carboxylic acids treatments. The % increase in weights of wool was 3.6, 3.2, 2.6 and 2.5 for wool pretreated with the aforementioned organic acids respectively. These increases in weight were found to correspond to the increase in the carboxyl content of wool from 421.7 meq/100 g fibres for untreated one to 622.1, 530.5, 457.3 and 425 meq/100 g fibres for the treated wool with the aforementioned acids respectively (6). The metal uptake of treated wool with oxalic acid increases as shown in Table 1.1. Other acids treatment did not enhance the metal uptake property. This may be due to the large molar volume of these acids which might restrict the penetration of metal ions into wool macrostructure (3).

The elongation %, tensile strength at break and alkali solubility of the untreated and treated wool with metal salts solution at 60ºC are illustrated in Table 1.2. The results indicated that nearly no changes in the mechanical properties of the treated wool were noticed. It is well known that the tensile properties of wool could be affected negatively during the dyeing process especially at high temperature (7) that might require using of protective agents. This treatment made it possible to dye wool at lower temperature and reflects more protection of wool from damage during the dyeing process (Table 1.2).

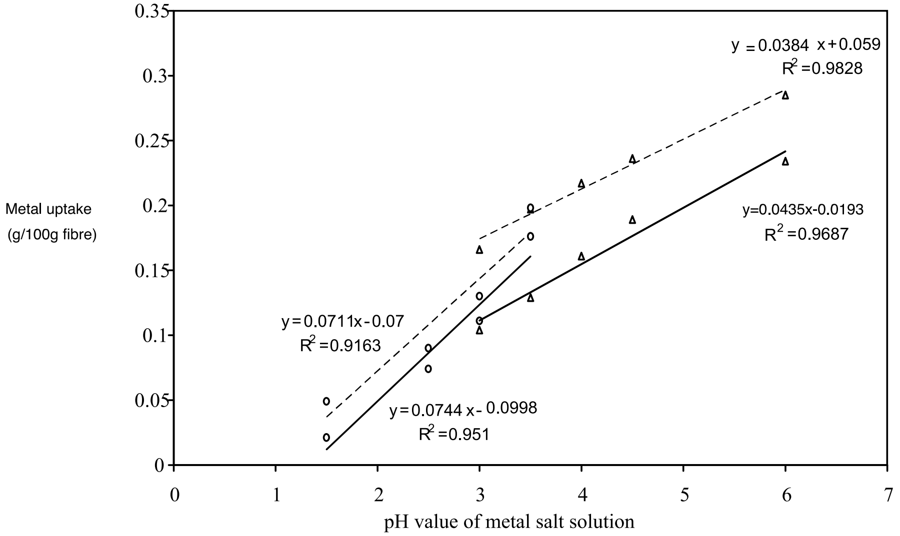

Fig. 1.1. Dependence of metal uptake by wool on the pH value of its solution at different temperatures. Treatment: 1.5 % (o.w.f), Δ-Δ copper sulphate, o-o ferric chloride, ___40° C, _ _60 °C, 30 min, liq. ratio 1:30.

Wool Samples		Metal uptake (mg/100 g wool)		
		Copper	Cobalt	Nickel
-Treated with metal salts		262.0	154.6	180.5
-Pretreated wool with:	Oxalic acid	366.0	172.1	196.71
	Maleic acid	157.1	21.9	44.3
	Succinic acid	150.4	11.0	19.2
	Adipic acid	129.2	8.2	19.9

Treatment: 0.03 M acid, 75 °C, 90 min., liq. ratio 1:50, 3 % metal salt, 60 °C, 30 min., liq ratio 1:30.

Table 1.1. Effect of pretreatment of wool with some organic acids on its tendency for metal uptake

Type of Sample		Elongation %	Tensile Strength (Kg)	Alkali Solubility
1-Untreated wool		26	41.5	8.82
2-Treated with:	Aluminum sulphate	25	45.5	8.67
	Copper sulphate	20	37.5	8.23
	Ferric chloride	22	43.5	8.42
	Cobalt sulphate	21	41.6	8.81
	Nickel sulphate	21	42.0	8.80

Treatment: 1.5 % (o.w.f.) metal salt solution; 30 min., pH 3.5; liq. ratio 1:30.

Table 1.2. Tensile strength, elongation % at break and alkali solubility of treated wool fibre with metal salts

Dyeability: Four steps could be envisaged in the process of dye uptake: a) diffusion into the fibre surface, b) transfer across the surface, c) diffusion within the fibre to appropriate sites and d) bonding to proper sites. Various algebraic expressions have been derived from Fick's laws of diffusion in an attempt to describe experimental dyeing rates. Near parabolic rates were seen (8). The equilibrium for the dye- wool interaction could be separated into the following:

$$W - NH_3^+.OOC - W \ + \ Dye \rightleftarrows W - NH_3^+.^-Dye \ +^- OOC - W$$

$$H^+ +^- OOC - W \rightleftarrows H.OOC - W$$

Probably the rate of the second step would be fast and thus the first step would be the rate determining. Combining the metal ions with carboxyl groups led to increasing the reaction in the forward direction and consequently increasing the rate of dyeing.

Pretreatment of wool prior to the metal treatment with some organic acids such as oxalic, maleic, succinic and adipic had enhanced the wool dyeability. Oxalic acid led to nearly complete exhaustion of dye from the dyebath after 30 min at 95ºC as compared to 90 % exhaustion for the untreated one dyed for 60 min. at the same temperature (Table 1.3). The dyeing rate constant and the diffusion coefficient increased by the aforementioned treatment while the half dyeing time decreased (Table 1.4). Both alteration (alt.) and staining (st.) washing fastness properties of wool dyed with acid dye at 95ºC were found to be good.

Type of Samples		Dye uptake (g dye / 100 g fibre)		
		Cobalt sulphate	Nickel sulphate	*Ferric Chloride
Treated wool		1.89	1.9	1.92
Pretreated wool with:	oxalic acid	2.0	2.0	1.96
	Maleic acid	1.99	2.0	1.96
	Succinic acid	1.94	-	-
	Adipic acid	1.96	-	-

Treatment: 0.03 M acid/100 g fibre, 75 °C, 90 min., liq. ratio 1:50, 3 %metal salt, 60 °C, 30 min., liq ratio 1:30. Dyeing: 2% C.I. Acid Red 41, * C. I. Acid Orange 19, 95ºC, 30 min, pH 4.5, liq. ratio 1: 50

Table 1.3. Dyeability of pretreated wool fabric with some organic acids followed by metal treatment

Type of Sample		$t_{1/2}$ min	k' x 10 $^{-4}$ (cm/sec) ^{½}	D x 10 $^{-7}$ cm^2 sec $^{-1}$
- Untreated wool and dyed at:				
	75˚C	14.5	4.976	2.7611
	85˚C	13.3	6.01	2.8151
	95˚C	9.0	8.12	3.5684
- Treated wool with aluminum sulphate at 40˚C, dyed at:				
	75˚C	12.2	7.417	2.7914
	85˚C	11.1	8.08	2.9277
	95˚C	7.8	9.901	4.2467
- Treated wool with aluminum sulphate at 60˚C, dyed at:				
	75˚C	10.0	8.487	3.0113
	85˚C	8.9	9.343	3.2365
	95˚C	6.7	10.954	4.5914

Type of Sample	$t_{1/2}$ min	k' x 10^{-4} $(cm/sec)^{1/2}$	D x 10^{-7} $cm^2 sec^{-1}$
- Treated wool with *copper sulphate at 40˚C, dyed at:			
75˚C	9.3	17.3	3.5014
85˚C	8.4	18.762	3.638
95˚C	7.4	20.692	4.1716
- Treated wool with *copper sulphate at 60˚C, dyed at:			
75˚C	8.8	18.1288	3.6961
85˚C	8.2	19.6198	3.6427
95˚C	6.5	22.3721	4.6041
- Treated wool with **ferric chloride at 40˚C, dyed at:			
75˚C	12.3	6.668	3.0978
85˚C	11.7	7.754	3.2777
95˚C	8.6	9.3165	4.3088
- Treated wool with **ferric chloride at 60˚C, dyed at:			
75˚C	11.7	7.1703	3.1014
85˚C	10.5	8.2731	3.3779
95˚C	8.0	9.7906	4.5258

Treatment: 1.5 % (o.w.f.) metal salt solutions, 30 min, pH 4.5, **pH 3.5, liq. ratio 1: 30.
Dyeing: 1% (o.w.f.), * 2% (o.w.f) C.I. Acid Blue 221, pH 4.5, liq. ratio 1: 50.

Table 1.4. Half dyeing time ($t_{1/2}$), dyeing rate constant (k') and diffusion coefficient (D) of untreated and treated wool with metal salts.

1.1.2 Treatment with sulphamic acid

Chemical treatments of wool and its blends with synthetic fibres are one of the goals to provide new characteristics and to promote their dyeabilities (10, 11). The advent of a new practical dye resist treatment, based on sulphamic acid for wool dyeing has brought about renewed interest in its dyeing capabilities especially for its acrylic blend. The application of sulphamic acid onto wool revealed a promoted possibility of cationic dyeing. The dye uptake usually resulted in higher dye exhaustion with level and full penetration of dye molecules into wool fibres. Sulphamic acid treatment offered the possibility of producing deeper shade on wool/acrylic blend without increasing the dye concentration used. Dyeing of the blend could be then achieved with single class of dye and possibly in one bath (12, 13). Wool fabric was immersed in sulphamic acid solution using concentration of 5-20 % (w/w), padded to pickup 70 %, dried at 80°C for 15 min., and then thermofixed at 160°C for 5 min. The treated wool was subjected to dyeing with cationic dye at 80°C for time intervals of 5–60 min. Wool pretreated with either 15 % (o.w.f) sulphamic acid solution attained nearly the same dye uptake upon dyeing with cationic dye under the same conditions. Alkali solubility of wool before treatment was found to be 15.6 % and that of the sulphamic pretreated wool was found to be 30 %, indicating that there is some damage of wool pretreated under these conditions. Infrared spectroscopy of the untreated and pretreated wool with sulphamic acid shows that no new peak appearance except SO_4^{-2} groups, which appeared at 1150 – 1050 cm^{-1} and also a peak belonging to sulphamic acid groups appeared at 1090 cm^{-1} as compared with the untreated one (14, 15). SEM of the untreated and the sulphamic acid treated wool shows that most of the scales have disappeared and wool attained a relatively smoother surface than the untreated one (Figs 1.2 and 1.3).

Fig. 1.2. SEM graph of untreated wool.

Fig. 1.3. SEM graph of sulphamic acid-treated wool.

1.1.3 Treatment with chitosan

Chitosan sorption on proteinic fibres is found to be due to ionic interaction between the negative charges of carboxylic groups in the polypeptide macromolecule and the protonated amino groups of chitosan, and possibly due to hydrogen bonding between the hydroxyl or amide groups of polypeptide chains and similar groups in chitosan. The application of chitosan onto wool reveals even dye uptake resulting in higher dye exhaustion with level and full penetration of dye molecules in wool fibres(16). The treatment of wool with chitosan permits the formation of an approximately uniform sheath on individual fibres. Chitosan treatment does not involve changes in colour fastness of the dyed wool to any extent, but may reveal some problems such as weak binding. Such problems are reported to be overcome upon applying chitosan onto wool with a nonionic surfactant (17, 18). The possibilities of improving the reactive dye affinity to wool fibres and their protection from damage by conducting chitosan treatments of wool before subjecting it to reactive dyeing were reported (10). Wool fabric was treated with chitosan and nonionic surfactant using diluted concentrations 0.1- 0.7 % (w/w) and then dyeing the pretreated wool with reactive dye at 80°C for 5-60 minutes. The pretreatment of wool with chitosan enhanced the colour intensity and the dye uptake as compared with the corresponding untreated one. The rate of dye fixation percentage of the dyed pretreated wool increased as compared with the corresponding untreated one. The rating of crocking and washing fastness was found to be higher than the corresponding untreated ones. Alkali solubility of wool and chitosan treated wool was 18.6 % compared to 15.6 % for untreated one, indicating that there is insignificant damage of treated wool. SEM micrograph of the chitosan treated wool is shown in Fig 1.4. Most of the scales have disappeared and wool attained a relatively smoother surface. Some holes were detected on the surface of treated wool.

Fig. 1.4. SEM of chitosan treated wool

1.1.4 Treatment with epichlorohydrin and alkoxides

Treatments of wool fabrics were performed using organic acids such as acetic, mono–, di –, trichloroacetic, propionic and butyric acids (19). Wool fabrics were treated with chitosan at different times and temperatures (17). The aforementioned treated fabrics were then dyed with reactive dye. The increase in the colour intensity and dye- uptake of the dyed fabrics was found to depend upon the type of the organic acid used in the pretreatment and the pK_a values of the acids used (20, 21). The acquired colour intensity and dye uptake of the pretreated wool increased compared to those of the untreated one. The dyeability of the treated wool and wool/polyester with some alkoxides using methyl, ethyl, propyl and butyl alcohols is improved towards acid as well as disperse dyes. Treatment of wool with epichlorohydrin (22) was found to improve its dyeability in comparison with the untreated one. Wool fabrics were firstly immersed in sodium thiosulphate or sodium bicarbonate mixture then treated with epichlorohydrin solution (0.25 mol/l) at temperatures 60°C and 80°C for different time intervals 10- 20 min. The treated fabrics were then dyed with a reactive dye for one hour at 80°C and the corresponding dye uptake was determined. Upon increasing the time of wool treatment with epichlorohydrin, an increase in colour intensity and dye uptake were attained. It was reported (23) that serine, tyrosine, aspartic and glutamic acids, arginine, lysine, histidine and the amino end groups in wool macromolecule are possibly the reactive sites for the interactions with epoxides. Water is required to enhance the reaction of epoxide with wool. A wide variety of chemical treatments have been used for wool having the objective of controlling the degradation of the fibre surface, with the least amount of damage. One of the early approaches was the use of alkalies dissolved in aliphatic alcohol to reduce the fibre swelling and to confine the beneficial effects on the fibre surface (24- 27).

1.1.5 Enzyme treatment

The possibility of obtaining various finishing effects on wool by the use of environmentally friendly treatments such as enzymes has been investigated. However the complexity of wool fibre makes it difficult to find the enzymes that are able to modify wool properties without excessive damaging its structure. Application of enzymes, particularly protease, to wool has been studied to achieve a non-felting fibre. The efficiency of shrink-resist protease treatment, the effect of treatment on the absorption of some reactive dyes, and the action of protease enzyme when added to the dyebath was reported to improve the dye absorption by wool fibres. The influence of pretreatment of wool fabrics with a lipase enzyme on its dyeability with reactive dyes was studied (28-30). The enzymatic treatments by exhaustion technique were performed in a bath of a liquor ratio, 1:40 for different intervals of time (10 min and 24h). The concentration of enzyme ranged between 0.2 - 2.0 % (o.w.f.). The pH of the treatment bath was adjusted to 10.7 using phosphate buffer. The enzyme treated fabric was then squeezed and air dried. Wool fabric was treated by padding technique after immersing in a 3 % enzyme solution buffered to pH 10.7. The fabric was padded and squeezed twice to have a pick up of 70 %. The padded fabric is then stored in an air tight polyethylene bag for 24 h. The treated fabric was then dried at room temperature before dyeing. The pretreatment of wool fabric with lipase enzyme has induced significant improvement on its dyeability with the reactive dyes (C.I. Reactive Blue 203 and C.I. Reactive Red 21). As the amount of the lipase increases, the rate of dye uptake increases. Lipase enzyme has been reported to remove the surface lipids of the fibre and thus enables improved penetration of solutions, including dyes, to the interior of wool fibres (28). The dye uptake of wool fabric is dependent on time of treatment. A complete exhaustion of C. I. Reactive Red 21 (1% o.w.f.) from the dyebath was achieved after about 10 min of dyeing of the enzyme pretreated wool at 80^{0}C compared to about 48% exhaustion for untreated one. Complete dye exhaustion has a positive impact on reduction of indoor pollution, cleaner production and energy saving. The half-dyeing time ($t_{1/2}$), specific dyeing rate constant (K′) as well as the diffusion coefficients (D) were calculated for untreated and pretreated wool fabric with lipase according to the following equation:

$$K' = 0.5 \cdot C_\infty \cdot (d/t_{1/2})^{1/2}$$
$$D = C_t / C_\infty \cdot \frac{d^2 \cdot 100}{t}$$

Where C_∞ is the % dye absorbed on the sample at equilibrium conditions between the sample and the dyebath divided by the weight of the sample, C_t is the dye uptake after 10 min and d is the fibre diameter in cm. Time of half dyeing ($t_{1/2}$) of pretreated wool fabric is less than that of untreated one. This can be contributed to the higher dyeing rate and higher dye diffusion of the treated wool fabric (Table 1.5). Using exhaustion or padding technique in treatment process (for 24 h at room temperature) resulted in the same effect in enhancing the dyeability of wool and reducing the half-dyeing time. The quantity of dye absorbed after short dyeing time (10 min) can substitute the diffusion values, so a modified Arrhenius relationship can be applied as follows :

$$\ln C = \ln C_0 \cdot \frac{-E}{RT}$$

Where C is the dye absorbed after a short dyeing time, C_o is constant, T is the dyeing temperature in ^{0}K and E is the activation energy of diffusion. Plotting ln C versus 1/T, two straight lines may be drawn, one at high temperature and the other at lower temperature. The two lines intersect at a point with approximately constant value of 1n C (ln C_i) and 1/T is increasing for treated wool fabric. The slope of the straight line is -E/R from which the activation energy of diffusion (E) can be calculated where R is the universal gas constant. For the early stage of dyeing where the outer layers of the fibre are involved, a certain number of dye sites in the outer layer of the fibres saturate slowly; diffusion towards these sites presents high activation energy (E_1) at dye concentration lower than C_i. Evaluation of E_1 for untreated and pretreated wool fabric was 15.4 and 6.6 kJ/kg.mol.^{0}K respectively. The enzymatic treatments led to first saturation at lower temperature, where it was 102^{0}C for untreated wool sample and 72^{0}C for pretreated one. Diffusion towards the other sites follows the first saturation and a decrease in activation energy was observed at a second linear relationship (E_2 at $C>C_i$), it was evaluated by 1.402 kJ/kg.mol.^{0}K for treated wool fabric. The kinetic investigation of the dyeing process revealed a decrease in half dyeing time, an increase in the dye rate constant and diffusion coefficient and also a decrease in the activation energy of diffusion.

Type of Sample	$t_{1/2}$ min	K' x10^{-5} (cm/sec)$^{1/2}$	Dx10^{-7} cm^2.sec^{-1}
-Untreated	16	1.14	1.980
-Pretreated by:			
exhaustion technique	7.5	2.08	3.803
Padding technique	7.5	2.08	3.803

Treatment: 2% (o.w.f.), 25^{0}C, 24h, Dyeing: 2% (o.w.f.) C.I. Reactive Red 21, 80^{0}C, pH 4.5, L.R. 1:50.

Table 1.5. Time of half dyeing ($t_{1/2}$), specific dyeing rate constant (K') and diffusion coefficient (D) of pretreated wool fabric with lipase.

1.2 Silk

1.2.1 Treatment with saccharin

Colouration of wool, silk and polyamide fibres are satisfactorily performed with acid dyestuffs. Energy saving as well as high fastness performance and reduction of costs can be reasonably gained by applying cationic dyes to the fibres used in carpet manufacture. An attempt has been directed to give evidence of the benefits of treatment of silk fibres with saccharin during dyeing (22, 25). Silk fabrics were treated with saccharin solutions (10 g/l); the treatment was carried out at 90°C for 1h. The effect of this treatment on the dyeing ability of silk fabrics with C. I. Basic Red 18 was studied. The pretreatment with saccharin had enhanced the colour intensity of the dyed fabrics, as compared to the untreated dyed one. The increase in colour intensity was found to be dependent on the temperature and the time of dyeing. The increased affinity of the saccharin treated fabric to the cationic dye can be attributed to the possibility of the breakdown of saccharin molecules liberating carboxylic acid groups. These groups have the ability to trap both cationic moiety as well as the NH_2 group of the fibres.

1.2.2 Treatment with organic solvents

Some studies on the solvent effects on shrink proofing of silk fabrics were reported(31, 32). The shrink proofing was obtained by treatment with dimethylsulphoxide, dimethylformamide, dimethylacetamide, sulfolane, and ethylene glycol in a closed curing system. The treatments with hexa-amino-cyclotriphosphazene in dimethyl sulphoxide, ethylene glycol, glycerol and the mixtures of (dimethylsulphoxide, ethylene glycol), and (dimethylsulphoxide, glycerol) were more effective for shrink proofing even with small amounts of resin deposition. These results showed that the molecular orientation and cross linking in medium crystalline regions played the important role for shrink proofing of silk crepe. Dimethylsulphoxide was one of the best solvents for the shrink proofing by phosphoric amides. Some of the fundamentals governing the shrinkage of silk goods were explained based on the release of the strains imposed during manufacturing processes and the swelling produced on wetting. The mechanism of the swelling by organic solvents was explained in terms of the solubility parameter of the solvents and hydrogen bonding and dipolar interactions between silk and the solvents.

1.2.3 Plasma treatment

Chemical modification of textile fabrics was early used as a tool for imparting new fibre properties and increasing its effective applications. However, these chemical methods are not always environmentally friendly and may also produce changes in the mechanical properties of the fabric which makes them less comfortable to wear. Nowadays, physical technologies can advantageously replace some of these chemical modifications as environmental friendly process. Plasma treatment is a rapid, innovative and environmentally amenable method which could replace wet chemical application to modify the surface properties of polymers and textile materials without significant effects in the bulk of fibres. Interest was directed to produce durable silk surface as well as use reactive dye for its printing. Plasma surface treatment of silk was carried out in atmospheric air at different discharge powers for different plasma exposure times. The effect of plasma treatment on the printability of silk fabric with reactive dye using conventional silk screen printing technique is investigated. The printability of silk was found to be markedly improved as well as its fastness properties. The whiteness of plasma treated silk increased by increasing the discharge power. The wettability of treated silk expressed as wetting time was found to depend upon the treatment time and discharge power (33).

2. Man made fibres

2.1 Polyester

Polyester fibers have attained a major position in the textile and non-textile uses, although polyester fibers have several drawbacks vis. low moisture regain (0.4%), a tendency to accumulate static charges, pick up soil dirt during wearing, difficulty of cleaning during washing, pill formation, thus spoiling fabric appearance and flammability. Modifications of polyester fibers can have an effect to overcome these disadvantages and can promote its permeability, hydrophilicity, hand and thermal properties (1, 2). Modification of polyester fibers is carried out via its treatments with alkalies, combined thermal and alkali, mono or multifunctional amines, organic solvents and acids as well as enzymatic hydrolysis. Thermal treatment of polyester fibers is a well known and important method in modification of the polymeric structure of the fibers. The purposes have increased to concern and cover the specific physico-chemical changes of the fiber structure to induce a certain tendency of crystallinity and orientation.

Unevenness is one of the major drawbacks in their dyeing. Drastic dyeing conditions are usually performed to overcome unevenness, to promote colour homogeneity and depth, which however endanger the properties of the fibres. The lower barré effect appears from the application of dyes having high diffusion efficiency in polyester fibres. It is an oversimplification to deem that polyester is a solid solvent for disperse dyes and other hydrophobic molecules (3). Some relationships exist between the rate of dye diffusion, temperature, steric structure of the dye, size of voids in the substrate and elasticity of the amorphous regions. Ensuring the benefits of chemical modifications of polyester fibres in order to introduce new possibilities by changing its dyeing characteristics was done (3 ,4). It is nearly impossible for a dye molecule to diffuse into the polyester structure at low temperature; adequate rates are only achieved when dyeing temperature exceeds the glass transition temperature of the fibre. Satisfactory dyeing of polyester fibres can be carried out by loosening the fibre structure. This can be achieved by high temperature treatments; or during high temperature –high pressure dyeing or via carrier dyeing. High temperature and carrier dyeing methods succeed in opening the fibre structure. As the fibre is being heated thermal motion of the polymer chains increases, thus allowing dye molecules to diffuse in. Dyeing begins in the least oriented regions of the fibres. The orientation of polymeric, chains directly determines the rate of diffusion and dyeing rate. Treatment with organic solvents increases the dyeability of polyester in spite of a significant increase in crystallinity. Preswelling and plasticization of polyester fibres promote its physico-mechanical properties as well as dyeability characteristics. Plasticizing effects occur due to carrier attack on polyester fibres resulting in larger and more accessible channels and voids giving more porous fibre into which dye and water molecules can diffuse more rapidly and uniformly(5-13).

2.1.1 Treatment with alkali

Alkaline hydrolysis has been used since several years to modify the physical properties of polyester. It is well established that the alkaline hydrolysis of polyester fibers using aqueous sodium hydroxide is confined to the polymer surface (3, 4). When using sodium hydroxide in alcoholic media, the attack is found to be more severe and weight loss occurs more rapidly. Sodium alkoxides form alkyl ester end groups during the ester interchange reaction with polyester, resulting in a more rapid loss in weight than using aqueous sodium hydroxide. Alkali treatment of polyester fibers in glycolic media was also tried. Combined thermal and alkali treatment was carried out (14-21).

Theory of Alkali Hydrolysis: Two separate kinds of chain cleavage may occur. The first may involve the reaction of single hydroxide ion with the chain to produce a carboxylate anion and hydroxyl end groups of the shortened chain. This reaction does not produce a weight loss directly but may increase the weight due to the addition of hydroxide ion. The second reaction involves the attack of two hydroxide ions essentially simultaneously some distance apart along the same polymer chain backbone (22). In this case, a low molecular weight segment of the chain is removed as a single unit, resulting in a loss in weight from the polymer. Further reaction of these low molecular weight segments occur in liquid phase and do not contribute further to the weight loss of polyester, but it does contribute to depletion of the caustic concentration of the solution. Both of these reactions occur at the interface between the caustic solution (liquid phase), and the fibre surface (solid phase). At the moment of reaction, molecular solvation of the polymer must be minimal. Accordingly, this step of the reaction must be slow. Another kind of reaction is a scission of an alreadycleaved chain at the carbonyl group distal to the free end group of the chain. The free end groups consist of either terephthalate anion or the hydroxyl ethyl group. The reactions leading to elimination of the terephthalate dianion or ethylene glycol by "un- zippering" (i.e., the progressive reaction of the chain with hydroxide ion, beginning at a free end group) occur at locations that may be solvated, and hence can be expected to have rates that are faster than the rates of chain cleavage. Hydrolysis at the end group produces one molecule of either ethylene glycol or the terephthalate dianion for the reaction of each hydroxide ion. Consequently, this sort of reaction is first order in hydroxide concentration, while chain cleavage may be either first order or second order in hydroxide concentration. Neither the density, the intrinsic viscosity, nor the number of carboxyl end groups changes appreciably as compared to the untreated one after treatment with 10% solution of aqueous caustic at 60°C for 2h, as the reaction does not occur in either regions of low order or high order and the attack is at the ends of the polymer (23, 24). A theoretical model has been developed to describe the kinetics of polyester fiber dissolution in alkaline solutions. The model is based on the surface reaction concept. The rate of dissolution is taken as being proportional to the surface area of fibers and to the concentration of OH^- ions raised to a certain power (order of reaction: 0, 1, or 2). Integrated forms of rate laws are derived for all possible orders of dissolution reactions. According to the results, the weight loss is not a simple linear function of time, as usually accepted. The kinetics of the process is characterized by the rate constant, which is, for a given system, independent of the content of OH^-, fibers, and water in the system (25-28).

Alkali Treatment in Aqueous Medium: Hydrolysis of polyester fabrics with sodium hydroxide was found to improve the hydrophilicity and other comfort-related properties of fabrics. Effect of the reaction parameters such as treatment time, sodium hydroxide concentration, and temperature on the extent of hydrolysis is examined. The modified fabrics are evaluated for their physical, mechanical and physico-mechanical properties (29, 30). Improved moisture absorbency of polyester fibers can be achieved by introducing hydrophilic block copolymers (31). In addition, penetration of water into the interior of the fibers has not been clearly shown to improve perceived comfort. Surface modifications can have an effect on hand, permeability, and hydrophilicity. Polyester fibers are susceptible to the action of bases depending on their ionic character. Ionizable bases like caustic soda, caustic potash and lime water only affect the outer surface of polyester fibers. Primary, secondary bases and ammonia can diffuse into polyester fibre and attack in depth resulting in breaking of polyester chain molecules by amide formation (32). The action of strong base leads to cleavage of ester linkages on the fibre surfaces (33, 34). The result is the formation of terminal hydroxyl and carboxylate groups on the fibre surface. Hydrolysis is believed to increase the number of polar functional groups at the fibre surface.

Caustic treatment in organic solvent medium

Some methods are involved to overcome the low water absorption of polyester fibers to improve its dyeability. The compactness of the structure of polyester fibers minimizes the rate of the dye diffusion. To overcome this difficulty, swelling agents or high temperature treatments are used. Preswelling and plasticization of polyester fibers promote their physico-mechanical properties, moisture regain, as well as dyeability characteristics. Treatment of polyester fabric with ethanolic sodium hydroxide solution showed a significant improvement in the absorbency behavior of the polyester fabric, such as the decrease in wicking time and relative increase in the moisture regain percentage, as compared with the untreated mate (35-40). It can be noticed from the scanning electron micrographs (Figs 2.1 and 2.2) of the untreated and treated polyester fabric with sodium ethoxide that there is a change on the surface of the polyester fabric without whole-fiber damage. This may be due to the use of alkoxide solutions causing a reduction in the whole-fiber swelling and thus imparting beneficial effects on the fiber surface (38).

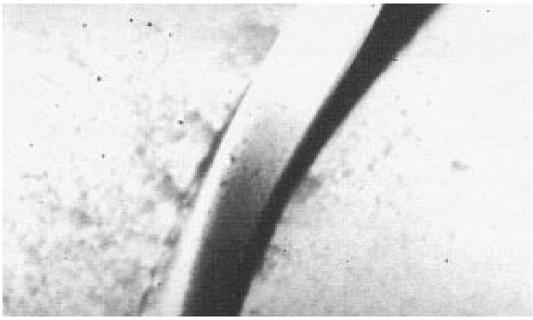

Fig. 2.1. SEM of untreated polyester fabric (16).

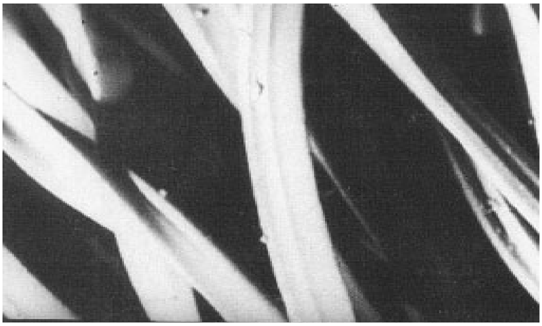

Fig. 2.2. SEM of treated polyester fabric with ethoxide (16).

The dyeability of the pretreated polyester fabric with disperse dye shows some progressive improvements with lowering the dyeing temperature and/or decreasing the time of dyeing. Ethoxide is found to be more effective in enhancing the dyeability of polyester fabric than either methoxide or propoxide. A decrease in the half dyeing time and an increase in the rate of dyeing of the pretreated polyester as compared with the untreated one are noticed (38). The influence of the variation of dye concentration in the solution on the extent of dyeing is studied by plotting rate of dyeing (tan α) against the dye concentration. This relation is illustrated in Fig. 2.3. The resultant curve is found to rise moderately at low dye concentration up to 0.2 g/L, and then the increase of tan α is slowed down by increasing the dye concentration up to 0.4 g/L for both dyed untreated and pretreated polyester fabric. The assumed equations of the curved line in Fig. 2.3 are:

$Y = -2.9369x^2 + 2.4799x$ for untreated polyester fabric;
$Y = -7.3587x^2 + 5.8675x$ for pretreated polyester with propoxide;
$Y = -7.8556x^2 + 6.4022x$ for pretreated polyester with ethoxide

Differentiating of the previous equations (y`) that represent the tangent of the curve at any point, it is found that $y`_{x=0.1}$ = 1.9 and $y`_{x=0.2}$ = 1.3 for the untreated sample, whereas the corresponding values for the pretreated sample with propoxide are 4.4 and 2.9 and that for the pretreated polyester with ethoxide are 4.8 and 3.2, respectively. These results indicate that the rate of tan α (y`) is found to decrease by increasing the dye concentration. This would enhance the evenness of the dyed pretreated polyester fabric despite increasing the rate of dyeing, as proved by the above-mentioned mathematical analysis (38).

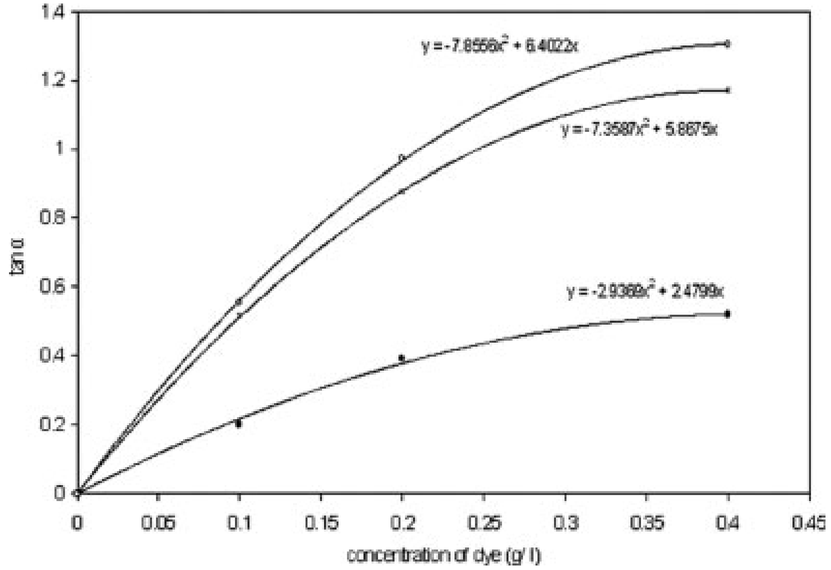

Fig. 2.3. Dependence of tan α value on the concentration of dye used in dyeing of polyester

Ethylene glycol is examined as an accelerating agent, but the improvement is not as good as methanol. Ethylene glycol and glycerin are used to replace the conventional water treatment of the alkaline solution. Both hydrolysis and glycolysis may shorten the treatment time and increase the hydrophilicity and dyeability of polyester (18). Treatment of polyester fibers with sodium hydroxide using propyl alcohol, propylene glycol and glycerol as a solvent was tried. The degradation rate in both propyl alcohol and propylene glycol is found to increase rapidly. The effect of treatment on some properties of polyester fabric are given through measurements of tensile strength, drapability, permeability, density gradient, crystallinity, moisture regain, and scanning electron microscopy. The use of this treatment can greatly shorten the treatment time to achieve results similar to those with the conventional aqueous system. The effect of concentration of sodium hydroxide in mono-, di- and tri-hydric alcohols on the weight loss of treated polyester fabric is illustrated in Fig. 2.4. The loss in weight resulted from treating of polyester fibres with sodium hydroxide in mono-hydric alcohol (propanol) more than di-hydric alcohol (propylene glycol) more than tri-hydric alcohol (glycerol). The loss in weight is about 10% in case of using propylene glycol corresponds to about 2% in case of glycerol, while using propanol as a medium of alkali hydrolysis leads to complete dissolving of polyester fibres after about 45 min at 65°C with 0.5 M sodium hydroxide (19).

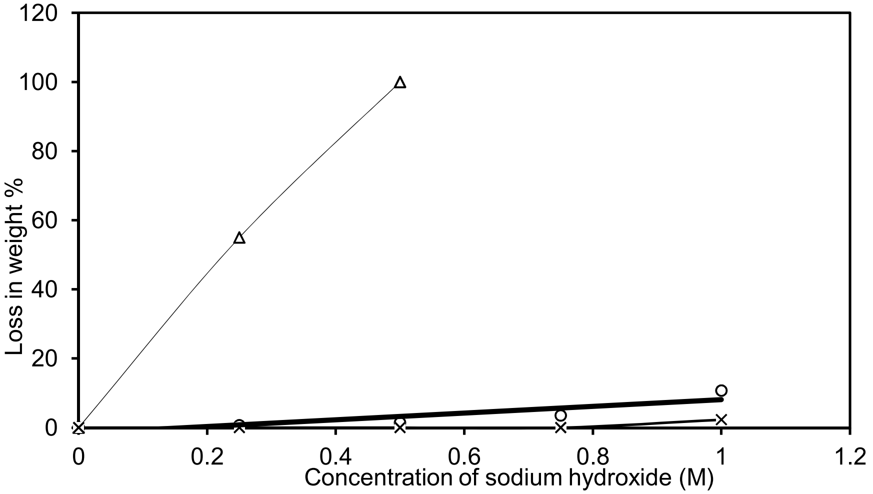

Fig. 2.4. Concentration of sodium hydroxide/ loss in weight of PET fibers, Treatment: 65°C, 45 min, L. R. 1: 25, x-x glycerol, o-o propylene glycol, Δ-Δ propanol

Combined thermal and alkali treatment

In textile processing, polyester fabric is usually heat set to improve dimensional stability and prevent creases during wet processing and handling. Heat setting of polyester fibers is processed to make a change in the fine structure and consequently dyeability and chemical reactivity (39- 49). The effect of heat setting temperature on the hydrazinolysis of polyester fibers was studied. Polyester partially oriented yarn (POY) is heat set at 100° to 220°C in a fixed state and then treated with hydrazine. Relatively smaller amines, such as hydrazine, swell the less ordered regions of the fibre and attack ester linkages in the molecular chain effectively. The weight loss of thermally treated POY is found to be minimum at 120°C and increased with increasing treatment temperature up to 220°C , while it is recorded to be 160°C for regular polyester because of the difference in the fine structure of the fibers. Hydrazinolysis with 40% aqueous solution of hydrazine monohydrate at 60°C for 120 min incorporates a hydrazide group at the end of the fibre's molecular chain. Hydrazinolysis builds inactive sites for adsorption acid dyes by modified polyester fibers. The crystallinity of the heat-set POY fibers increases with hydrazinolysis as well as the heat setting temperature. Scanning electron microscopy (SEM) photographs of the hydrolyzed POY fibers show appearance of cracks on the fibre surface which differs with variation of heat setting temperature and becomes deeper in the inner regions. Polyester fibre is heat set at 100°-220° C and then hydrolyzed with 10 % aqueous sodium hydroxide solution at 90 °C for 1 and 2h. The disperse dye exhaustion of the heat set/ alkali hydrolyzed polyester is found to decrease with increasing the temperature up to 180 °C. The amorphous/ crystalline ratios are the controlled parameters in dyeing of PET fibre with disperse dye and consequently the applied method in thermal treatment (20). Other attempts were carried out to improve the dyeability of polyester fabric with disperse dyes at the boil without using carriers or using HT/HP dyeing technique. Some alkyl and/or alkylol amines as well as hydrazine hydrate treatments are carried out by padding technique at room temperature prior subjecting it to the thermal treatment in air and slack conditions. Methylamine, ethylamine, ethanolamine and hydrazine hydrate (5-20 % v/v) solutions are used in this study as pretreatment reagents by padding technique then squeezed up to 100 % pick up, followed by thermal treatment at 160ºC for 15 min in air under slack conditions. The pretreated fabric is dyed at the boil with disperse dye without using carriers. Treatment of polyester fabric with hydrazine hydrate before thermal treatment led to high enhancement of the fibre dyeability with disperse dyes as well as decreasing the setting temperature of polyester to 160ºC. Applying the padding technique in treatment of PET may decrease the consumption of chemicals in the dyeing process as well as reducing the pollution impacts (40, 48). The effect of pretreatment of polyester fibers with some amines such as methylamine, ethylamine and ethanolamine followed by thermal treatment is shown in Table 2.1 (40).

PET sample	Color intensity (K/S)					
	0	5%	10%	15%	20%	30%
-untreated	4.9	-	-	-	-	-
-thermally treated	6.1	-	-	-	-	-
-treated with ethanolamine		7.0	9.2	10.0	11.6	-
-treated with methylamine		6.1	6.3	6.5	7.1	8.0
-treated with ethylamine		7.2	7.9	8.3	8.9	9.8

Treatment: 160ºC, 15 min, Dyeing: 1% (owf) C.I. Disperse Red 60, 100 ºC, pH 4.5, L.R. 1:100.

Table 2.1. Dyeability of pretreated polyester fabric with various concentrations of some amines.

The depth of disperse dye inside the interior structure of pretreated PET fabrics increases by the effect of steam and hydrazine hydrate treatments (Table 2.2). Polyester fabrics pretreated with steam have lower Tg values. The chemical/thermal pretreatment of polyester fabrics with hydrazine hydrate causes a decrease in T_g. The glass transition temperatures of pretreated polyester fabric with ethanolamine, ethylene glycol and 2-hydroxy-4-methoxybenzophenone are reported to be 63º, 68 º and 63º C respectively (40).

Polyester sample	Dye depth in cross section %	T_g °C
-untreated	38.4	72
-hydrate hydrazine treated	46.5	70
-Steam treated	39.5	69.0

Table 2.2. Dye depth and glass transition temperature of polyester fabric.

2.1.2 Enzymatic hydrolysis

Application of biotechnology to textile finishing is an example of more environmentally compatible processes. Enzymes are produced from fermentation of microorganisms (renewable resources) and are biodegradable. Amylases and cellulases hydrolyze starch and cellulose respectively and can be used in desizing of textiles. Hydrolases are capable of hydrolyzing fatty acids or carboxylic esters. Lipases have been reported to biodegrade polyesters. The insoluble nature of polyester fibers in an aqueous medium may limit enzymatic hydrolysis to the surface, thus improving the fibre wettability. The water wetting contact angle of the untreated polyester is evaluated as 75.8º. Polyester fabrics are immersed in the buffer solution (organic and inorganic) at 35ºC for 1h. The organic buffer, tris (hydroxyl methyl)-aminomethane, lowers the wetting contact angle of polyester fabric to

67.5°. The inorganic buffer, sodium phosphate, increases the contact angle to 81.9°. Any improvement in surface wetting can be due to the hydrolyzing action of the lipase. Some types of lipases are found to decrease the water wetting contact angle to 57.4° without significant change in breaking tenacity and strain of pretreated polyester fabric. The lipase hydrolysis resulted in better wetting surfaces than aqueous alkaline hydrolysis. The improved wettability due to enzyme treatment is accompanied by full strength retention compared to the significant reduced strength and mass from alkaline hydrolysis. The water contact angle is found to decrease from 75.8° to about 52°. As the contact angle decreases, the wettability increases and consequently the dyeability is improved (50-56).

2.1.3 Other trends in dyeing

Organic Solvents: The solvent treatment of synthetic fibres influences strongly dye-diffusion characteristics as well as the equilibrium dye-uptake. Interaction of solvents with synthetic fibres can affect fibre swellability, segmental mobility, irreversible structural changes, shrinkage and shifts in glass-transition temperature. Small amounts of organic solvents such as alcohols were added in the aqueous dyeing baths of synthetic and natural fibres to assist the dyeing process (5-13). The effect of plasticizing of benzyl alcohol /chloroform (6: 4) mixture on polyester is presumed to increase the degree of crystallinity and the perfection of the apparent size of the crystallites. This effect might occur by reducing the forces of entanglement points between the macromolecular chains. Chain segments thereby acquired relatively sufficient free movement into a crystal arrangement. Part of the amorphous region remains intact and tends slowly to crystallize at an extremely slow rate. The solvent molecules were expelled from the crystal, but still persist to influence the amorphous portion, which exhibited some mobility. Change in the tendency of the modified polyester to uptake disperse dyestuff was also noticed. Polyester structure modification due to binary solvent interaction showed some promising improvement in the accessibility of the substrate to dyeing (57, 58). Treatments of polyester fibres were performed with non-hydrogen bonded solvents vis. 1, 4-dioxan, N, N'-dimethylformamide, cyclohexanone and with hydrogen-bonded reagents such as formic and monochloroacetic acids (59). The non-hydrogen bonded-type of solvents were found to be more efficient in improving the colour intensity than the pretreatment with some hydrogen-bonded solvents. Adsorption behaviour of these modified polyester fibres is examined via studying the nature of the dye, maximum adsorption temperature, and dipole moment of the dye molecules (60-64).

Acids: Moderate treatment of polyester and Quiana polyamide fibers with sulfuric acid solution is studied (65). Significant improvements in the dyeabilities of both fibers with cationic dyes below the boiling point, without appreciable reduction of the fabric dimension are attained. Kinetic characterization of the dyeing process reveals that the time of half dyeing decreased pronouncedly in case of the modified substrates and, consequently, the specific dyeing rate constant increases. A rapid decrease in the relative diffusion coefficient of the sulfuric acid pretreated substrates is observed upon increasing the temperature of dyeing. The dye affinities increase and the corresponding heats of dyeing practically decrease for both modified fibers. The kinetic reactions between both polyester and Quiana polyamide fibers and sulfuric acid were studied (66). The moisture regain and dye uptake of treated polyester increased (67-70).

Super Critical CO_2: The dyeing of polyester textile in supercritical carbon dioxide is investigated experimentally. The influence of temperature and density of the SC-CO_2 on the process was studied in the ranges 85—125°C and 400—550 kg/m^3. The dye saturation concentration in the polyester increased and the distribution coefficient decreased with temperature, the latter showing a logarithmic dependence on the reciprocal of temperature. Increasing the fluid density led to an increasing saturation concentration and a decreasing distribution coefficient. When the right temperature and solvent density were chosen for the supercritical process, the same dye concentration could be attained as in aqueous dyeing. The experiments showed that the dyeing was exothermic, with a negative change of entropy. The thermodynamic characteristics of supercritical and aqueous dyeing were concluded to be roughly the same, with similar saturation concentrations, thermodynamic affinities and heats and entropies of dyeing (71). One-bath dyeing of polyester/cotton blends with reactive disperse dyes is investigated using supercritical carbon dioxide (SC-CO_2) as a solvent in the range of 353 to 393° K and 10 to 20 MPa. The dyeing behavior is compared with the thermosol dyeing method using the same dye. Samples are subjected to a color fastness test and colorimetric measurements. Good color intensity and wash fastness are obtained by the SC-CO_2 dyeing method at 393 K and 20 MPa. The color fastness properties of fabrics dyed in SC-CO_2 are superior to those of fabrics dyed by the thermosol dyeing method (72). Supercritical carbon dioxide is a suitable solvent for dyeing even for the most sensitive textiles up to 140°C. The treatment time at 160°C should not be longer than 1 hour (73). Supercritical dyeing can be an interesting alternative to traditional dyeing due to the unquestionable advantage of the use of a clean solvent that can be easily recovered and separated from the excess dye at the end of the process. Set up a pilot plant of supercritical dyeing could be performed with yarn bobbins for polyester textiles (74).

Dyeing with Carriers: Carrier dyeing is a method of dyeing polyester materials that is used when necessary. Although usage of carriers in dyeing enables the dyeing of polyester materials at atmospheric pressure, the undesirable properties of the carriers are drawbacks. Disperse dyes are classified under different energy levels and the dyeing methods and color and fastness properties of dyed materials are associated with this classification. Carriers can be used when dyeing at higher temperatures than 100°C to promote the leveling of the more difficult disperse dyes (75, 76).

Dye Absorption after Thermal Treatment: Thermal treatment of polyester fibers can lead to variation in the absorption behavior as appeared in its dyeing properties, iodine sorption as well as swellability. The rate of dyeing of polyester is dependent on temperature, time and thermal history of the polyester fibers. The dye uptake of disperse dyes by thermally- set polyester initially decreases as the temperature of pre-heating is raised. At higher temperatures the dye uptake increases with temperature and can be greater than that of the untreated polyester fibers depending also on the dye molecule (77). The variations in dyeing properties of polyester fibers in terms of structure is described using two- phase theory of structure involving crystalline and amorphous regions. The competition between crystallization (with reduction of rate of dyeing) and disorientation of the amorphous region (leading to increased dye uptake) explains the variations of dyeing behavior of polyester fibers with heat setting. The effect of heat setting at various temperatures and draw ratios on the diffusion of disperse dyes into polyester fibers is studied in relation to the measurements of the dynamic loss modulus of the fibers. The diffusion is controlled by the chain mobility of polymer as indicated by measuring the glass transition temperature (T_g). The diffusivity and dye saturation values depend on the difference between the dyeing temperatures and glass–transition temperature. The dye molecules penetrate the polymeric fiber structure upon movement of the chain segments producing spaces suitable to the size of the dye molecules. The larger the dye molecule, the higher might be the dyeing temperature to permit the formation of spaces of sufficient size by the segmental motion of chains (78, 79). The physical characteristics of polyester fibers such as solubility, dyeability and iodine absorption are related to the orientation and crystallinity of fibers. The absorption of iodine by polyester fibers decreases on increasing the thermosetting temperature from 180° to 220° C. Increasing the applied tension on the fiber during thermal treatment hinders the iodine absorption due to better microstructure orientation (80- 82). The dyeability of the micro-denier polyester fabric is compared with the normal denier polyester. The rate of dyeing is found to be higher in the case of micro denier polyester. The fastness property has not been influenced by the rate of heating during dyeing with disperse dyes (83, 84).

2.1.4 Plasma treatment

Polyester (PET) swatches are treated with electrical discharge plasma of a reactive atmosphere (tetrachlorosilane) to graft chlorosilane groups, subsequently hydrolyzed to very hydrophilic hydroxysilane groups. The results show that the surface parameters are considerably modified by the treatment (85). Low-pressure glow discharges are efficient in generating uniform plasmas. They have been applied in the surface modification of a variety of materials. Through the discharge of mixture of argon and oxygen, Ar-O_2 (10:1), polyester fabric is continuously modified. The results reveal that the dyeability of the polyester fabric is dramatically improved. The improvement of dyeability is attributed to the introduction of functional groups on the surface during the treatment (86). Polyester fabrics are treated with radio-frequency plasma (in air) at different power levels and time intervals, and moisture content and surface resistivity behavior. The surface resistivity of polyester is dramatically reduced after plasma treatment. The fabrics are subjected to further plasma initiated grafting of acrylamide and acrylonitrile. Polyester has a moisture content of up to 3% after plasma initiated grafting. The surface resistivity of polyester is drastically lowered after grafting (87). Polyester fabrics are dyeable and printable with disperse dyes. Since the dyeability of PET fabric has been related to hydrophilicity and/or increase of micro roughness and surface area therefore, plasma treatment can improve the colouration of fibres (88). The printability of treated fabric with plasma/Al_2O_3 at 1.3 watt for 2 min was tried. The colour intensity of treated sample increased from 13.4 for untreated sample to 15.2 for treated one. The washing fastness properties of coloured treated samples are almost the same as the untreated one (4-5).

2.1.5 Microwave irradiation

Microwave drying is substantially more effective than convection oven drying. Microwave exposure has no effect on the elongation of polyester (89). Aliphatic polyesters have been studied mainly for medical applications. High energy radiation induced processing is an established technique that is used in polymer science. Radiation is used to initiate radical polymerizations and for modifications such as degradation, cross-linking, and graft-copolymerization (90).

2.2 Polyamide

Prospects of low waste or clean technology in textile dyeing can be realized by preserving the quality of both fibres and dyeing during processing. To meet new demands for energy conservation, high production rates (1, 2) and strengthening the dye-fibre bond formation, various redox systems were incorporated in the dyebath vicinity. Redox systems have been utilized to induce covalent fixation of dye moieties on proteinic and polyamide fibres. Radical formation is usually the consequence of a bimolecular reaction between oxidant and reductant. Its rate can be adjusted almost by suitable variation of reactant concentration. The organic substrate may participate in a two-electron transfer process without radical formation (1-5). Introduction of glyoxal- hydrogen peroxide as a redox system to accelerate the polyamide dyeability with acid dyes is performed. An increase in colour intensity of the substrate dyed in the presence of the redox system as well as rapid exhaustion of the dyebath was observed. Time of half dyeing, specific dyeing rate constant and diffusion coefficient show some advancement as compared with the untreated polyamide. The activation energy of dyeing of the pretreated substrate decreased (1). Addition of 2 % alcohols to the pretreatment bath reveals nearly complete exhaustion of the dyebath after 30 min. at 70°C. The alcohol effectiveness can be ordered methanol > ethanol > propanol. Complete dye exhaustion at lower dyeing temperature and time can save energy, time as well as minimize pollution effects. Half dyeing time at 60ºC decreased by the applied treatment from 13.5 min for untreated sample to 2.5 min for glyoxal pretreated sample in methanol/water (2:98), as compared with the given $t_{½}$ at 80ºC which decreased from 6 min to 1 min. Both dyeing rate constant (k`) and diffusion coefficient (D) at 60ºC and 80ºC have increased by the same pretreatment (Table 2.3).

Type of Sample	$t_{1/2}$ (min)		K'		D (cm ^{2} sec $^{-1}$) x10^{-4}	
	60ºC	80ºC	60ºC	80ºC	60ºC	80ºC
1- Untreated	13.5	6	0.01	0.0245	0.176	0.291
2-Pretreated with glyoxal in:						
-propanol/ water	5.0	1.0	0.0283	0.0632	0.311	0.422
-ethanol/ water	3.5	1.0	0.0338	0.0632	0.328	0.422
-methanol/ water	2.5	1.0	0.04	0.0632	0.345	0.422

Treatment: 0.5 g glyoxal/ 100g fibre , solvent/ water ratio 2:98 , 50ºC, 1h.,Dyeing: 1% (o.w.f.) C. I. Acid Red 41, pH 4.5, liq ratio 1: 100, 0.3 % H_2O_2

Table 2.3. Half dyeing time ($t_{½}$), dyeing rate constant (K'), and diffusion coefficient (D) of polyamide 6 fibres dyed with C. I. Acid Red 41.

The activation energy decreased from 41.5 kJ/g mol for untreated one to 24.9 kJ/g mol for pretreated polyamide 6 fabric with glyoxal/H_2O_2 in methanol/water (Table 2.4). The decrease in the half dyeing time and the activation energy and the increase in dyeing rate constant and diffusion coefficient led to saving in time. The colour intensity was improved upon applying continuous dyeing technique.

Samples		E (kJ/ g mol)
1- Untreated		41.5
2- Pretreated with glyoxal in:	methanol / water	24.9
	ethanol / water	26.9
	propanol / water	26.9

Treatment: 0.5 g glyoxal / 100 g fibre, solvent / water ratio 2: 98, 50ºC, 1h, Dyeing: 1 % (o.w. f.) C. I. Acid Red 41, pH 4.5, liq ratio 1: 100, 0.3 % H_2O_2

Table 2.4. Activation energy (E) of dyeing for pretreated polyamide 6 fibres

Techno-economic estimation of dyeing PA6 fabric

The cost of energy is continuously increasing and is becoming a significant share of total cost of processing textiles. Lowering the dyeing temperature brings down the energy requirements which can be done by employing some dyebath additives or by giving some pretreatment to the material to be dyed, during which improvement of the dyeing behaviour of the fibre can be achieved (6). Pooling of techno-economic knowledge across research and application would improve the productivity when faced by lower cost competition (7). The intention is to achieve lower machinery cost, less chemicals and energy consumption, easier wash-off, better reproducibility and rapid as well as easier technical changes for higher value-added products. Attempts are undertaken to perform a comparative techno-economic investigation of two dyeing methods of polyamide fabrics; a conventional dyeing method normally as applied in industry versus a proposed modified one which depends on the usefulness of chemical pretreatment of polyamide fabric with acetaldehyde or a redox system at ambient conditions. The economic aspects of the dyeing processes are pursued, where the variables are brought together, to determine the production costs. The pretreatment of polyamide 6 with either reagent reveals some improvements in dyeing characteristics. This is reflected on the possibility of saving considerable amount of energy, shortening the time of dyeing, increasing the production rate and so lowering the total cost of the dyeing process as well as reducing the environmental impacts (8). Conventional exhaust dyeing of PA-6 fabric was performed at nearly the boil (9). Pretreated PA-6 wet fabrics with either acetaldhyde or glyoxal/H_2O_2 were exhaust dyed at different temperatures (60°, 70˚ and 80°C). The pH value of the dyeing bath was adjusted at 4.5 by adding acetic acid (about 1 ml/ litre) and using a liq. ratio of 1:10 (1, 10). The process is wet on wet. Pretreated PA-6 fabrics with acetaldehyde had exhausted the same amount attained by conventional dyeing method (0.92g dye/100g fibre) after about 45 min at 80°C (10). Pretreated PA-6 fabric with the redox system exhausts almost completely the dye from the bath at different temperatures (60°, 70° and 80°C) after about 40, 20 and 10 min respectively (8).

Cost of chemicals and water in conventional and modified dyeing method

Table 2.5 illustrates comparatively the cost of chemicals, dyes and water consumed in the investigated dyeing processes. PA-6 fabric pretreated with glyoxal/H_2O_2 attained the lowest cost and on the other hand acetaldehyde pretreated PA-6 fabric is relatively the highest. Specifically, this held true in the element of water consumption.

Dyeing Process	Dye	Chemicals	Water	Total
Conventional dyeing at the boil.	2.0	0.78	0.025	2.805
Dyeing of pretreated fibre with acetaldehyde.	2.0	1.555	0.039	3.594
Dyeing of pretreated fibre with (glyoxal/ H_2O_2).	1.84	0.837	0.015	2.692

Table 2.5. The costs of chemicals and water consumed (LE/kg fabric)

Steam consumption

The amount of steam required to offer necessary heat to the wet processes can be estimated from the following equation (11):

$$Q=W.\ Cp.\Delta t$$

Where Q is the heat required, Cp is the specific heat of matter to be warmed up, W is the weight of the material to be warmed up; and Δt is the temperature difference involved, An initial temperature of 20°C is assumed for water. The heat loss by radiation and by other means can be calculated by assuming that the total heat is twice the heat required for heating up (12). Table 2.6 shows the cost of heat energy per kg of fabric. It is clear that the glyoxal / H_2O_2 pretreated fabric attained the lowest value.

Dyeing process		Energy/cycle Kcal	Cost/cycle	Cost/kg
Conventional dyeing Method		497280	29.8368	0.0995
Pretreated with acetaldehyde.		372960	22.3776	0.0746
Pretreated with glyoxal/H_2O_2				
and dyed at:	60°C	154716	9.283	0.031
	70°C	162876	9.772	0.0325
	80°C	171036	10.262	0.034

Assuming that 10^6 Kcal energy = 60 LE

Table 2.6. Cost of energy consumption for the different dyeing process in (LE)

Fixed costs

In addition to the expenditure on dyes, chemicals, water and energy, the layout on the equipment and operating personnel carrying out the dyeing process have to be considered, besides the general costs and overheads. The general costs have to be a common item not to be included in the calculations.

Machinery

The suggested dyeing processes have to be compared with the conventional one. The price of Jet machine is considered as one million Egyptian pounds. For suggestion of dyeing methods, a stainless steel tank of $4m^3$ is required for preparation and storing the pretreatment solutions of either acetaldehyde or glyoxal. A stainless steel pump (5 Hp) is also required. The total cost of the pump and the storage tank is assumed to be about 10.000 LE, supposing the use of two Jet machines in this study.

Depreciation for 10 years as: $\frac{1}{10} \text{ X } \frac{\text{cost of machine}}{\text{production rate (kg/year)}}$

Interest =10 % of the capital cost.
Repairs = 5 % of the capital cost.
Labour /kg fabric = (Man hour x no. of hours/shift x no. of shifts/day x no. of labours/shift) ÷ (no. of batches/day x Production rate/ batch)

Table 2.7 represents the total fixed operating costs/kg fabric for all dyeing processes in this study. It can be noticed that the investigated pretreatments led to decreasing the operating costs as well as increasing the production rate.

Table 2.8 illustrates the total production cost/kg fabric. Glyoxal/H_2O_2 pretreated fabric attained a lower production cost than both conventional dyeing method and that pretreated fabric with acetaldehyde. It can be noticed that pretreatment of PA-6 fabric with redox system (glyoxal/H_2O_2) led to a decrease in the total production cost/kg fabric in the range of 7-11% as well as increasing the production rate/year and decreasing the pollution impacts without impairing the tensile properties of the fibre.

Dyeing process	Depreciation	Interest	Repairs	Labour	Total
Conventional dyeing Method	0.278	0.278	0.139	0.048	0.743
Pretreated with acetaldehyde	0.255	0.255	0.127	0.044	0.681
Pretreated with glyoxal/H_2O_2 and					
dyed at 60°C	0.255	0.255	0.127	0.044	0.681
70°C	0.234	0.234	0.117	0.04	0.625
80°C	0.2	0.2	0.1	0.034	0.534

Table 2.7. Fixed operating costs in LE/kg fabric

Dyeing process	Variable cost LE/kg		Fixed cost	Total
	Chemicals	Energy	LE/kg	LE/kg
Conventional dyeing Method	2.805	0.0995	0.743	3.65
Pretreated with acetaldhyde	3.594	0.0746	0.681	4.35
Pretreated with glyoxal/ H_2O_2 and dyed at				
60°C	2.692	0.031	0.681	3.4
70°C	2.692	0.0325	0.625	3.35
80°C	2.692	0.034	0.534	3.26

Table 2.8. Production costs in LE/kg fabric

2.3 Cellulose acetate

Dyeing acetate fibers is reviewed thoroughly to show some new possibilities of improving its dyeability with disperse, azoic, acid and cationic dyes. The fastness, techniques and conditions of dyeing, dye-absorption, fixation, leveling and vapor phase dyeing of acetate fibers are also reported (1-3).

Dyeing characteristics

Acetate fiber was the first man-made fiber which could not be dyed with conventional dyes used for cotton, wool and silk (4). Dyeing of acetate fibers by the method used for cellulosic fiber was found to be difficult because of the saponification possibility of acetate groups in alkalies. When dyeing was carried out at room temperature, no swelling of acetate fibers took place; consequently the diffusion of the dye component into the fiber was hindered. Dyeing behavior of acetate fiber was found to be very similar to that of synthetic fibers, particularly the affinity for water-insoluble dyes. Acetate fiber was dyed with selected types of cationic and acid dyes. The former produced a brilliant shade, while the latter produced a medium shade. Disperse dyes are generally suitable. Developing dyes of deep, wet-fast shades can be applied to acetate fibers. Pigment dyes were used only in exceptional cases and only for only pale shades. The effect of aromatic amines on dyeing intensity of triacetate fibers was related to change in the fibers' structure, determined by the interaction of amines with cellulose triacetate fiber (2, 5).

Disperse dyes: The migration of disperse dyes in the dyeing of triacetate fibers was determined by dissolving the fibers in either chloroform or an acetone-water mixture (4:1) (6, 7). The influences of temperature, liquor ratio, carrier, and acetyl value were determined.

Increasing the temperature accelerated the migration, giving higher values for the desorption constants than for the absorption constants. Increasing the liquor ratio was more favorable for the dyes having a higher solubility in water. Use of carriers promoted the migration because of the increase in dye solubility. When the acetyl value decreased, the rate of migration was found to increase (2, 8). Acetate fibers were dyed with disperse dyes in tetrachloroethylene in presence of water at a temperature above that of the tetrachloroethylene-water azeotropic mixture under pressure for 30 min. to give fast deep shade. The presence of tetrachloroethylene as a carrier gave fast shade at higher yields than in the presence of aromatic chlorinated hydrocarbons (9-12). Cellulose triacetate was exhaust dyed at 50°-75° in an aqueous bath containing disperse dye, 10-50% methylene chloride or methylene bromide, and a dispersing agent. The result was a level dyeing with good penetration and excellent fastness (13-15). Dyeing acetate yarns with dyeing liquor exposed to ultrasonic waves increased the dye absorption. The dyeing liquor was exposed to ultrasonic waves by passing the liquor through an ultrasonic generator. Acetate yarns were immersed in the resulting liquor for 20 min. at 85 °C to give dyed yarns with the amount of the dye absorbed 50% greater than that obtained without passing the liquor through the ultrasonic generator. In the dyeing of triacetate fibers with disperse dyes in organic solvents; the affinity and the heat of dyeing were much smaller than those in an aqueous system. The diffusion coefficients varied with different fiber solvent combinations (13- 17).

Acid dyes: Acid dyes are used for dyeing acetate, nylon, and acrylic fibers. These dyes were originated from basic dye acidification and have a complete color range. The light fastness ratings were generally very good and not affected by gas fading (5). The impregnation of acetate fabrics with liquors containing an acid dye and storing the fabric in ammonia vapor to give dyed fabrics with improved wash fastness was studied. An acetate taffeta fabric was immersed in a bath containing 20% g/l acid dye and 50 g/l thiourea to 50% pick up, dried, and stored in water vapor containing 28% ammonia for 4 h at room temperature, washed, and dried to give dyed fabric with wash fastness rating (2, 18).

Direct dye: Acetate samples treated with methylamine, dimethylamine and trimethylamine and dyed with direct dye gave satisfactory results. The maximum color intensity was obtained in case of the treatment with diethylamine as compared with the relatively lower color intensities for ethylamine and triethylamine. This can be explained on the basis of higher basicity of diethylamine which led to a higher hydrolyzing effect changing the acetyl groups to hydroxyl groups (1).

In dyeing processes, the use of cyclodextrin (CD) can improve the dye uptake of CA because CD increases the tendency of disperse dye solubilization in aqueous solutions. CD is characterized by a hydrophobic internal cavity and by a hydrophilic exterior. This can give different inclusions of dye molecules depending on the size of the cavity. The formation of complexes between the dye molecules and CD has been thoroughly described and can be used as an alternative to dyebath additives. The structure of CD shows an ability of inclusion of complexes with compounds having a molecular size complementary to the cavity dimensions. No covalent bond is established between the dye molecules as a guest in the CD host molecules. Consequently, the dissociation–association equilibrium in solution becomes one of the characteristic features of the guest/host association. One of the modification possibilities of the fiber surface to alter its properties is attained by a successful binding of CD to the fibers (19). CA samples of known weight were treated with both CD and MCT-CD by a padding technique. The samples were then subjected to the dyeing process. A systematic study on the influence of CD treatments on the dyeing of CA fabric with disperse dye was performed to optimize new possibilities to dye CA fabric at a lower temperature than the conventional dyeing one without using additives as well as enhancing the fastness properties and increasing the dye penetration into the interior of the fiber structure to ensure homogeneity and leveling of the dye. Disperse dyes are hydrophobic compounds, it was anticipated that CD could serve as host sites if incorporated into the molecular structure of a warp size. CD treatment offered a significant dyeability effect on CA than MCT-CD. The color intensity of the dyed CA was found to depend on the CD concentration. The differential thermal analysis data of the untreated CA and that one pretreated with CD is given in Table 2.9. A slight decrease in glass transition temperature (Tg), crystallinity temperature (Tc), and melting temperature (Tm) was observed. CD treatment of CA fabric imparts no effect on the thermal properties of CA.

CA Sample	Tg (ºC)	Tc (ºC)	Tm (ºC)
Untreated	64.5	168.8	260
Pretreated with CD	62.1	163.0	259

Treatment: padding, pick up 100%, 0.2 g CD/100 g fiber, pH 8.0, 150ºC, 3 min.

Table 2.9. Differential Thermal Analysis of Untreated and Pretreated CA Fabric With CD

Scanning electron micrographs (SEM) of the untreated and pretreated CA fabric with CD are depicted in Figure 2.5(a, b). Some changes on the surface features of the pretreated CA were observed. The mean depth of the disperse dye inside the pretreated CA fiber was found to be twice more than that of the dyed untreated one. The % mean depth of dye into the dyed fiber is ranged from 60 to74% for CD-treated CA compared to 20–21% for untreated one. A mean dye depth <30% inside the fiber is defined as ring dyeing.

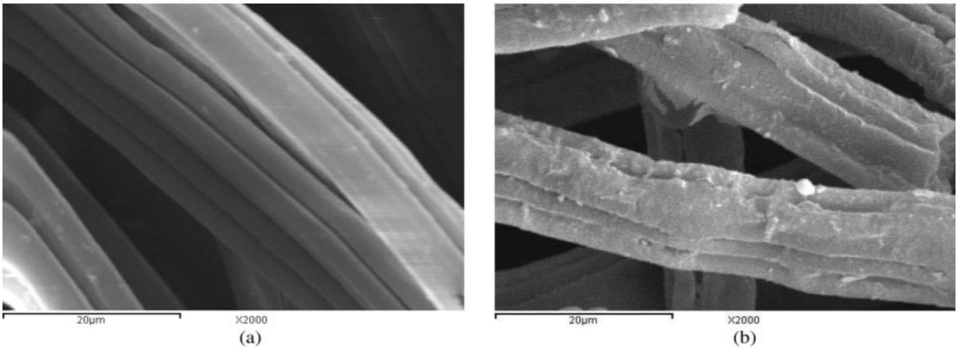

Fig. 2.5. (a) SEM of untreated CA fabric. (b) SEM of treated CA fabric with CD.

Dyeing behaviour of laser treated fabric: The excimer UV-laser treatment can improve the dyeability of polyester fibres. The maximum colour intensity of untreated one could be attained at shorter time. Also, the half dyeing time of laser treated sample decreases from about10min for untreated one to 7 min. The main factor which explains the improvement of the dyeability of the irradiated CA fabric is the increase of the overall surface area as a result of the morphological modification induced by excimer laser. The mean depth % of dye into the dyed treated CA sample is that 43.9 % compared to 20.2% for untreated one (20).

3. References

3.1 References - Proteinic fibres

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15

Effect of Plasma on Dyeability of Fabrics

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1. Introduction

The unique physical and chemical characteristics of the plasma environment make it attractive for textile processing. Plasma is an ionized gas, i.e. it contains electrons, ions and neutral atoms and/or molecules. However, not all of the ionized gases used in textile processing will exhibit the properties associated with plasmas, mainly because of their low charge state densities compared to the neutral gas density or are produced by transient phenomena.

Plasma activation is being used in several fabric and nonwoven applications in the textile industry. (Pane *et al.*, 2003)

There are many industrial applications of thin film deposition by plasma sputtering or plasma polymerization in the technical textile and nonwoven industry. Roughly, the coatings deposited in those industries can be categorized under either (permanently) hydrophilic coatings or hydrophobic/oleophilic coatings. In most cases, the deposited coatings give rise to unique products that are difficult or even impossible to produce using other technologies.

The textile market is trying to make deep, dark colours and this is not easy to achieve. (Svensson, 2004)

One way to do this is to reduce the specular component of reflection of the fabric surface after dyeing. A plasma etching leads to a controlled nano or micro-roughness, increasing diffuse reflectance and minimizing the specular component. In consequence, the dyed fabric will have an intense darker colour after plasma etching.

In various research programs, it has been shown that pick-up of dyestuff can be strongly improved after plasma pre-treatment of natural and synthetic fibre fabrics.

Polypropylene fibers have such excellent properties as low specific weight (0.91 g/cm^3 only), high strength (42-53 CN/ Tex) and good resistance to acids and alkalis, and they also possess good thermal resistance and antibacterial properties. The poor wettability (only 0.05 % at 20 ^{o}C) and dyeability have, however, limited the application of these fibers in garments and other industries (Huang et al, 2006). It is of importance to improve the wet ability and dyeability of PP fabrics for many applications. Although chemical modification of the fibers has been somewhat successful in improving hydrophilic and antistatic properties, there are environmental concerns related to the disposal of chemical after treatment. Plasma treatment, as a clean, dry and environmental friendly physical technique, opens up a new possibility in this field. So in this chapter we focused on investigation about the improving the dye and printability of PP fabrics in section 2 to 4.

In the other point of view, natural dyes are generally understood to be colorants (dyes and pigments) that are obtained from animal or vegetable matter without chemical processing. They are mainly mordant dyes, although some natural vat, solvent, pigment, direct and acid types are known. In recent years, concern for the environment has created an increasing interest in natural dyes. Conventional wisdom leads to the belief that natural dyes are friendlier to the environment than their synthetic counterparts, although the issue is not necessarily quite so straightforward. The natural dyeability of wool fabrics is investigated in section 5-6. In textile processing, the interactions of the plasma generated species with and on the surfaces in contact with the plasma are of great importance and these are discussed in this chapter, respectively.

2. Effect of using cold plasma on dyeing properties of polypropylene fabrics

The dye-ability of hydrophobic fabrics, such as the PP fabrics is very poor. (Chun Liu et al, 2006) It is known that introducing hydrophilic sites on the hydrophobic fabrics can improve the dyeability of these fibers. Plasma modifications resulting in unsaturated bonds and/ or free radicals on the surface of the fabrics have a significant influence on the overall surface changes and consequently on dyeability (Shahidi et al, 2007). PP fabrics have been treated with Low Temperature Plasma (LTP) of oxygen and nitrogen for different period of times, different condition of power and pressure. The best condition was treatment for 7 min at the power of 120 watt and pressure of 5×10^{-2} torr. As it can be seen in Figures 1 to 4, the reflection factors of dyed LTP treated samples were less than dyed untreated sample. The results show that the O_2 and N_2 plasma treatments are effective in increasing the dye exhaustion of PP with anionic, cationic, disperse and direct dyes. Furthermore, the colors achieved much more brilliant shades with the LTP treatment. The results show that, the average of K/S between wavelength of 350-500 was first increased with prolonged LTP exposure time, reached a maximum generally at about 7 min, and then decreased since by increasing time of exposure some Al particles are deposited on the surface of the samples. (Shahidi et al, 2007). As it can be seen in Figures, and as is evident from the FTIR measurement, O_2 plasma treated PP incorporates oxygen in the form of C-O and O-H (negative sites) in the fiber surface and increases electronegativity. So the dye exhaustion for cationic (basic) dye with positive sites increases considerably. It can be seen that, average K/S value of O_2 -7 min sample, which was dyed with this dye, is 3 times more than average K/S value of untreated one. Furthermore, by creating N-H groups (positive sites) on the surface of PP fabrics with N_2 LTP treatment, the dye exhaustion for direct and anionic dyes (with negative sites) increases. Note that there were no significant color changes either with repeated washing cycles or with a long period of storage, which indicates that the stability of dye attachment to the fabrics. It can be seen in Figure 4 that the reflection factor of dyed O_2 LTP treated sample with disperse dye is less than Dyed N_2 LTP treated one. It shows that the disperse dye exhaustion of O_2 LTP treated sample is more than N_2 LTP treated one. But it is not noticeable because Disperse dyes don’t have any positive or negative sites.

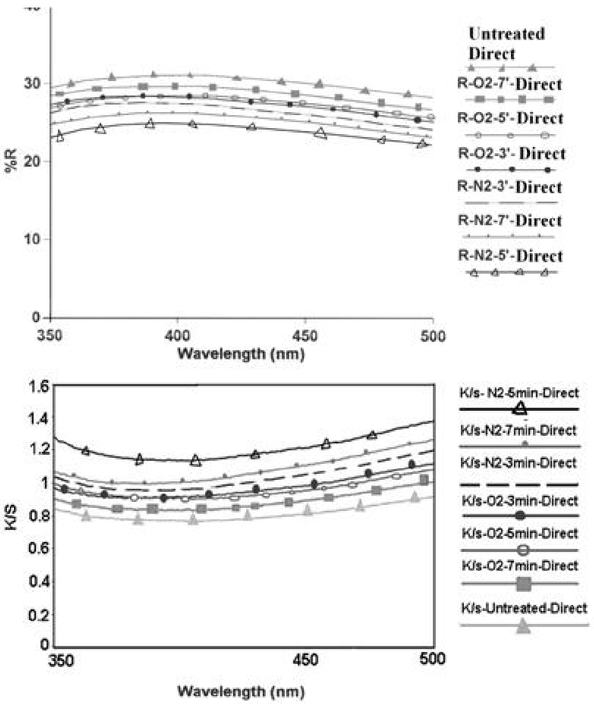


Fig. 1. R% and K/S Value of dyed samples with Direct Dyes

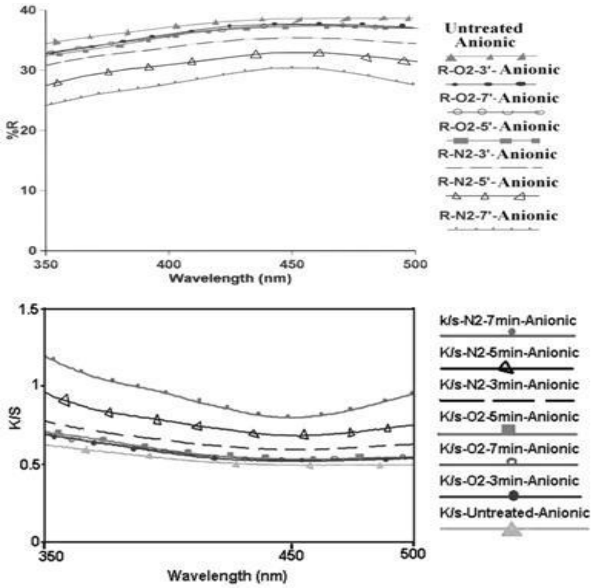


Fig. 2. R% and K/S Value of dyed samples with Anionic Dyes

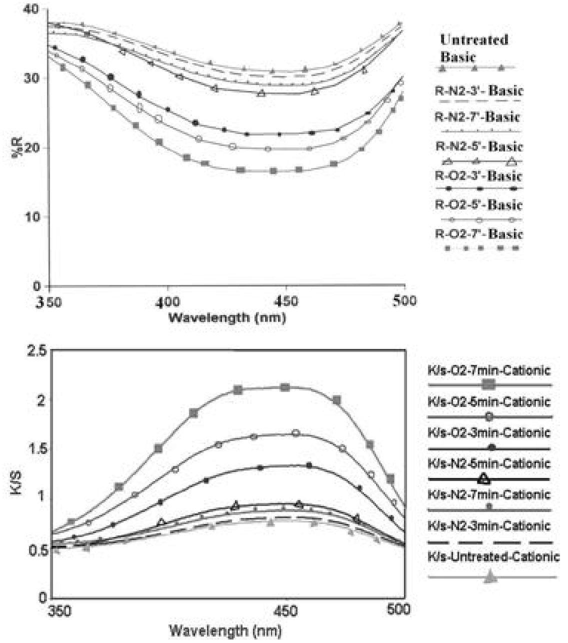


Fig. 3. R% and K/S Value of dyed samples with Cationic Dyes

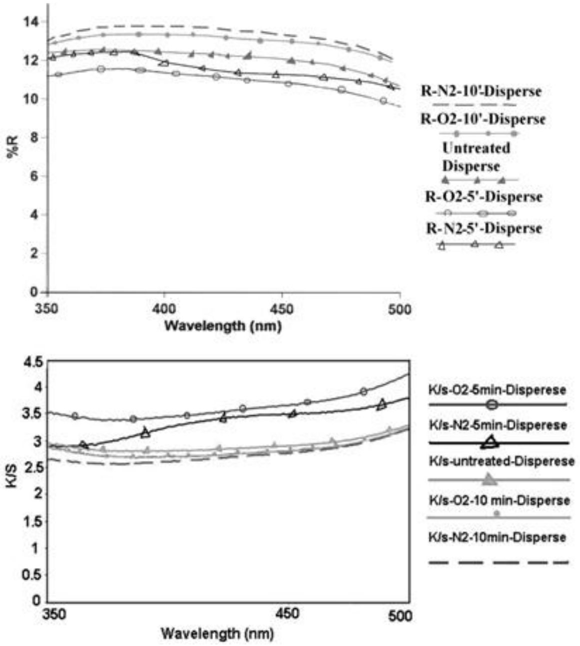


Fig. 4. R% and K/S Value of dyed samples with Disperse Dyes

SEM micrographs of PP fabric treated, respectively, with the two non-polymerizing plasma gases (O_2, N_2) are shown in Figure 5, only 3 and 7 min treated samples being presented here. It can be seen that, after prolonged LTP treatment, ripple like patterns oriented in a fiber axis are developed (see Figure 5 (d, e)). O_2 plasma gives more distinct effect than N_2 plasma.

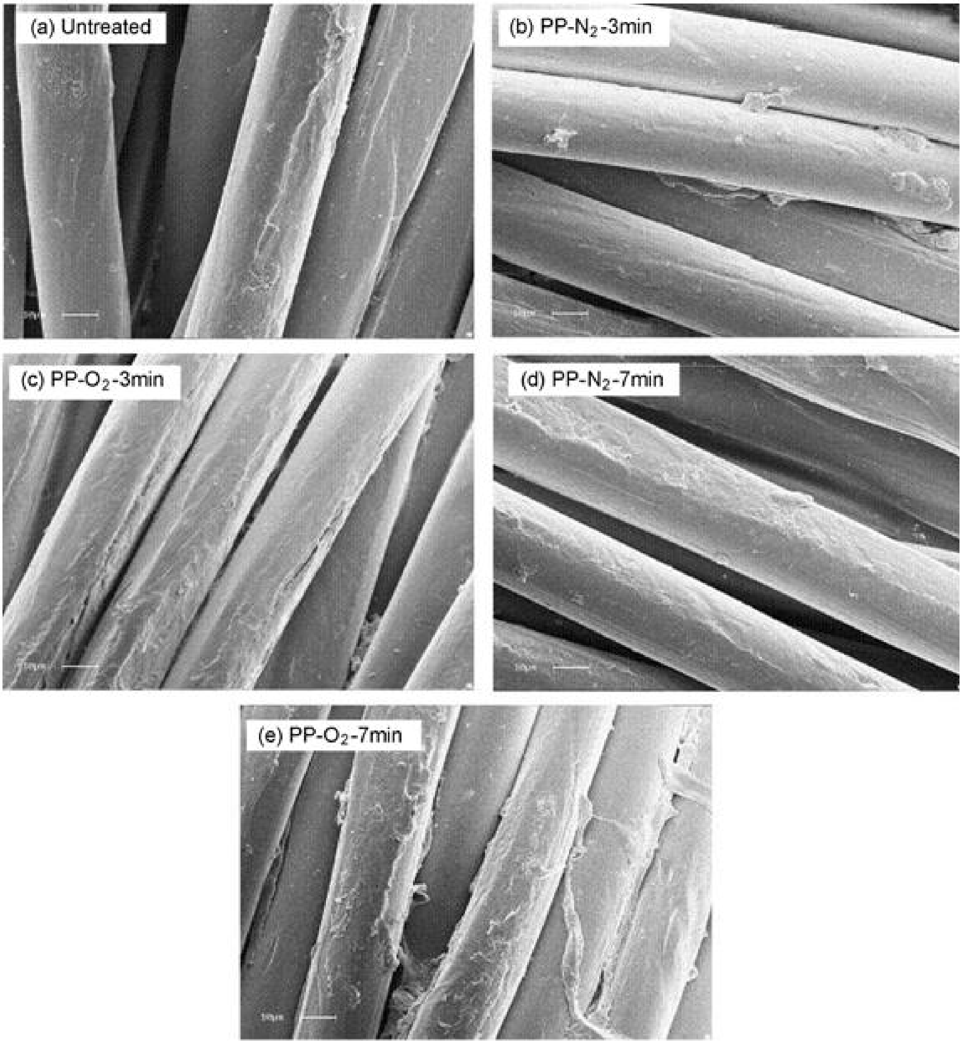


Fig. 5. SEM Images of Treated and untreated samples

X-ray diffraction (XRD) is a crystal structure analysis method using the atomic arrays within the crystals as a three dimensional grating to diffract a monochromatic beam of X-rays. The angles at which the beam is diffracted are used to calculate the interplaner atomic spacing (d-spacing) giving information about how the atoms are arranged within the crystalline compounds. X-ray diffraction is also used to measure the nature of polymer and extent of crystallinity present in the polymer sample. The results of XRD analysis are reported in Figure 6. Study of the data of this analysis shows no noticeable changes in the value of d or FWHM (size of crystals) of the PP fibers, but the LTP treatment slightly increased the total crystallinity. This indicates that the treatment has not changed the arrangement or decreased the strength of the fabrics.

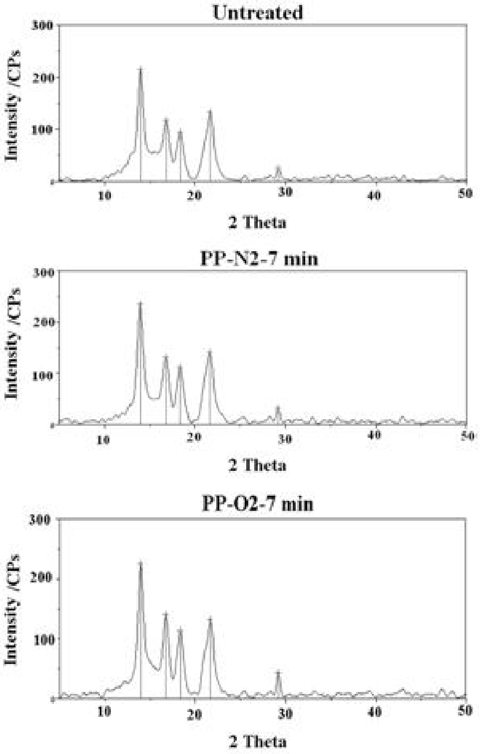


Fig. 6. XRD Results of Treated and Untreated Samples

In this research work, the dye-ability of Polypropylene Fabrics was improved by using low temperature plasma treatment. The dye-ability of PP fabrics treated with LTP of N_2 is increased with anionic dyes, and by creating OH and C=O groups on the surface of the fabrics with O_2 LTP treatment, the dye exhaustion for cationic dye increases noticeably. So we can dye PP-O_2 LTP treated sample with cationic dyes easily (Shahidi et al, 2007). And we can have new usage of PP fabrics as textile garments. The present examples show that plasma technology performed under reduced pressure, leads to a variety to processes to modify fiber or textile materials to fulfill additional highly desirable requirements. It is to be expected that, this technology, which has been known for a long time and is being used in different branches of industry, in the near future will conquer textile as well (Errifai et al, 2004; Shahidi et al, 2007).

3. Effect of electron irradiation on printability of polypropylene (PP) fabrics, (novel method for decoration of PP fabrics)

Textile printing is the area of textile processing used for applying color in a localized design or pattern to textile material, normally fabric. Depending on the fiber composition and the construction of the fabric to be printed, as well as the proper selection of dyes or pigments, the printed patterns can exhibit good to excellent colorfastness. From a practical point of view, textile printing is the process which incorporates artistic design, engineering, and chemical technology to produce unique patterns which can then be accurately repeated on large volumes of the fabric. Textile printing is probably best described as an industrial art, having a long history and an assured future. Printing is actually local dyeing. The dye is a part of a printing paste, which is applied on the textile material by different printing techniques. After printing, it is usual to steam the textile material, to achieve colorfastness (wash, light, and rubbing fastness).

Textile print was created thanks to man's desire to decorate fabrics designated for clothing, and later for home decoration (Petrinic, Andersen, Ostar-Turk, & Le Marechal, 2007). It has logically gone through many development steps. The steps were aimed at improving the mechanization and automation of each printing technology phase. Each printing technique was created and improved step by step (Burton, 2005).

In traditional textile printing, colored images on the fabrics are produced by using textile print paste which consists of highly concentrated thickened solutions of textile dyes or pigments. Unfortunately, the use of these print pastes can lead to intensely colored waste products.

Environmental issues are of major concern to most textile printers (Moser, 2003). For many years, improving the quality of prints was the main goal in product development. Lately, economic, environmental, and toxicological considerations have become more important. Using more environmentally friendly print paste preparations and auxiliary products, for example reducing or to eliminating formaldehyde on the fabric, is currently one of the major concerns in the textile printing industry (El-Molla & Schneider, 2006).

In many cases relating to the processing of fibers, powders, and films, the modification of polymer surface functional groups composition is often required.

The development of methods for the controllable modification of polymers in order to adjust their physicochemical, mechanical, optical, and other properties without any chemical processing is one of the most important areas of polymer science and technology.

Accelerated electrons generated by an electron beam (EB) may be considered one of the most important sources of ionizing radiation in the recent years. The effects of ionizing radiation, in general, and accelerated electrons in particular range from the basic phenomena of interaction of radiation with matter, radiation physics and chemistry to industrial applications. Among the different chemical systems, polymeric materials show marked changes when subjected to the action of ionizing radiation. These changes are mainly cross-linking or degradation, which result in the formation of products with modified physical and chemical properties.

Radiation curing by EB has become a well accepted technology, which has found a large number of industrial applications mainly in the coating and printing fields, in the manufacture of adhesives, and in microelectronics (El-Naggar, Zohdy, Said, El-Din, & Noval, 2005).

The modification of polymers is an important area of EB technologies providing an effective way to surface modification of various chemically inert materials, such as polyethylene imparting them with the reactivity required for the formation of polymer blends and grafted layers. Particularly, the high density EB treatment of polypropylene (PP) was found to promote the formation of oxygen-containing groups (mainly C=O) on the polymer surface and enhancement of PP compatibility with hydrophilic inorganic materials (El-Naggar et al., 2005; Ibrahim, Salmawi, & Ibrahim, 2005; Iller, Kukiełka, Stupińska, & Mikołajczyk, 2002; Kondo et al., 2006; Leonhardt, Muratore, & Walton, 2004; Mahapatra, Bodas, Mandale, Gangal, & Bhoraskar, 2006; Timusa, Cincub, Bradleyc, Craciuna, & Mateescua, 2000; Vasiljeva, Mjakin, Makarov, Krasovsky, & Varlamov, 2006; Zagórski, 2004; Zsigmond, Halasz, & Czvikovszky, 2003).

I.S. Bhardwaj and his coworkers researched on the modification of PP fiber with EB. In this work, PP filaments were irradiated by different doses of EB in the presence of monomers like acrylic acid, 2-4 vinyl pyridine. The solubility, crystallinity, and tenacity of the treated fibers has been determined. There appears to be a marked improvement in the tenacity of the fiber and dye take-up (Bhardwaj & Heusinger, 1978). Also, EB treatment studies have been carried out by H.M. Abdel-Hamid to investigate the potential for improvements in the dielectric properties of the PP film (Abdel-Hamid, 2005). F. Poncin-Epaillard reported that, surface grafting of polymeric materials, such as films and fibers, may improve their surface properties and this improvement on PP active sites should initiate a surface postgrafting that can be formed by an EB irradiation. EB modified PP was also functionalized through an aging reaction, emphasized by a high radical concentration. Active surface films are susceptible to react with monomers in a postgrafting reaction (Poncin-Epaillard, Chevet, & Brosse, 1994).

In this work, the PP fabric is irradiated with electrons to form oxygen containing groups on its surface. By creating these functional groups, the uncovered part of PP fabric can be dyed by cationic dyes easily without any hazardous materials (Shahidi et al, 2007). Thus, just by dyeing the fabrics can be printed.

The aim of this research is the development of an environmental-friendly process with no thickeners in order to enable good quality printing and to minimize water pollution.

Due to low surface energy, polypropylene has very weak hydrophilic properties and doesn’t have any affinity to cationic dyes. In this study, some parts of polypropylene fabrics (PP) have been covered by mask, and then they were irradiated by electrons with different energies (Figure 7). After electron irradiation, the samples have dyed with cationic dyestuff. The electron irradiated parts can be dyed and by this work we can print or decorate the polypropylene fabrics and films easily. The treated surfaces were characterized by Scanning Electron Microscopy (SEM), reflective spectroscopy and FTIR. Also, light and wash fastnesses of printed samples were measured. As we know, pigment printing method requires additional materials such as gauze, screen, screen frame, screen lake, etc. and these affect product costs. Moreover, this process requires longer times compared to Electron Beam (EB) designing. On this account EB designing is more advantageous. One of the advantages of the EB designing is the good repeatability of the designs. Besides, desired physical effects can be fully ensured. In pigment printing method printing time is lengthening and reproducibility decreases due to the difficulties such as paste preparation, squeegee motion, clogging of the screen and the necessity to print the same area for each sample. Moreover, EB designing process does not include any after-treatments such as drying and fixating which increase the production time and costs. The results from this work show that the EB-based designing process represents a serious competitor of the conventional technologies. And just by dyeing the electron irradiated samples, the printed look appeared on the surface of PP fabrics, it is because of this matter that, PP doesn't have any affinity to cationic dyestuffs, but after EB treatment, cationic dye can be absorbed by irradiated parts of fabrics easily.

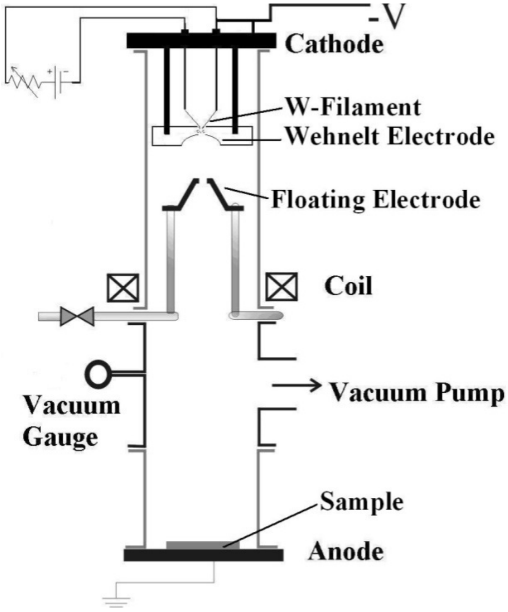


Fig. 7. The Schematic view of experimental setup.

In order to study the chemical modification of the electron irradiated part of fabrics, Fourier transform infrared spectroscopy is used. FTIR was used to examine the functional groups of the corresponding samples investigated in Figure 8. As shown only slight increase in absorbance at 1720 cm^{-1} (C=O) band and 3400 cm^{-1} (O-H) band and 1080-1300 cm^{-1} (C-O) after electron irradiation can be noticed. The improvement of dye-ability properties of these uncovered parts confirmed that, electron bombardment activated successfully the surface of uncovered PP fabrics. The main effect of electron beam treatment of a polymer is the transfer of energy towards the respective polymer surface .In function of the molecular structure of the polymer, one of the following events could proceed : cross-linking , chain scission or radical stabilization. In the case of polymer treatments by Electron Beam, electrons are accelerated towards the exposed surface and lead to an increased reactivity of the respective surface. This fact is possible due to the breaking of the different bonds and further formation of free radicals. After the polymer samples are brought out from the reactor, the reaction of the oxygen from the atmosphere with the free radicals takes place, and thus surface functionalization is obtained. This functionalization is more important for the materials that have no oxygen-containing groups in their initial composition. The improvement of dye-ability properties of these uncovered parts confirmed that, electron bombardment activated successfully the surface of uncovered PP fabrics.

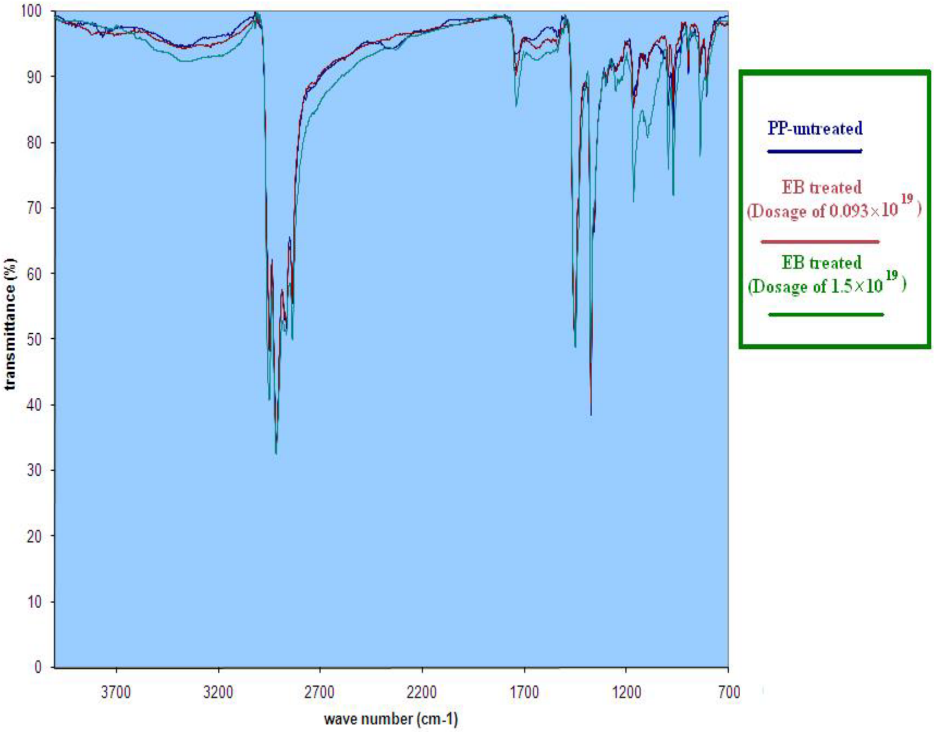
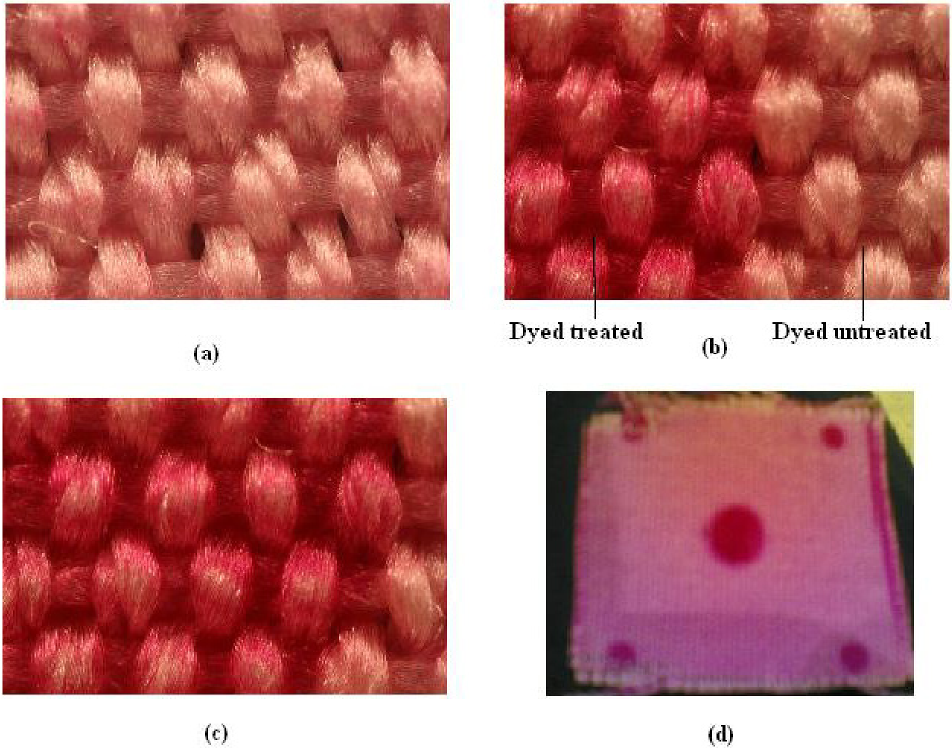


Fig. 8. The FTIR results of untreated and treated samples.

In this study, Electron Beam Irradiation has been used as a novel method for decoration of PP Fabrics. The highest relative color strength (K/S) is obtained and the fastness properties range between good and excellent for samples printed using electron irradiation, this is true irrespective of the type of printed fabric. In this research work, the physical and chemical properties of PP fabrics were improved by using electron beam irradiation with different energy of bombardment. By this treatment, the wet ability and Dye ability of PP were increased significantly through creating (-O-H), (C=O) and (C-O) groups on the surface of samples where hydrophobic properties changes to hydrophilic.

And we could dye the uncovered electron irradiated parts of PP fabrics with cationic dyestuff and decorate the PP fabrics without any thickener and auxiliaries as it can be seen in Figure 9(d). It is expected that, EB irradiation which has been known for a long time and is being used in different branches of industry, in the near future will conquer polymer as well (Payamara et al, 2010).



(a) (b) (c) (d)

Fig. 9. The photo of printed samples

4. Ion beam modification of polypropylene fabrics

The main goal of this work was examination of structural and compositional changes in the polypropylene (PP) fabrics caused by ion irradiation. In this work, the PP fabric has been irradiated with CO_2 ions. The implantation conditions (i.e, exposure time, beam current, and discharge power) were changed to control the extent of surface modification. And the effects of irradiation were studied using different instruments. Also dye ability of the untreated sample and treated under different conditions were investigated by using a 3% wt aqueous solution of a basic dyestuff. The obtained data show that, ion beam processing of PP fabrics allows an adjustable modification of their surface properties. The functional groups on the surface of samples were examined using FTIR spectrometer. Moreover, dyeing properties for treated fabrics have been tested. Significant increase in color strength has been achieved. Morphology of samples was examined by Scanning Electron Microscopy (SEM). The PP fabric was mounted on a sample holder and placed inside a vacuum system Fig 10. Carbon dioxide ion beams at energies of 1 and 2 keV were implanted, using an Ion Beam Sputtering system with Kauffman Ion Source, at the Plasma Physics Research Center (Tehran, Iran). Vacuum chamber was evacuated to the base pressure of 9×10^{-3} torr using rotary pump, and then to pressure of 10^{-5} torr using turbo pump. After filling the chamber with 10^{-2} torr of working gas (CO_2), the filament, discharge, accelerator and focusing system were generated , respectively. The ions were produced via a multi-step process: that is, ions are initially formed by stripping electrons from source atoms in plasma. The beam of ions is then accelerated using a potential gradient column. A series of electrostatic lens elements shapes the resulting ion beam and scans it over an area in a work chamber containing the samples to be treated. One side of samples was treated for duration of 3 minutes. The dosage of 1×10^{11} ions/cm^2 was used, and the implantation was done with different beam current below 1mA to avoid excessive heating and thermal degradation.

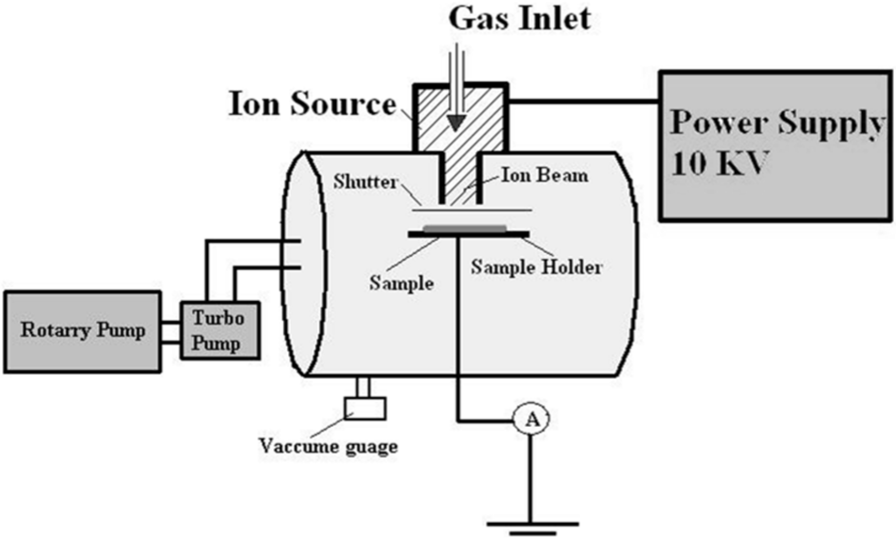


Fig. 10. Schematic view of Ion Implantation set up.

In this research work, the dye-ability of polypropylene fabrics is improved by using ion implantation treatment. The cationic dye-ability of treated PP fabrics by creating OH and C=O groups on the surface of the fabrics increases noticeably. So we can dyes PP-Ion implanted samples with cationic dyes easily. And we can have new usage of PP fabrics as textile garments. The present examples show that ion implantation technology performed under reduced pressure, leads to variety to processes to modify fiber or textile materials to fulfill additional highly desirable requirements. However it should be mentioned that, the dye ability of PP fabrics using electron beam can be improved significantly in same dosage of energetic particles. Ion implantation is promising for the compatibilization of PP fiber and matrix with various compound in blends and production of multilayered composites for versatile applications such as laminates and supported compound. (Payamara et al, 2008)

5. Study of surface modification of wool fabrics using low temperature plasma

Owing to the selective modification of wool surface, LTP leads to the formation of new surface groups. Plasma treatment of wool is confined to the fabric surface, leaving the bulk properties unchanged. In this work, plasma was produced by DC glow discharge in a cylindrical glass tube evacuated up to 10^{-3} torr by mechanical pumps. The surface characterization was performed using XRD, FTIR and SEM imaging, so allowing the selection of treatment parameters for reproducible, efficient and stable surface modification. The absorption time were utilized to analyze the result of the treated samples. The changes in these properties are belived to be related closely to the inter-fiber/ inter-yarn frictional force induced by LTP treatment. For sample preparation, size residue and contamination on the fabrics were removed by conventional scouring processes, which the fabrics were washed with 0.5 gl^{-1} sodium carbonate and 0.5 gl^{-1} anionic detergent solution (dilution ratio to water =1:10) at 80^0C for 80 min and then washing was conducted twice with distilled water at 80^0C for 20 min and once at ambient temperature for 10 min. The DC magnetron sputtering reactor has been used to treat the wool fabrics, and non-polymerizing reactive gases, such as O_2, N_2 and Ar were used to modify the wool surface. In the reaction chamber, a sheet of wool fabric was placed on the anode or cathode. Details of samples are shown in Table 1. Before the process started air and old gases had to be pumped out by the vacuum pump, thus almost a vacuum level was created in the reaction chamber. Afterwards, plasma gas was introduced into the reaction chamber. Discharge voltage was 500V, discharge current was 200 mA and the inter-electrode distance was 35 mm. The pressure remained at 0.02 Torr for the entire glow-discharge period.

Sample	Description
No1	Sample was placed on the cathode. Ar gas was used for 7 min
No2	Sample was placed on the cathode. O_2 gas was used for 7 min
No3	Sample was placed on the Anode. O_2 gas was used for 7 min
No4	Sample was placed on the Anode. N_2 gas was used for 7 min

Table 1. Description of samples.

The SEM analysis of surface morphology reveals slight changes which occur on the surface of wool fibers as a result of plasma modification. The rising parameters of LTP treatment (time and power) lead to a slight increase in these changes causing a rounding of scales, microcracks, recesses and tiny grooves, all caused by the etching of the material . SEM micrographs of wool fibers after plasma modification are shown in figure 11. As it can be seen in Figure 11, the scale of samples which were put on the cathode was destroyed more than other samples. It showed that by putting samples on the cathode the rate of etching is increased and it can help to anti felting of wool fibers. For N_2 and O_2 plasma treatment, that, samples that were put on the anode, minimal damage occurs to the scale structure as a result of the glow discharge treatment. The most important effect of LTP treatment of wool is the change in the character of the wool fiber surface from hydrophobic to hydrophilic and anti felt.

For dyeing process, aqueous solutions, containing 3.0 wt. % of the acid dye were employed for dyeing wool fabrics. The bath ratio was 1:100 (1 g of fiber in 100 ml of dye solution). The following dyeing condition was adopted: Initial temperature 40 ^{0C}, followed by a temperature increase of 3 ^{o}Cmin^{-1} up to 80 ^{o}C, holding for 30 min at 80 ^{o}C. 5 g/lit of acetic acid for pH adjustment, were added for anionic dyeing processes. After dyeing, the fabrics were rinsed with cold-hot-cold water and then dried at room temperature. As it can be seen in Figures 12, the reflection factor of dyed LTP treated samples was less than dyed untreated sample. The results show that the O_2 and Ar-Cathode plasma treatment are more effective in increasing the dye exhaustion of wool with anionic dye. Furthermore, the colors achieved much more brilliant shades with the LTP treatment.

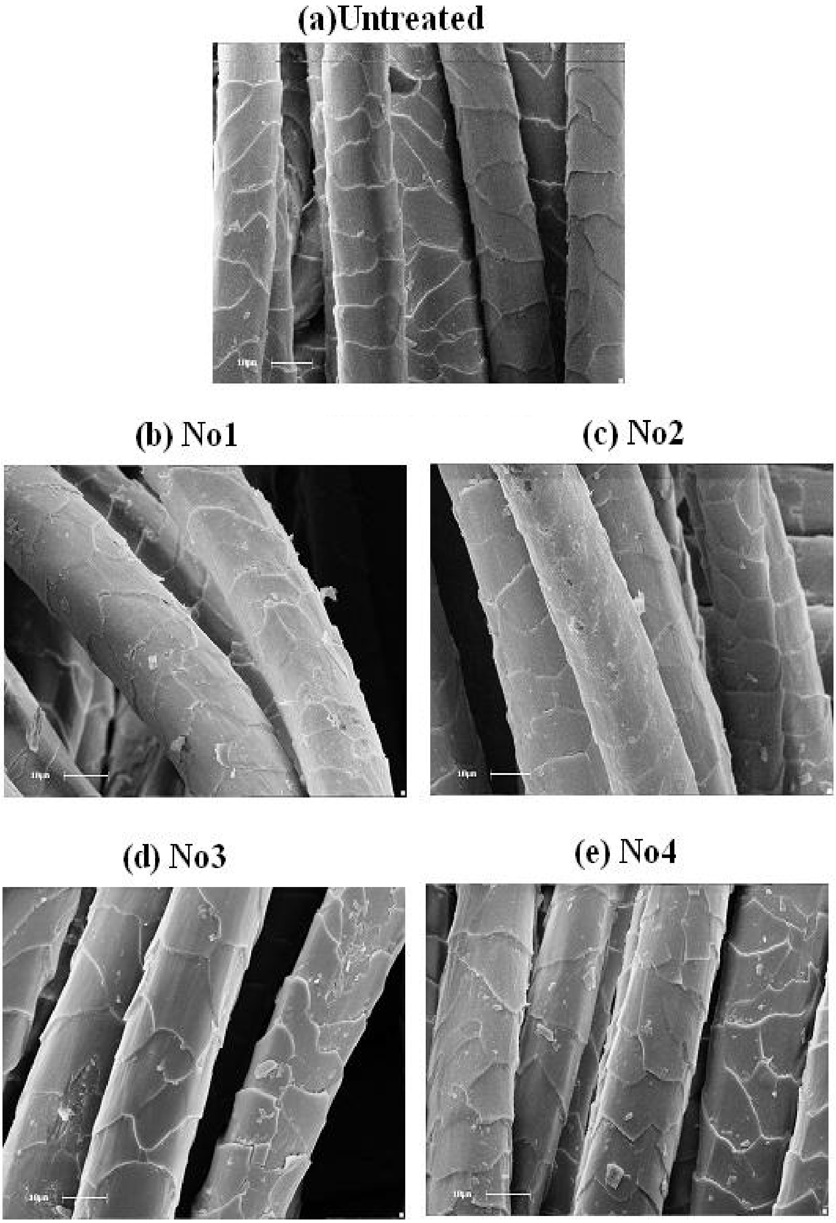


Fig. 11. SEM images of treated and untreated samples.

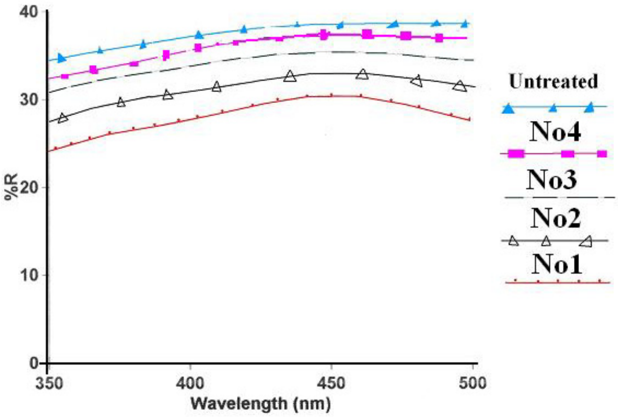


Fig. 12. Reflection spectroscopy of untreated and treated samples.

The quality of water repellency of the samples were evaluated by water drop test in which drops of controlled size were placed at a constant rate upon the fabric surface and the duration of the time required for them to penetrate to the fabrics have been measured. The results are shown in Table 2 in which the absorption times have been recorded for different treated and original samples. As seen after LTP treatment the water absorption time is much decreased. However this time is very low for O_2 –cathode LTP treatment.

Sample	Absorption time
Untreated	20 min
No1	5 sec
No2	1 sec
No3	2 sec
No4	3 sec

Table 2. Absorption time of treated and untreated samples

In this research work, the surface of wool samples were changed both physically and chemically by using LTP treatment. The situation of wool samples in LTP reactor is very important factor. By putting samples on the cathode and using oxygen as a working gas, the wet ability and dye ability of wool samples were increased (Shahidi et al, 2010)

6. Influence of plasma sputtering treatment on natural dyeing and antibacterial activity of wool fabrics

In this paper, the effect of plasma sputtering treatment on the natural dyeing properties of wool and the possibility of substituting it for mordant treatment have been studied. Madder and weld as natural dyes and copper sulfate ($CuSO_4$) as a metal mordant have been used. Also, copper as the electrode material, in a DC magnetron plasma sputtering device was used. The color strength of samples was analyzed using a reflective spectrophotometer and washing and light fastnesses were investigated according to I.S.O. standard recommendations. The results show that, the color strength and fastness of dyed wool samples have been improved after plasma treatment. The antibacterial counting test was also used for determining the antibacterial efficiency of plasma treated and mordanted samples and the durability of antibacterial properties of them was compared. The scoured wool fabric was divided in 2 parts, one was mordanted by copper sulfate, and the other deposited by a plasma sputtering device. The chamber was evacuated to the pressure of 2×10^{-5} torr, using a rotary and also a diffusion pump, and then argon gas was introduced

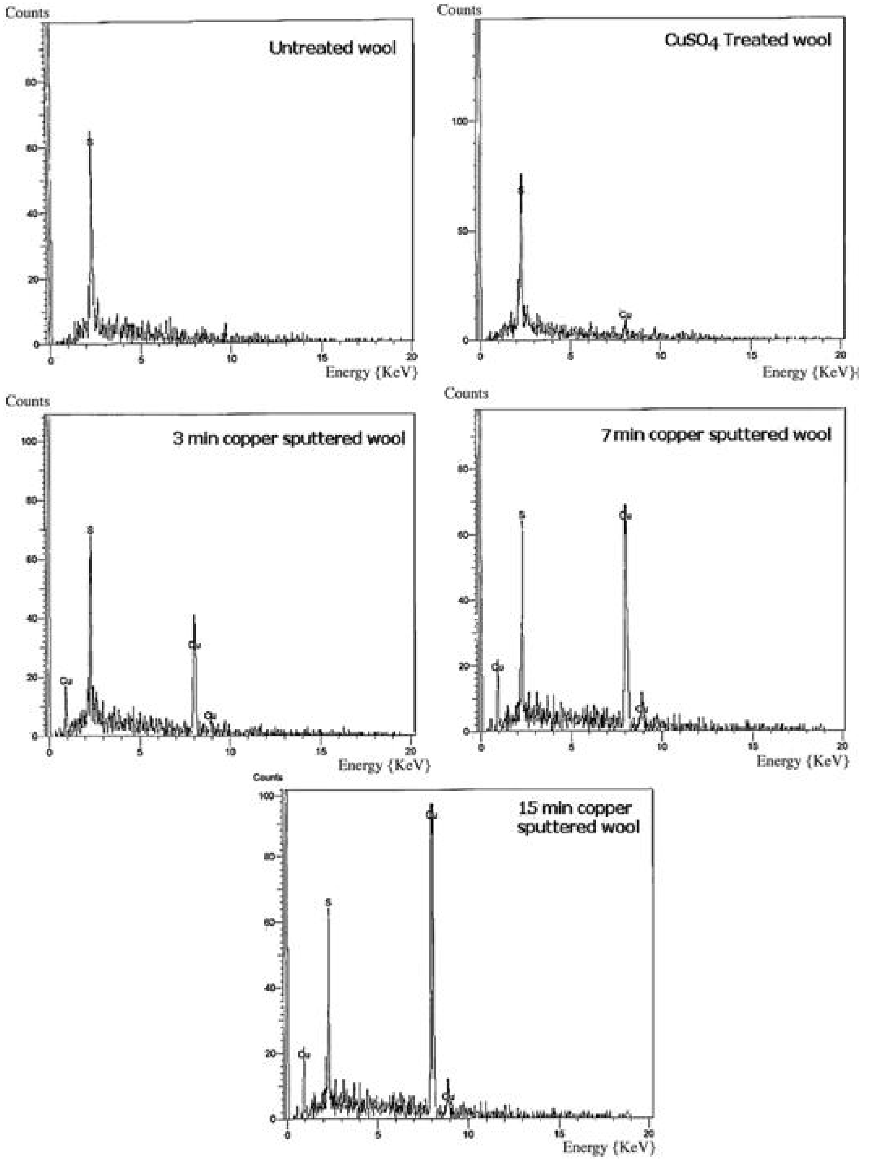


Fig. 13. The EDX results of sputtered wool

into it at a pressure of 2×10^{-2} torr. Voltage was kept at 2000 V and the discharge current was 220 mA. The duration of Cu deposition was 3, 7 and 15 min for different samples. All samples were analyzed using EDX for comparing the amount of copper on the samples. As it is shown in Figure 13, the amount of copper on plasma sputtered samples is more than $CuSO_4$ treated one which demonstrates that in a very short time of plasma sputtering, large amount of copper has covered the surface of the samples. Thus by increasing the time of sputtering, it is possible to increase the amount of copper sputtered on the samples.

After dyeing the samples, the color intensity of them has been measured and compared using a reflective spectroscopy in the range of 400-700 nm. The results are shown in Figure 14 and 15. As it can be seen in Figure 14, the reflection factor for the mordanted sample by

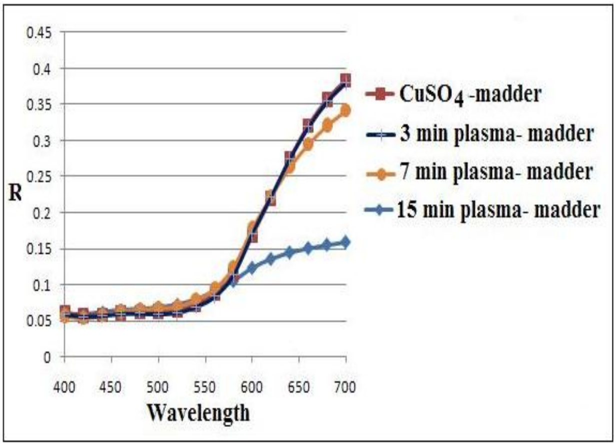


Fig. 14. The Reflection factors of dyed samples with madder

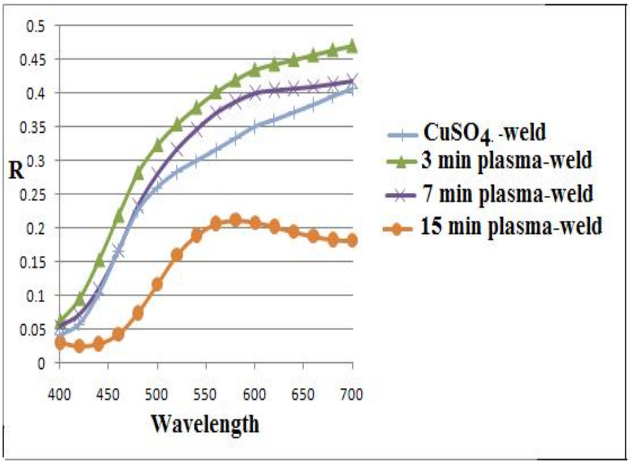


Fig. 15. The reflection factor of dyed samples with weld

$CuSO_4$ when dyed by madder is very close to the Cu-deposited samples with 3 minutes plasma treatment. However in Figure 15 which shows the case of dyeing with weld, the reflection factor of 7 min Cu-sputtered sample is close to the reflection factor of $CuSO_4$ mordanted sample. The K/S values of the samples corresponding to the cases of Figures 14 and 15 are shown in Figures 16, 17 respectively. The Figures show that by choosing a proper condition for sputtering, it is possible to improve the natural dying properties of wool

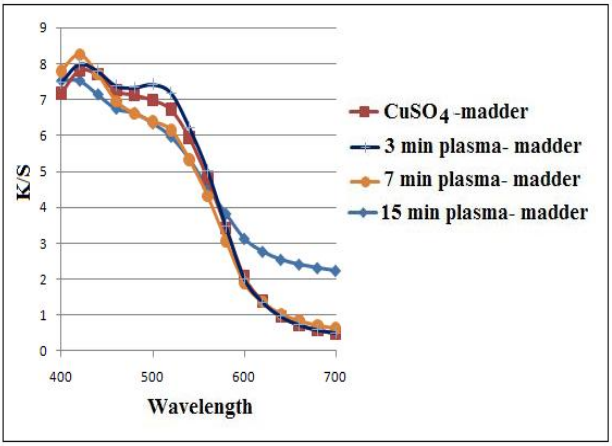


Fig. 16. The K/S values for dyed samples with madder

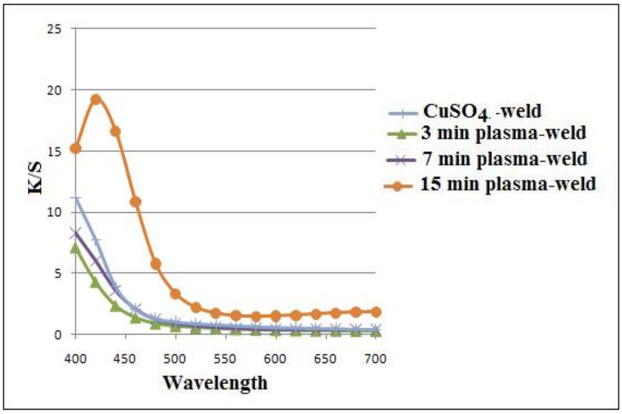


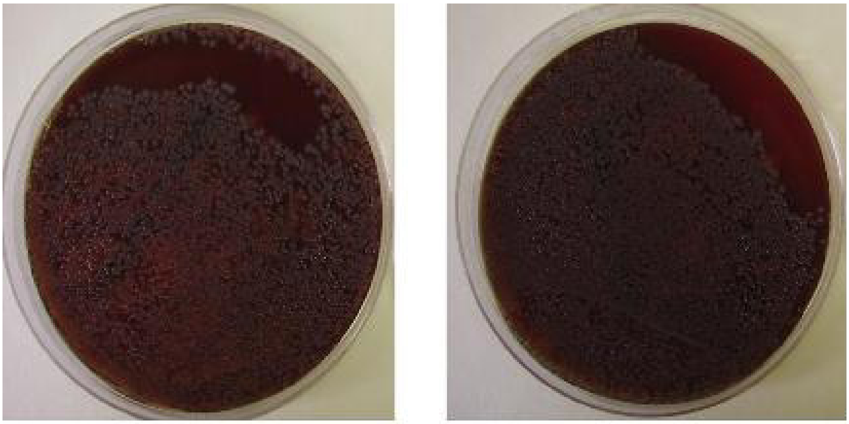
Fig. 17. The K/S values for the dyed samples with weld

As we mentioned before, the durability of dyed wool fabrics has been also evaluated in terms of fastness towards washing and light, using the gray and blue scale according to ISO standard recommendations. The results are shown in Table 3. Assessment of fastness involves a visual determination of either change in shade or staining of an adjacent material and the graduation of the gray tones in the scales is defined as the smallest difference in depth, which is of commercial significance. As shown in Table 3, the fastness properties of the Cu sputtered dyed fabrics are improved and fastness in range between good to excellent has been achieved. As mentioned before, the wash and light fastness of natural dyes are not satisfactory, so many research are carried out for improving these fastnesses. Here it has shown that by using plasma sputtering technique we can dye wool samples by natural dyes easily with very good wash and light fastness. This technique may found many applications in carpet industry as well.

Samples	Wash Fastness	Light Fastness
$CuSO_4$ treated madder dyed wool	4	5-6
3min-coated-madder dyed wool	4	5-6
7min-coated-madder dyed wool	4-5	7-8
15 min-coated-madder dyed wool	4-5	7-8
$CuSO_4$ treated weld dyed wool	3-4	5
3min-coated-weld dyed wool	5	7-8
7min-coated-weld dyed wool	5	7-8
15min- coated-weld dyed wool	5	7-8

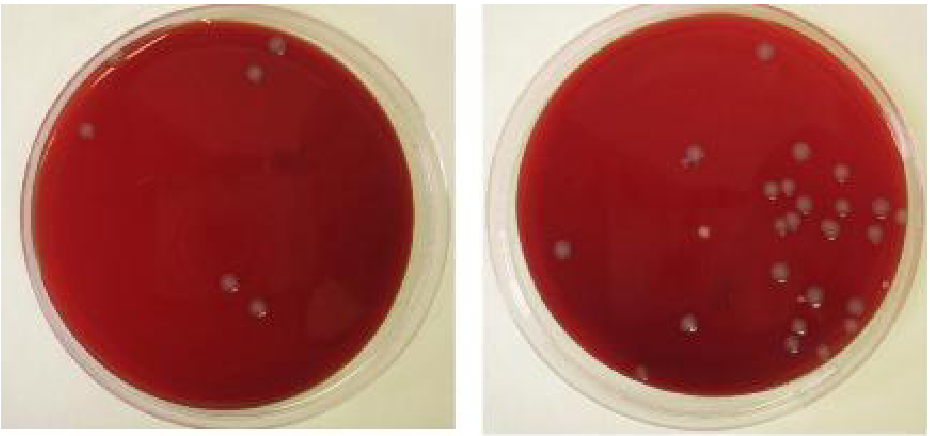
Table 3. The results of wash and light fastness

In another point of view, in recent years, the demand for antibacterial fabrics in domestic and abroad markets has grown significantly because of more awareness of the potential threat of spreading diseases. Bio-protective fabrics such as medical clothes, protective garments, and hygienic textiles are the main application of the antibacterial fibers (Schmidt-Przewozna et al. 2008). Natural textiles such as those made from cellulose and protein fibers are often considered to be more vulnerable to microbe attack than man-made fibers because of their hydrophilic porous structure and moisture transport characteristics. Thus, the use of antibacterial agents to prevent or retard the growth of bacteria is becoming a standard finishing for textile goods. However, conventional finishing techniques applied to textiles (dyeing, stain repellence, flame retardance, antibacterial treatments) generally use wet-chemical process steps and produce a lot of wastewater. Plasma treatment, on the other hand, is a dry and eco-friendly technology, which offers an attractive alternative to add new functionalities such as water repellence, long-term hydrophilicity, mechanical, electrical and antibacterial properties as well as biocompatibility due to the nano-scaled modification on textiles and fiber. Moreover, the bulk properties as well as the touch of the textiles remain unaffected (Hegemann et al, 2007 ; Yuranova et al, 2003 ; Chen et al, 2008 ; Yu et al, 2003, Park et al, 2008 ; Ghoranneviss et al, 2007). In this paper in addition to investigation about the effect of plasma sputtering and mordant treatment on wool natural dyeing, the antibacterial efficiency of both plasma treated and mordanted samples have been also studied. The tests done to evaluate antibacterial textiles were divided into two types, agar based zone of inhibition tests and bacteria counting tests. The agar culture medium is transparent, when the bacterium is inhibited from growth, a transparent area in the form of a halo around the fabric will be observed. No halo for untreated wool fabrics has been observed. This control test shows that the original fabric does not have any antibacterial property, while the $CusO_4$ treated and Cu-coated samples show very good antibacterial activity. The reason is that the interaction between copper ions and bacteria can change the metabolic activity of bacteria and eventually cause its death. The diameter of the halo is shown in Table 4. As it is shown, coating the samples by Copper has produced an antibacterial effect in it. Figure 18 illustrates the results of counting test for untreated wool sample. As it is seen, too many bacteria are spread over the plate. The results of treated samples are shown in Figure 19. As shown, coating the samples by copper for 7 minutes has significantly decreased the amount of survival bacteria colonies. Similar results were achieved for the rest of the coated samples. We should mention here that the amount of bacteria spread over the agar plate is also decreased for the $CuSO_4$ treated samples. However these process which are done in a wet medium under a long duration, at least 60 minutes [Chen et al, 2008 ; Hong and Sun, 2008 ; Kumar et al, 2005 ; Chen & chiang, 2008], are not comparable with easily obtained treatment through plasma sputtering technique.



E.Coli **S.Aureus**

Fig. 18. The photo of bacteria spread over the plate in case of untreated wool



S.Aureus **E.Coli**

Fig. 19. The antibacterial activity of copper coated sample for 7 min.

Samples before dyeing	Counting test (Reduction percentage of bacteria), S.Aureus	Counting test (Reduction percentage of bacteria), E.coli	Inhibition zone, S.Aureus	Inhibition zone, E.coli
$CuSO_4$ treated wool	99.4	99.4	4 mm	4 mm
3 min copper sputtered wool	99.5	99.5	4 mm	4 mm
7 min copper sputtered wool	99.5	99.5	4 mm	4 mm
15 min copper sputtered wool	99.6	99.5	4 mm	4 mm

Table 4. The antibacterial activity of the treated samples before dyeing

So by Cu-sputtering , not only the wool fabrics could be dyed easily in a short time without need to any wet medium , but also they could gain very good antibacterial properties. The results show that, the sputtering has improved the natural dying properties of wool fabrics. It has also improved the wool resistance to washing and light. The dyed treated samples have also gained very good antibacterial properties (Shahidi et al, 2011).

7. Conclusion

As has been demonstrated, plasma treatments of textiles look very promising. They can be used both in substitution of conventional processes and for the production of innovative textile materials with properties that cannot be achieved via wet processing. They are applicable, in principle, to all substrates, even to those that cannot be modified by conventional methods. In general, no significant alteration of bulk properties is produced.

They are fast and extremely gentle, as well as environmentally friendly, being dry processes characterised by low consumption of chemicals and energy. When they cannot replace an existing wet process (dyeing and some finishing), if used as pre-treatments, they can reduce markedly the amount of chemicals required by the process and the concentration of pollutants in the effluents.

The great advances of the last decades in the field of the science of materials are now ready to enter into the field of textiles and it is already possible to envisage that, in the next ten years, the clothing–textile industry will undergo a dramatic revolution. Smart textiles, completely new fibres (nanofibres, etc.), and new textile applications in unexpected fields can be expected. Also, our way to consider clothing is going to change completely. Environmental aspects are going to play a more and more important role. Under these perspectives, plasma processes are certainly going to supersede many traditional finishing processes.

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16

Dyeing and Fastness Properties of Disperse Dyes on Poly(Lactic Acid) Fiber

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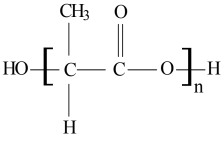
1. Introduction

Poly(lactic acid) or PLA is an aliphatic polyester being considered as a green material due to its natural-based origin and biodegradability properties. Lactic acid obtained from the fermentation of sugar and vegetables e.g. corn and cassava is used as a monomer for PLA polymerization. Production of PLA polymer can be achieved by 2 major synthesis routes viz., direct condensation polymerization of lactic acid and ring-opening polymerization of lactide, a cyclic dimer of lactic acid, yielding poly(l-lactic acid), poly(d-lactic acid) or poly(d,l-lactic acid) depending on lactic acid isomers employed. The chemical structure of PLA is shown in fig. 1. PLA possesses desired properties required for packaging materials. Major market share of PLA therefore falls in the packaging industry. At the same time, its interesting properties have drawn attention from the textiles industry. An attempt to use PLA as a textile fiber has been pursued with the aim of replacing poly(ethylene terephthalate), PET, fiber with this green polyester fiber. PLA fiber can be produced by both melt and solution spinning processes (Gupta et al., 2007) but the former is used more regularly due to the more eco-friendliness and ease of processing. Thermal degradation of the PLA polymer during melt spinning can be prevented by addition of a thermal stabilizer. The processing of PLA fiber/yarn is one of the important parameters in controlling the properties of PLA. PLA yarns which are formerly passed through different yarn processing possess different physical properties and morphological characteristics, which subsequently influence the accessibility of the chemicals into the fiber during textile wet processing for example, dyeing and finishing (Suesat et al., 2003).



$$HO-\left[\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-O\right]_n-H$$

Fig. 1. Chemical structure of PLA

PLA fiber has superior elastic recovery and a slightly higher hydrophilicity as compared with PET. It also exhibits lower flammability and less smoke generation. One of the important properties influencing dyeing properties of PLA is claimed to be the effect of its lower refractive index. It was informed by NatureWorks, Co., Ltd. that refractive indices of PLA and PET were 1.35-1.45 and 1.50, respectively while Yang & Huda claimed that they were 1.45 and 1.58 for PLA and PET, respectively (Yang & Huda, 2003). The lower refractive index of PLA causes a deeper shade of the disperse dyes obtained on PLA at the same applied dye concentration (Lunt & Bone, 2001). Thermal properties of PLA were reported to be similar to that of polypropylene. The glass transition temperature (T_g) of PLA is 55-65°C. The melting temperature (T_m) of PLA, containing the L- or D-isomeric form alone, is between 171-180°C whereas that of the stereocomplex analogue is 220°C (Perepelkin, 2002). The T_m of PLA is dependent on the molecular weight, thermal history, and isomeric composition of the polymer (Södergård & Stolt, 2002). The most typically used PLA for textile application is poly(*l*-lactic acid) or PLLA. PLA has a lower melting temperature than PET. Fig. 2. shows the DSC scans of the fabrics derived from PLA and PET fibers. The melting temperature of PLA is at 170°C while PET melts at 260°C. This allows PLA to be processed at a lower temperature, for example disperse dyeing of PLA is done at 110°C while PET is dyed at 130°C, heat setting of PLA is carried out at 130°C whilst PET is heat set at 180°C (Phillips et al., 2003). These lower thermal properties are a cause of sensitivity of PLA fabric to high temperatures employed in textile processing and the conditions being experienced during its service life. Exposure to high temperatures could harm the fiber. Therefore, precaution is taken for the textile products obtained from PLA fiber to avoid ironing at high temperatures which can cause fiber damage. Alternatively, PLA is recommended for knitted goods rather than wovens in order to avoid such problems.

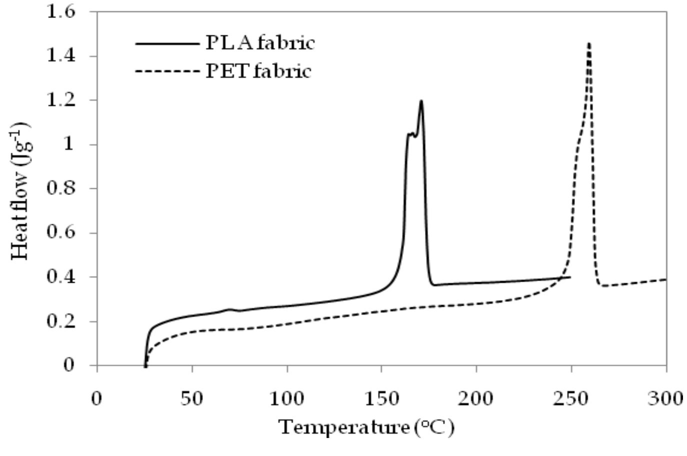


Fig. 2. DSC scans of the knitted fabrics derived from PLA and PET fibers

As PLA fiber is rather thermally sensitive, even the heat generated by scanning electron microscope (SEM) during a measurement performed at 15 kV could cause the fiber to melt and fuse together after being exposed to electron beam within a few seconds as seen in Fig. 3.a), while no damage was observed on PET fiber (Suesat, 2004). The same electron beam damage has also been found on the low melting point polymer such as polypropylene.

Jamshidi et al. claimed that PLA was relatively sensitive to thermal degradation, especially at a temperature higher than 190ºC. It was explained that the degradation reactions involved cleavage of the ester bonds on the main chain of the polymer. In addition, the presence of low molecular weight compounds e.g. water, monomers, oligomers, and catalysts in the polymer seemed to influence the reduction of the molecular weight at high temperatures (Jamshidi et al., 1988).


a) b) c)

Fig. 3. SEM photographs of damage on PLA fiber caused by ; a) electron irradiation of SEM; b) and c) peroxide bleaching used for PLA/cotton blend

PLA is not only thermally sensitive but it is also sensitive to alkali. It can be destroyed more easily by alkaline hydrolysis than PET. Thus, it can be deteriorated by those using alkaline wet processing in textiles production. Under alkaline conditions, PLA can be damaged by an alkaline hydrolysis reaction. The fiber surface is eroded and its strength is impaired, especially at high temperatures. An example of the alkaline preparation process is peroxide bleaching used to whiten the cotton component in the PLA/cotton blend. The alkaline hydrolysis takes place and the fiber surface is eroded as depicted in Fig. 3.b) and c), resulting in a substantial reduction of the fiber strength (Phillips et al., 2004a). Therefore, the preparation, dyeing and finishing processes for PLA should be milder than those used for PET. It is suggested to process PLA fiber at lower alkalinity, processing temperature and time.

2. Dyeing PLA fiber with disperse dyes

Although PLA fibers exhibit many attributes similar to other synthetic fibers, they are a new category that requires modified dyeing and finishing techniques to maximize their benefits. The dyeing properties of PLA have been investigated, especially in comparison with PET fiber. The dyeing of 100% PLA fiber has been intensively studied (Scheyer & Chiweshe, 1999; Nakamura et al., 2001; Phillips et al., 2003, 2004a, 2004b, 2004c). Owing to its relatively hydrophobic nature like PET, PLA can normally be dyed with disperse dyes. The optimum dyeing conditions for dyeing PLA are 110ºC for 30 mins under an acidic pH (pH 5) (Fig. 4.) whereas PET dyeing is normally carried out at 20ºC higher (130ºC) under a more acidic condition (pH 4) (Phillips et al., 2004b). Disperse dyes which show good dyeing properties on PET do not always provide good dyeability on PLA. According to the study of DyStar (2004), the disperse dyes recommended for dyeing PLA fiber are the medium-energy azo dyes which exhibit a superior degree of exhaustion as compared with other dye types. The disperse dyes based on benzodifuranone structure are not recommended due to their low uptake and poor build-up on PLA, therefore, a heavy depth of shade seems to be commercially infeasible (Phillips et al., 2003).

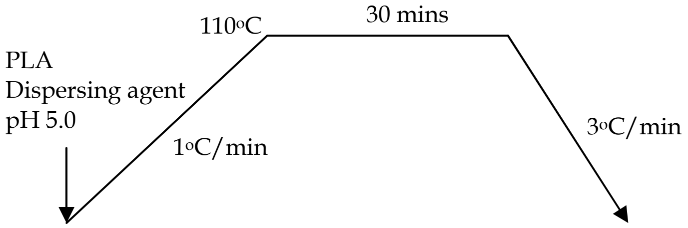
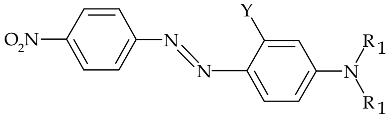


Fig. 4. Typical dyeing profile of PLA with disperse dye

Dyeing of PLA blended fibers has also been given a great attention as PLA blended with other fibers has been developed in order to improve some inferior properties of PLA and to gain a new type of fiber with better characteristics. One important blend is PLA/cotton. Due to a high price of PLA fiber, the blend of PLA/cotton was primarily produced so as to provide more economical PLA-based products with better desired properties. This PLA/cotton blend brought about a subsequent dyeing issue to be figured out. As PLA is alkaline sensitive, it should be noted that the cotton dyeing condition should not be harmful to PLA fiber. Reactive dyeing of cotton involves the use of the alkaline condition for dye fixation, so this should be carefully controlled. Nevertheless, under acidic and neutral conditions, PLA was reported to be severely damaged when it was treated for a longer time at higher temperatures, with neutral conditions exhibiting a more severe effect in deteriorating PLA strength. The hydrolysis reaction taking place in such conditions was reported to occur in a bulk erosion manner whereby hydrolysis degradation of the polymer occured simultaneously all over the fiber cross section. The hydrolysis mechanism of PLA was said to be strongly pH dependent and it was claimed to undergo bulk erosion under acidic and neutral conditions whereas under concentrated alkaline media, it was dominated by surface erosion (Yuan et al., 2002, 2003; Burkersroda et al., 2002). The effect of preparation and dyeing processes on the strength of PLA contained in the PLA/cotton blend was investigated and it was illustrated that these processes did weaken the PLA fiber but its retained strength after processing was in a commercially acceptable level. However, dyeing PLA/cotton using 1-bath, all-in process with Kayacelon React dyes under neutral conditions at 110°C did ruin the strength of PLA beyond acceptability (Phillips et al., 2004a, 2004c). This experience suggests that the use of higher temperatures or longer times of dyeing can cause degradation of the polymer, an observation confirmed by Kameoka et al. (1997) who claimed that the temperature, time and pH of dyeing resulted in a significant reduction in the molecular weight of the polymer.

2.1 Dyeing and build-up properties of disperse dyes on PLA fiber

Concentrations of disperse dye applied on PLA and PET fibers with the aim to achieve the same level of visual color yield on both fibers were examined and the values found indicates a less amount of dye required for PLA. Table 1 depicts the amount of disperse dyes used for dyeing PLA compared with those used to apply on PET. As seen that in order to gain the same K/S level of 10, a lower amount of % dye applied is required on PLA. One explanation can be made from the lower refractive index of PLA as compared with PET, rendering a deeper shade observed visually. Another important explanation is applied by the findings from the solvatochromism study of disperse dyes mentioned in our previous work (Suesat et al., 2011). The light absorption capacity of the dye is influenced by polarity of the polymer medium. It was found that the azo disperse dyes exhibited a higher molar extinction coefficient (ε_{max}) when dyed on PLA as compared with PET. Therefore, when the dyes are applied on the two fibers at the same concentration, a more intense color will be observed on PLA, in other words, less dye is needed on PLA so as to gain the same visual color yield compared with PET.

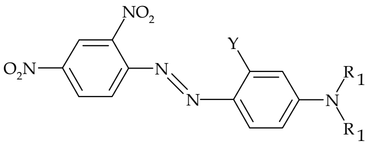


Dye	Y group	R_1 group	Concentration applied (%owf)	
			on PET	on PLA
D1	H	C_2H_5	0.16	0.12
D2	H	$C_2H_4OCOCH_3$	0.26	0.17
D3	CH_3	C_2H_5	0.16	0.10
D4	CH_3	C_2H_4OH	0.31	0.24
D5	CH_3	$C_2H_4OCOCH_3$	0.25	0.20

Table 1. Concentration of dyes applied to achieve the visual color yield (K/S) of 10 on PLA and PET fibers

The dyeing properties viz. % exhaustion, K/S values and λ_{max} of selected azo disperse dyes are shown in Table 2. A marginally higher degree of dye exhaustion was observed on PLA for this series of azo disperse dyes. At about the same %dye exhaustion, a higher visual color yield (K/S values) obtained on PLA. The difference in visual color yield observed on the PLA and PET can be considered from two important parameters, namely degree of exhaustion and the tinctorial strength (i.e. ε_{max}) of the dyes. High visual color yield on the fiber is expected to be obtained when the dyes render a high exhaustion percentage on the fiber. However, if the dye used is tinctorially weak, the deeper shade would not be able to be obtained. Therefore, high visual color yield achieved on polyester fiber involves the use of the disperse dyes which are tinctorially strong and well exhaust on the fiber. Yang & Huda studied the exhaustion of 10 disperse dyes on PLA and PET fabrics and found that, although the degree of dye exhaustion of all the disperse dyes on PLA was lower. The color yield of dyed PLA was higher than that of PET because of the lower reflectance of PLA (Yang & Huda, 2003). The λ_{max} of the dyes depicted in Table 2. was also shifted to a shorter wavelength on PLA. The higher K/S values and shorter λ_{max} of the dyes on PLA is explained by the effect of the polymer on the spectroscopic properties of the dyes which will be discussed in detail in the next section.

Another interesting property is the build-up characteristics of the dyes on PLA. The build-up properties of disperse dye on PLA has been studied in comparison with those of PET fiber. Fig. 5. and 6. show build-up curves of the selected azo disperse dyes on PLA and PET, respectively. All disperse dyes built up differently on the two fibers.



Dye	Y group	R_1 group	Exhaustion (%)		K/S		λ_{max} (nm)	
			On PLA	On PET	On PLA	On PET	On PLA	On PET
1	H	C_2H_5	99.30	96.43	17.67	11.94	530	550
2	H	$C_2H_4OCOCH_3$	98.30	91.55	9.82	7.97	490	520
3	CH_3	C_2H_5	99.12	98.48	15.41	12.46	540	550
4	CH_3	$C_2H_4OCOCH_3$	99.10	98.27	9.78	8.93	510	520

Table 2. Dyeing properties of azo disperse dyes on polyester fibers when applied at 0.2%owf

On PLA, these dyes exhibited a larger variation in build-up characteristics although their basic molecular structures were the same. At the same time, a less variation in build-up characteristics was found in the case of PET fiber. These results showed that the same set of azo disperse dyes performed differently on PLA as compared with PET. A change in the substituted group on the same basic structure of these azo disperse dyes did affect their build-up properties on PLA whereas this influence of the substituted groups was lower on PET. This property variation observed may be a result of the poorer fiber-dye interaction in the case of PLA.

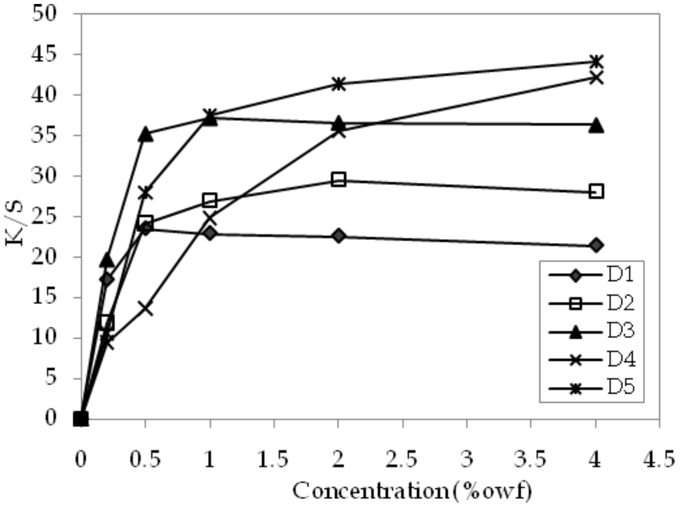


Fig. 5. Build-up curves of azo disperse dyes on PLA fiber (Structures of the dyes are in Table 1.)

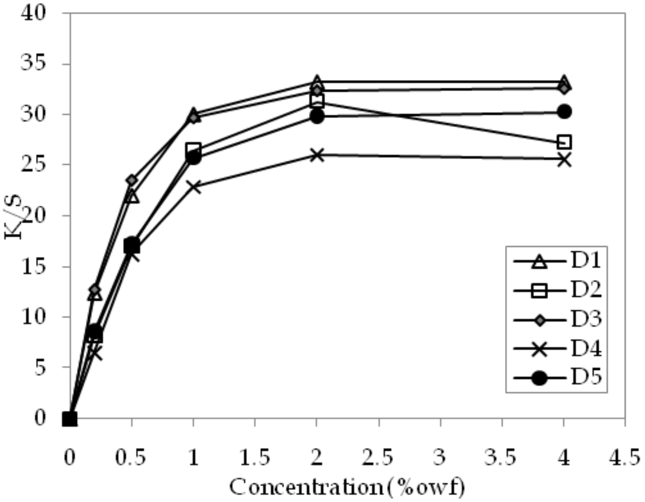
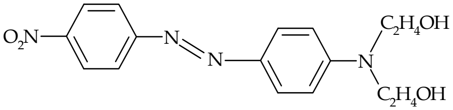


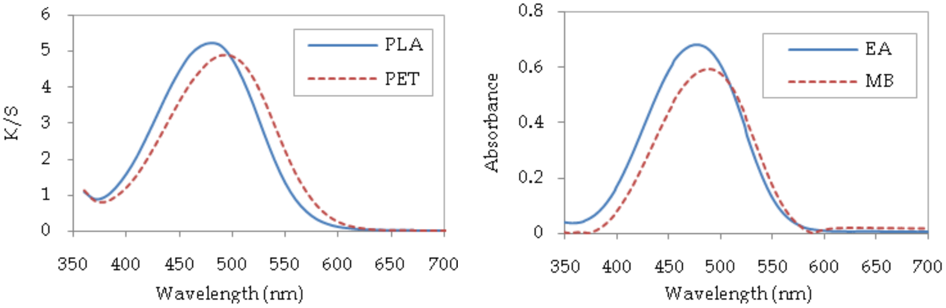
Fig. 6. Build-up curves of azo disperse dyes on PET fiber (Structures of the dyes are in Table 1.)

2.2 Study on the spectroscopic properties of disperse dyes on PLA in comparison with those on PET

PLA and PET polymers have different reflectance properties. As mentioned in the previous section that the different refractive index of the fibers affected the shade of dye obtained on the fibers (Lunt & Bone, 2001). The lower refractive index of PLA enhances a deeper shade as compared with PET. When the dye is applied at the same depth on the two fibers, the brighter shade is observed on PLA. Several studies reported that shades of the disperse dyes observed on PLA differed from those obtained on PET, the orange and red dyes appeared yellower whereas the yellow and blue dyes became greener on PLA (Choi & Seo, 2006; Avinc, 2007). Nakamura et al. studied the absorbance of C.I. Disperse Red 60 on PLA fabric. The results exhibited that the λ_{max} of the dye on PLA occurred at a shorter wavelength (Hypsochromic shift) as compared with that on PET (Nakamura et al., 2001). These works confirm the difference in spectroscopic properties of disperse dyes on these two polyester fibers.

In order to gain a clear understanding on the influence of the polymer on the spectroscopic properties of the dyes, a study has been conducted. The polymer (fiber) is considered as a medium (solvent) having the dye molecules dissolving in. PLA and PET fibers have different molecular characteristics, for example molecular size/structure, polarity, dipole moment, etc. These different molecular properties could influence spectroscopic properties of the dyes that stay in the polymer media. Suesat et al. reported that different spectroscopic properties of azo disperse dyes on these two polyesters could be explained in the same way as a solvatochromic effect. The organic solvents, ethyl acetate and methyl benzoate, having similar molecular structure were selected as representatives of PLA and PET, respectively, for this investigation. The chemical structures of ethyl acetate and methyl benzoate are shown in Table 3. compared with those of PLA and PET, respectively. Refractive indices of ethyl acetate and methyl benzoate are 1.372 and 1.517, respectively (wypych, 2001) being closely similar to those of PLA (1.35-1.45) and PET (1.54). As a chemical structure resemblance of ethyl acetate and methyl benzoate with the two polyesters, they could be used to dissolve disperse dyes and imitate the environment of the dyes in PLA and PET and their influence on the dye could then be monitored (Suesat et al., 2011).





(a) (b)

Fig. 7. The K/S spectra curves of disperse dye in a) PLA and PET; b) ethyl acetate (EA) and methyl benzoate (MB)

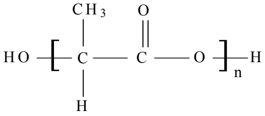
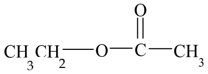
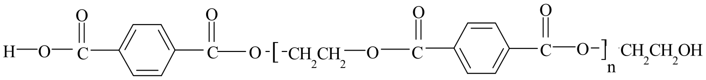
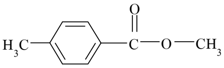
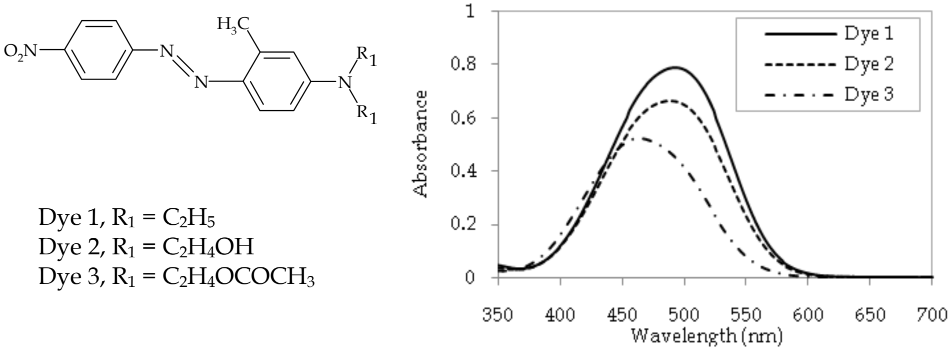
Polymer structure	Solvent Structure
 PLA	 Ethyl acetate
 PET	 Methyl benzoate

Table 3. Chemical structures of ethyl acetate and methyl benzoate versus PLA and PET

The absorption spectral curves of the dyes in the representative solvents are illustrated as seen in Fig. 7.b). The same tendency was noticed when compared the absorbance curves of the dye in the solvents with the K/S curves of the same dye when applied on the polymers (Fig. 7a)). The λ_{max} of the dyes exhibited a hypsochromic shift when dyed on PLA and dissolved in ethyl acetate. About a 10 nm difference was observed between λ_{max} of the dyes on the two fibers and in the two solvents. The shift of λ_{max} on K/S spectra of the dye on PLA and PET, being dyed with the same dye, is a reason for differing in shade of the dyes obtained on the fibers. This change in spectroscopic properties of disperse dyes is affected by the difference in the interaction between the dye molecule and the polymer (solvent). Avinc (2007) mentioned that the difference in λ_{max} values of azo disperse dyes when dyed onto PLA and PET was about 10 nm or higher whilst such a difference was lower in the case of anthraquinone disperse dyes.

When the dyes were dissolved in methyl benzoate and ethyl acetate, the color of the dye solutions was different. This is the effect of the solvatochromism. The solvatochromic effect happened as a consequence of polarity of the solvent used, influencing λ_{max} to shift towards shorter or longer wavelengths depending on types of the interaction between the solvent and the dye molecule in its ground and excited states. For the dye molecules, their excited state is more polar than their ground state. When polar solvent interacts with the molecules in their excited state, it results in a bathochromic shift because the energy gap between their ground and excited states (HOMO-LUMO gap), is lowered (Bamfield, 2001). The polarity of ethyl acetate and methyl benzoate is 0.795 and 0.836, respectively (Wypych, 2001). Thus when a given dye was dissolved in ethyl acetate (less polar), poorer stabilization of the dye's excited electronic state brought about a higher energy gap between the ground and excited states of the dye molecules and a hypsochromic shift was observed, compared with methyl benzoate. The corresponding explanation could be used to describe the influence of the polyester polymers on the spectroscopic properties of the dye.

One more interesting point obtained from Fig. 7.a) and b). is that the magnitude of the spectral curves was higher in the case of PLA and ethyl acetate compared with those of PET and methyl benzoate. This indicates that not only shifting of the dye spectra, but the polymer/solvent also affects the molar absorptivity (ε_{max}) of the dyes.

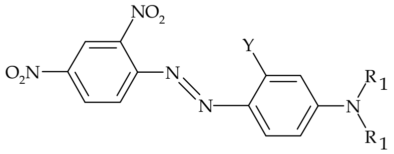


Dye 1, $R_1 = C_2H_5$
Dye 2, $R_1 = C_2H_4OH$
Dye 3, $R_1 = C_2H_4OCOCH_3$

Fig. 8. Absorption spectra of the selected azo disperse dyes in ethyl acetate at concentration of 6.25 mg/l

The substituted group on the dye molecule is also influenced the absorption properties of the dyes. Fig. 8. shows the absorbance curves of the aminoazobenzene based disperse dyes in ethyl acetate. Shift in spectral curves and change in their magnitudes were observed when the substituted groups were changed on the dye molecules. The λ_{max} and ε_{max} values varied depending on the degree of electron donating/withdrawing capacity of the substituted groups.

Table 4. shows the numerical data of the dye properties influenced by the solvents and the polymers. The difference in λ_{max} suggested a different color of the dyes'solutions in the solvents, with a hypsochromic shift being obtained in ethyl acetate. Nakamura et al. found that the maximum absorption of C.I. Disperse Red 60 on PLA appeared at a shorter wavelength than on PET (Nakamura et al., 2001). Apart from the shifting of λ_{max}, the molar extinction coefficients, ε_{max}, were also found to be influenced by the solvents as their surrounding environment, the values being higher in ethyl acetate compared with those in methyl benzoate. Thus, the dye tended to be stronger and brighter in ethyl acetate than in methyl benzoate. This infers that a stronger shade of the dyes is expected on PLA than on PET. The brightness of the dyes is represented by half-band width ($\Delta\lambda_{1/2}$) of the dye spectra. The lower $\Delta\lambda_{1/2}$ values indicate a brighter shade. A brighter shade of the dyes was discovered on PLA, this corresponding to the dye properties observed in the solvents.



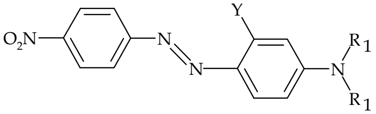
Dye	Y group	R_1 group	Properties in organic solvents				Properties in polyesters			
			λ_{max} (nm)*		ε_{max} ($l\ mol^{-1}cm^{-1}$)*		$\Delta\lambda_{1/2}$ (nm)**		K/S**	
			Ethyl acetate	Methyl benzoate	Ethyl acetate	Methyl benzoate	PLA	PET	PLA	PET
1	H	C_2H_5	522	538	40,600	37,400	104	114	17.67	11.94
2	H	$C_2H_4OCOCH_3$	496	509	33,100	30,100	111	118	9.82	7.97
3	CH_3	C_2H_5	534	552	39,300	37,500	110	114	15.41	12.46
4	CH_3	$C_2H_4OCOCH_3$	509	522	35,800	32,100	114	118	9.78	8.93

*measured on the dye solutions.

**measured on the dyed fabrics with % exhaustion of higher than 90% when dyed at 0.2%owf.

Table 4. The spectroscopic properties of azo disperse dyes measured in the solvents and polyester fiber

The color properties of the disperse dyes on PLA and PET are compared in Table 5. The dyed polyester fabrics with the same level of color yield (K/S=10) showed a differed shade, depicted by the L*, a*, b*, C* and H* values. The L* values representing lightness of shade were higher on PLA, indicating a lighter shade as compared with those on PET. A yellower shade was noticed on PLA with higher b* values whereas the C* (chroma) and H* (hue) were also higher on PLA. This points out that the shade obtained on PLA differs from that on PET. It was reported that the shade difference was observed on PLA and PET when the two fibers were dyed at the same level of visual depth (Suesat et al., 2011). In addition, a brighter shade obtained on PLA was found (Choi & Seo, 2006; Blackburn, 2005).



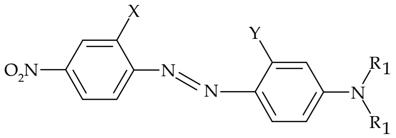
Dye	Y group	R_1 group	Fiber	L*	a*	b*	C*	H*
D1	H	C_2H_5	PET	49.1	50.68	25.56	56.76	26.77
			PLA	55.71	51.32	45.73	68.74	43.01
			Diff.	6.61 L	0.64 R	20.17 Y	11.98 B	16.24 Y
D2	H	C_2H_4OH	PET	54.52	46.44	34.19	57.66	36.36
			PLA	56.67	42.5	44.22	61.32	46.49
			Diff.	2.15 L	-3.94 G	10.03 Y	3.66 B	10.13 Y
D3	H	$C_2H_4OCOCH_3$	PET	56.67	42.5	44.22	61.32	46.49
			PLA	66.55	41.82	65.32	77.56	60.12
			Diff.	10.07 L	-5.13 G	13.94 Y	7.96 B	12.54 Y
D4	CH_3	C_2H_5	PET	43.29	48.74	12.69	50.37	14.6
			PLA	52.18	51.64	30.61	60.03	29.96
			Diff.	8.89 L	2.90 R	17.92 Y	9.66 B	15.36 Y
D5	CH_3	C_2H_4OH	PET	46.5	46.97	23.23	52.4	26.32
			PLA	52.3	48.34	35.66	60.07	36.2
			Diff.	5.80 L	1.37 R	12.43 Y	7.67 B	9.88 Y
D6	CH_3	$C_2H_4OCOCH_3$	PET	51.14	48.21	37.57	61.12	37.93
			PLA	58.97	47.53	53.83	71.81	50.2
			Diff.	7.83 L	-0.68 G	16.26 Y	10.69 B	12.27 Y

**Diff.= the values difference of PLA and PET

Table 5. Color properties of azo disperse dyes applied at visual color yield of 10 on PLA and PET

2.3 Parameters influencing dyeing properties of disperse dyes on PLA

The dyeing properties of disperse dyes on PLA have been studied by many researchers in order to gain an understanding as what the factors affecting dyeability of PLA are. Several papers involved the explanation of disperse dye sorption on polyester by solubility parameter concept (Gerber, 1978; Karst & Yang, 2005; Choi et al., 2010). Gerber stated that the azo disperse dye suited for dyeing polyester fiber should have a closely similar solubility parameter (δ) value to that of the fiber (Gerber, 1978). This concept was later used by Karst & Yang to correlate with disperse dye sorption on PLA fiber. They calculated the δ values of PLA, PET and disperse dyes by means of group contribution method. The δ values of PLA and PET were reported to be 20.2 $(J.cm^3)^{0.5}$ and 21.7 $(J.cm^3)^{0.5}$, respectively. The important point drawn from their work was that the dyes having the δ close to that of the PLA would exhibit a high exhaustion. From their study, the dyes with the δ values below 25.0 $(J.cm^3)^{0.5}$ had high sorption whereas those with δ values above 25.0 $(J.cm^3)^{0.5}$ exhibited lower than 70% sorption on PLA when dyed at 110°C and the dyes with the δ values close to that of PLA were mainly azo dyes. In our work (Suesat et al., 2011), a correlation between the solubility parameter and the dye exhaustion was also established from a set of experimental data obtained from 22 azo disperse dyes on PLA and PET. The δ values were also calculated by means of group contribution methods mentioned in Karst & Yang (2005). The exhaustion of the dyes was acquired experimentally by dyeing at 0.2%owf on PLA and PET fabrics. The correlation between the δ values with the % exhaustion of the dye on PLA has been made as shown in equation (1). The δ values of each azo dye were used to calculate the dye exhaustion in equation (1) and the predicted dye exhaustion was obtained. The predicted values of dye exhaustion were plotted against the exhaustion observed from the experiment as seen in Fig. 10. The linear regression with the R^2 of 0.819 was obtained for the case of PLA whereas the correlation of the same set of azo disperse dyes on PET as shown in equation (2) had a lower R^2 of 0.764. The plot between the predicted and observed dye exhaustion on PET is shown in Fig. 11. The two equations indicate that the solubility parameter correlates well with the degree of exhaustion of azo disperse dye on the fibers. The dye having the solubility parameter close to that of the polymer would have high exhaustion. However, this establishment only experimented on the azo disperse dyes with the basic structure shown in Fig. 9. Application of the correlation for other type of disperse dyes may be impractical as reported by Karst et al. (2007).



Where X = H, Cl, CN and NO_2
Y = H and CH_3
R1 = C_2H_5, C_2H_4OH and $C_2H_4OCOCH_3$

Fig. 9. Structure of the azo disperse dyes used

$$\text{Exhaustion} = 145.282(\pm 5.344) - 2.314(\pm 0.225)\,\delta \tag{1}$$

$$R^2 = 0.819,\ n = 22,\ F\ \text{change} = 90.328,\ s = 2.54$$

The explanation on molecular parameters affecting the dyeability of disperse dyes on polyester was also given by several researchers. Kim & Son described that the degree of disperse dye exhaustion was related to the solubility and hydrophobic/hydrophilic properties of the dyes which was, in turn, varied by the types of substituted group on the dye molecule. The hydrophobic/hydrophilic properties of the dyes could be considered from dipole moment values of the dyes. The dye having low dipole moment (low polarity) tended to be hydrophobic. This would result in their solubility in hydrophobic medium, like polyester fiber (Kin & Son, 2005). In addition, the dye-fiber interaction was reported by Karst et al. to play an important role on the disperse dyeing properties on PLA fiber. The substituted groups on the dye molecule that formed strong interaction with PLA were $-N(C_2H_4OCOCH_3)_2$, $-(CO)_2NC_3H_6OCH_3$, $-SO_2NHC_6H_5$, $-NO_2$, $-CN(NH)C_6H_4$ and $-CH(CO)_2C_6H_4$, while those with –Br and –Cl were among the weakest. The dyes which interacted strongly with PLA would have more negative interaction energy with PLA, bringing a high sorption on the fiber (Karst et al., 2007).

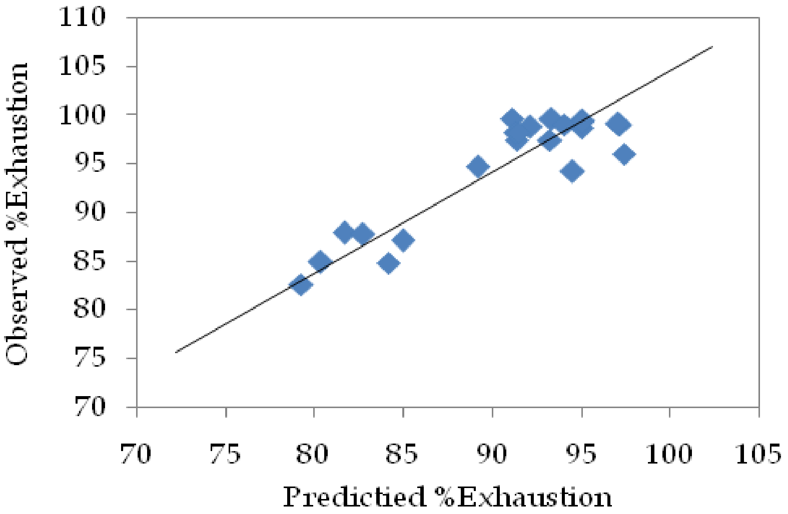


Fig. 10. Relationship between predicted and observed % exhaustion of the azo disperse dyes on PLA fabric

$$\text{Exhaustion} = 173.915(\pm 10.320) - 3.491(\pm 0.434)\ \delta \qquad (2)$$

$$R^2 = 0.764,\ n = 22,\ F\ \text{change} = 64.755,\ s = 4.91$$

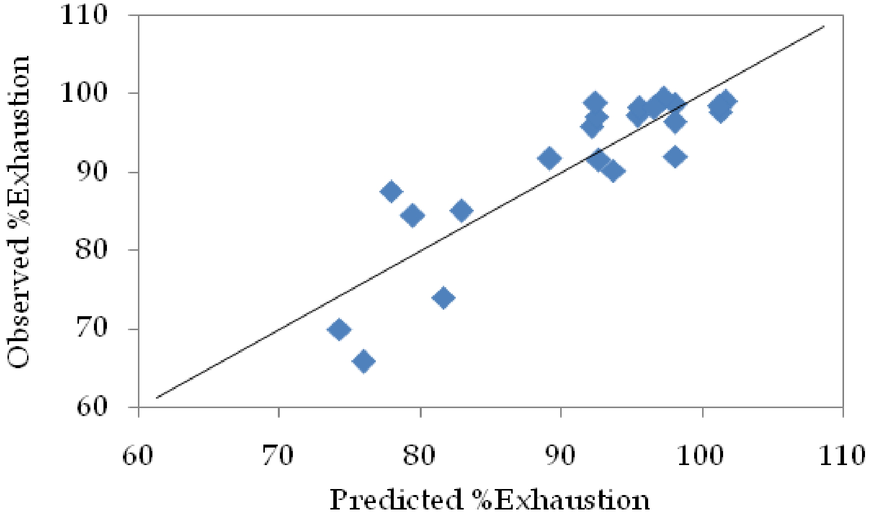
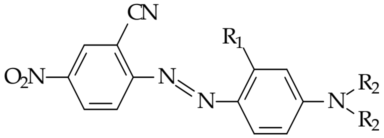


Fig. 11. Relationship between predicted and observed % exhaustion of the azo disperse dyes on PET fabric

3. Color fastness properties of disperse dyes on PLA

3.1 Color fastness of dyed PLA vs PET

The color fastness of dyed PLA in comparison to dyed PET has been studied by many researchers. It has been claimed that the color fastness properties of disperse dyes on PLA were generally lower than those on PET. Yang and Huda studied the wash, rub and light fastness properties of PLA and PET dyed with ten disperse dyes from all three energy levels; low, medium and high-energy dyes. At the same 2%owf, PLA dyeings possessed 0.5 to 1.0 point lower wash fastness than those on the corresponding PET dyeings. The results indicated no significant influence of energy levels of the disperse dyes on the wash fastness grade. They also suggested that the wash fastness of PLA can be effectively improved in the range of 0.5 to 1.5 points by the appropriated reduction clearing process. Both dry and wet rub fastness of dyed PLA were either the same or up to 1.0 point lower than those of PET. Light fastness of disperse dyes on PLA and PET was very similar, even though the dye concentration on PLA was much lower than that on PET (Yang & Huda, 2003). The other factors, besides the concentration of dye, such as the interaction between the dye and fiber, the distribution of the dye in the fiber and the chemical structure of dye and fiber can also play important roles in light fastness (Yang & Huda, 2003; Kim & Park, 2001). The work of Choi and Seo is in agreement with Yang and Huda. They investigated wash and light fastness properties of PLA and PET fabrics dyed with eight disperse dyes at 4%owf. The PLA dyeing exhibited the same or 0.5 to 1.0 point lower wash fastness than its PET counterpart. Light fastness for seven of the eight dyes observed on PLA compared with PET showed no difference. There was no influence of the chemical classes of the dyes investigated, i.e. nitrodiphenylamine, monoazo and anthraquinone, on the light fastness. However, the differences in color (ΔE^*) upon light fastness testing were greater in the case of the PLA dyeing as compared with PET (Choi & Seo, 2006). Choi et al. investigated the wash and light fastness of PLA dyed with the commercial disperse dyes that were initially intended for the production of high light fastness polyester fabrics or for cellulose diacetate dyeing. The wash fastness results in terms of staining to acetate and nylon fabrics showed that the PLA dyeings were 1.0 up to 2.0 points lower than the PET counterparts. The significantly higher diffusivity of disperse dyes was allowed more in PLA than in PET. Therefore, the greater amount of dyes was able to migrate from the PLA fabric during wash fastness testing and stained heavier on the adjacent fabric, leading to lower wet fastness properties. The light fastness rating of PLA dyeings was 0.5 to 1.0 grey scale units lower than the corresponding PET dyeings because PLA allowed more UV transmittance than PET. Dorospers G/YEL KBGL was recommended as a good choice for dyeing PLA to meet the super light fastness requirement (Choi et al., 2007). Mogi et al. investigated the light fastness of monoazo and anthraquinone disperse dyes on PLA fabrics using a carbon arc light source. The results indicated that the photofading behaviors of disperse dyes increased with increasing the exposure time. Moreover, a deeper color fabric tended to give a higher light fastness than a paler color one which indicated that the light fastness depended on the concentration of dye inside the fabric (Mogi et al., 2001a, 2001b). Batch et al. reported that PLA dyed with C.I. Disperse Red 167:1, C.I. Disperse Blue 79 and Serilene Black RFS in super critical carbon dioxide gave good to very good wash and rub fastness. They also suggested the after-clearing process of dyed PLA in order to obtain high wet fastness properties (Batch et al., 2006). Our work with light fastness of monoazo dyes on PLA and PET fabrics, as shown in Table 6, also showed that the dyed PLA exhibited slightly lower light fastness properties, about 0.5 to 1.0 point, than the dyed PET.



Dye	R_1	R_2	Light fastness	
			PLA	PET
1	H	C_2H_4OH	3	3-4
2	H	$C_2H_4OCOCH_3$	3-4	4-5
3	CH_3	C_2H_4OH	3	3-4
4	CH_3	$C_2H_4OCOCH_3$	4	4-5

Table 6. Light fastness of monoazo disperse dyes 1-4 on PLA and PET

Color fastness is also correlated with the chemical structures of disperse dyes on PLA. The monoazo disperse dyes having cyanoethyl or acetoxyethyl group in the coupling component provided high light fastness properties such as C.I. Disperse Red 50, C.I. Disperse Red 82, and C.I. Disperse Orange 30. Cyano and chloro groups had a positive effect on the light fastness, while methyl group showed a negative effect (Mogi et al., 2001a). Dyes 1 and **3** in Table 6. containing acetoxyethyl groups (R_2) also showed better light fastness properties. A methyl group (R_1) had no significant effect on the light fastness of the dye on PLA and PET fabrics. Phenoxy substituents on anthraquinone disperse dyes, such as C.I. Disperse Red 127 and C.I. Disperse Violet 26, showed high light fastness properties on PLA fabrics (Mogi et al., 2001b). Wash and light fastness properties of the substituted aminoanthraquinone disperse dyes on PLA were reported by He et al. The substituted amino groups had little effect on the wash fastness, but obviously influenced the light fastness. The results showed that all selected substituted amino groups gave good wash fastness ratings. Light fastness was higher with the introduction of aromatic amino or cyclo-fatty amino groups into the anthraquinone disperse dyes. In addition, the longer the aliphatic fatty amino group, the lower the light fastness on PLA was (He et al., 2009).

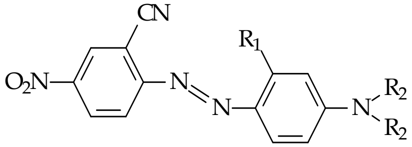
3.2 Thermal migration of disperse dyes on PLA

Thermal migration of disperse dyes is the movement of dye during post-heat treatment as a result of the breakage of the interaction between dye and fiber, leading to an accumulation of dye at the fiber surface and some limited sublimation of the dye to the bordering atmosphere. Even if the loose surface dyes were reduction cleared after dyeing, the heat treatment can promote the diffusion of the dye inside the fiber to fiber surface because of weak interactions between polyesters and disperse dyes which are mainly van der Waals forces and hydrogen bonding. A heat treatment for PLA fabrics is generally either to provide dimensional stability or in the application of a chemical finishing agent. The degree of thermal migration of a disperse dye is an important factor in determining the subsequent wet fastness properties of PLA fabrics (Avinc et al., 2009; Kim et al., 2004; Phillips et al., 2004b).

Phillips et al. reported that the wet fastness properties (wash and perspiration fastness) of dyed PLA fabric, dyed with three blue azo disperse dyes, were the same before heat treatment with almost no staining on the adjacent nylon. After the PLA fabric was heatset for 30 s at 130°C, both wash and perspiration fastness properties became lower as compared with the non-heatset counterpart. In order to determine the amount of dye migrated to the fiber surface, the heatset fabric was immersed in cold toluene and then the absorbance of the solution was measured at the assigned time. The amount of dye at the fiber surface was estimated from the extrapolated absorbance at time, t=0 min. The difference between the amounts of dyes at the fiber surface before and after heat treatment represented the amount of dye that had migrated to the fiber surface on heat treatment. In addition, the amount of dye lost from PLA fabric during heat treatment due to sublimation to the atmosphere was estimated from a monochlorobenzene extract containing both dye and PLA substrate. The calculation of the amount of lost dye via sublimation was also from the difference between the amount of dye on PLA fabric before and after heat treatment. As a result of heat treatment, the wet fastness properties reduced for all three disperse dyes studied. The amount of dye migrated to the PLA fiber surface was about 1.4%. The authors suggested that the high degree of thermal migration of the disperse dyes at the surface of PLA was because the absence of π-π bonding forces between the disperse dye and the polymer chain. They also concluded that the wet fastness of the heatset PLA fabric was not directly proportional to the amount of disperse dyes that has migrated to the fiber surface (Phillips et al., 2004b). Avinc et al. investigated the influence of different heat treatment conditions on the wet fastness properties viz. wash, alkaline perspiration and wet rub fastness of three red disperse dyes (Serilene Red 3B-LS, Foron Rubine S-2GFL and Dianix Deep Red SF) on PLA fabric. The wet fastness properties of PLA were reduced after subjecting the fabric to the heat treatment process due to thermal migration of dye on PLA (Avinc et al., 2009). The amount of dye thermally migrated on the PLA fabric finished with different softeners was examined in terms of their color fastness (Avinc, 2007). No clear relationship was found between the hydrophobic nature of the disperse dye and the ionicity character of the softener on the color fastness of finished PLA fabric. For example, softened PLA fabrics dyed with C.I. Disperse Red 167.1 showed greater thermal migration, resulting in lower color fastness than the corresponding PET fabrics. In contrast, softened PLA fabrics dyed with Dianix Deep Red SF exhibited less thermal migration, leading to higher color fastness than the corresponding PET fabrics. The application process also influenced the thermal migration of disperse dyes. Softened PLA fabrics from the exhaust process gave higher wet fastness up to 1.25 points more than the one from the padding process. The exhaust method allowed less thermally migrated dye onto the PLA surface than the pad method (Avinc et al., 2009). Dry heat fastness of Dyes 1-4 on PLA and PET fabrics with K/S = 10 was evaluated according to ISO 105-P01:2006(E)(150°C) as shown in Table 7. The dry heat fastness properties of the dyed PLA fabric exhibited 0.5 grey scale units being lower than those of the dyed PET fabric. The dye migrated to the fiber surface by thermal migration, leading to lower dry heat fastness properties.

Our work on thermal migration of disperse dye on PLA fabric was carried out by using six commercial disperse dyes from all three different sublimation classes. The quantity of dye migrated to the fiber surface and dye lost by sublimation to the atmosphere after heat treatment at 130°C for 30 s was investigated according to the procedure in Phillips et al.

(2004b). Moreover, the wet fastness properties (wash, perspiration, and rub) were compared between the dyed PLA before and after heat treatment. Table 8. showed that the amount of dye migrated to the PLA surface as a result of the heat treatment being in a range of 0.04 to 3.04%. However, the amount of disperse dye that has migrated to the PLA fiber surface was not dependent on the sublimation class. Besides the molecular size of the dye, the other parameters such as the chemical structure, polarity and hydrophobicity of the dye can also affect the movement of disperse dye from the interior of the fiber to the surface. Loss of disperse dye due to sublimation was observed only from the low energy dyes, approximately 2%. Low-energy dyes tended to loss via sublimation easier than the other two higher energy classes. Table 9 illustrated the wet fastness properties of the dyed PLA after heat treatment which was slightly lower than the one before the treatment. The migrated dyes as a result of heat treatment led to lower wet fastness properties of dyed PLA fabric. Nevertheless, the wet fastness properties of dyed PLA fabric were not directly proportional to the amount of dye migrated to the fiber surface.



Dye	R_1	R_2	Color change (PLA/PET)	Staining (PLA/PET)	
				Nylon	Polyester
1	H	C_2H_4OH	4-5/4-5	4-5/4-5	4-5/4-5
2	H	$C_2H_4OCOCH_3$	4-5/4-5	4-5/4-5	4-5/4-5
3	CH_3	C_2H_4OH	4-5/4-5	4/4-5	4-5/4-5
4	CH_3	$C_2H_4OCOCH_3$	4-5/4-5	4/4-5	4-5/4-5

Table 7. Heat fastness of monoazo disperse dyes 1-4 on PLA and PET

Dye	Commercial name	Sublimation class	Dye migrated to surface (%)	Dye lost by sublimation (%)
1	Dianix Orange E-3R	Low energy	3.04 ±0.12	2.12±0.13
2	Dianix Blue E-R 150%	Low energy	0.37 ±0.07	1.66± 0.43
3	Dianix Rubine SE-B	Medium energy	0.44 ±0.10	0
4	Dianix Yellow Brown XF	Medium energy	0.04 ±0.003	0
5	Dianix Yellow Brown S-2R 150%	High energy	0.25 ±0.06	0
6	Dianix Red S-BEL	High energy	0.47 ±0.06	0

Table 8. The amounts of dye migrated to the fiber surface and lost by sublimation on heat treatment of PLA fabrics

Dye	Wash* (C06/B2S, 50°C)		Acid perspiration* (E04)		Alkaline perspiration* (E04)		Rub* (X12)	
	PET	Nylon	PET	Nylon	PET	Nylon	Dry	Wet
1	4 (4)	2-3 (2-3)	4-5 (4-5)	4 (4)	5 (4-5)	4 (3-4)	4-5 (4)	4 (3-4)
2	3 (3-4)	2 (1-2)	4-5 (4)	4-5 (3)	4-5 (4-5)	4 (4)	5 (4-5)	4-5 (4)
3	3-4 (3)	3 (2-3)	4-5 (4-5)	4-5 (4-5)	4-5 (4-5)	4-5 (4-5)	4-5 (4-5)	4 (4)
4	4 (3-4)	4-5 (4)	4-5 (4)	4 (3)	4-5 (4-5)	4 (3-4)	5 (5)	4-5 (4-5)
5	4 (3-4)	4-5 (4)	4 (3-4)	3-4 (3)	3-4 (3-4)	3 (2-3)	5 (5)	4-5 (4-5)
6	4 (2-3)	4 (2-3)	4-5 (4-5)	4-5 (4)	4-5 (4-5)	4 (4)	4-5 (4-5)	4-5 (4-5)

* Values in parentheses are those after heat treatment for 30 s at 130°C

Table 9. Wet fastness properties of disperse dyes on PLA before and after heat treatment

4. Conclusion

With promising properties, PLA has been intensively studied in order to gain its maximal benefit as a textile fiber for the textile industry. PLA fiber possesses many comparable properties to the conventional polyester, PET, but its thermal and alkaline sensitivities are inferior, therefore, milder processing conditions used in textile production are suggested for PLA. PLA can be dyed with disperse dyes to provide a stronger and brighter shade as compared with PET. The differences in dyeing properties of disperse dyes on PLA and PET are explained to be a result of different interactions between the polymer (fiber) and the dye molecule. The polymers (PLA and PET) are influential on the spectroscopic properties of the dyes. PLA provides less stabilization of the dye molecules in its excited states as compared with the case of PET, consequently, different shade and strength of the dyes are observed. The difference in dyeing properties of disperse dyes on PLA and PET was explained by several researchers that the key factor affecting this was the solubility parameter. The dye having a solubility parameter close to that of PLA, would exhibit high sorption on the fiber whereas those with solubility parameter being largely different from the fiber, would have low sorption. A new concept was proposed that there were other important factors, apart from solubility parameters, being influential on the dyeability of disperse dyes, for example hydrophilic/hydrophobic nature of the dye and the dye-fiber affinity. A study on color fastness of disperse dyes on PLA in comparison with PET indicates that fastness properties of the dyed PLA is slightly lower (about 0.5-1.0 unit of grey scale) than those on PET. A higher degree of thermal migration of the dye was found on PLA after subjected to heat setting or chemical softening, resulting in a poorer wet fastness of the dyed PLA as compared with PET. A greater degree of thermal migration of the dye on PLA is explained to be due to higher dye diffusivity and lack of π-π bonding between the dye molecule and the polymer (fiber).

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17

Application of Cyclodextrins in Textile Dyeing

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1. Introduction

1.1 Dyeing auxiliaries

Auxiliaries are compounds which are not an integral part of the dyeing process but by adding them to the dye bath the dyeing can be improved. The main functions of auxiliaries are to prepare or improve the substrate in readiness for colorants (by wetting, providing sorption sites, improving or resisting the migration of dyes), to stabilize the application media (by improving dye solubility, stabilizing a dispersion or solution), to protect or modify the substrate (by creating or resisting dyeability, protecting against the effects of temperature and other processing conditions), to improve the dyes fastness (by various after-treatments) and to enhance the properties of laundering formulation. The main ranges of dyeing auxiliaries are: crease inhibitors, wetting agents, defoamers, diffusion accelerants, carriers, dispersing agents, dye-protective agents, fibre-protective agents, fixing agents, levelling agents, migration-inhibiting agents, pH regulators, buffers, sequestering agents, UV absorbers, fibre stabilizers, UV protective agents and wash-off agents.

1.2 Levelling agents

For all dye-fibre systems, level dyeing problems can be divided into either *gross unlevelness throughout the substrate* which is related to the dyeing process or *localized unlevelness* which is related to non-uniformity of the substrate (Burkinshaw, 1995). The receptivity of different regions of a fibre or of different fibres in a mixed yarn may not be the same for a given dyestuff, thus causing uneven dyeing. These undesired effects can be eliminated or diminished by the use of levelling agents. Levelling agents usually contain functional groups which are similar to those by which the dyestuffs are attached to the fibre. There are two mechanisms involved in the activities of levelling agents: there is a competition for sites on the fibre between dyestaff and levelling agent; or the agents can slow down the migration of dye by forming complex micelles with the dyestuff molecules which are released slowly to the fibre. A very large number of levelling agents have been developed in attempts to get the right balance of properties for particular types of dyestuff and fibres, cyclodextrins could be one of the most promising.

2. Supramolecular chemistry

Supramolecular chemistry is the discipline of chemistry which involves all intermolecular interactions where covalent bonds are not established between the interacting species: i.e., molecules, ions, or radicals. The majority of these interactions are of the host-guest type. Among all potential hosts, the cyclodextrins seem to be the most important ones, for the following reasons (Szejtli, 1998; Vögtle, 1991).

1. Cyclodextrins are seminatural products; they are produced from a renewable natural material, starch, by a relatively simple enzymatic conversion.
2. They are produced in thousands of tons per year by environmentally friendly technologies.
3. Because of their huge production, the initially high prices of cyclodextrins have dropped to levels where they become acceptable for most industrial purposes. The total output of β-cyclodextrin is in excess of 1000 tons/year, and the price is only several dollars per kilogram, depending on quality and delivered quantity. Also α- and γ-cyclodextrins, as well as several derivatives, (hydroxypropyl-β-cyclodextrin and -γ-cyclodextrin, randomly methylated α- and β-cyclodextrin, maltosyl-β-cyclodextrin, acetylated cyclodextrins, etc.) are produced industrially. A large number of other derivatives are available as fine chemicals, and used in various chromatographic methods, or are studied as potential drug carriers, stabilizers, catalysts, etc.
4. Cyclodextrin molecules are of a great interest for scientists because of their capacity to include guest molecules in their cavities. Such inclusion is considered as a molecular encapsulation and it results in better stability of guests to air, heat or light, higher water solubility, possible increase in bioavailability, slow release and others.
5. In general, cyclodextrins are not toxic, but any of their toxic effects are of secondary character and can be eliminated by selecting the appropriate cyclodextrin type or derivative or mode of application.

2.1 Cyclodextrins

Cyclodextrins (CDs) comprise a family of three well-known industrially produced substances. The practically important, industrially produced CDs are the α-, β-, and γ-cyclodextrins (Fig. 1). There are some rare, minor cyclic oligosaccharides as well which are due to their costs not applicable to textiles (Vögtle, 1991).

The three major cyclodextrins are crystalline, homogeneous, nonhygroscopic substances, which are torus-like macro-rings built up from glucopyranose units. The α-cyclodextrin (Schardinger's α-dextrin, cyclomaltohexaose, cyclohexaglucan, cyclohexaamylose, α-CD, ACD, C6A) comprises six glucopyranose units, β-cyclodextrin (Schardinger's β-dextrin, cyclomaltoheptaose, cycloheptaglucan, cycloheptaamylose, β-CD, BCD, C7A) comprises seven such units, and γ-cyclodextrin (Schardinger's γ-dextrin, cyclomaltooctaose, cyclooctaglucan, cyclooctaamylose, γ-CD, GCD, C8A) comprises eight such units (Fig. 1). Cyclodextrins can be obtained by enzymatic degradation of starch. In this process compounds with six to twelve glucopyranose units per ring are produced. Depending on the enzyme and the way the reaction is controlled, the main product is α, β or γ-cyclodextrin (6, 7 and 8 glucopyranose units, respectively). They are of circular and conical conformation, where the height is about 800 pm. The inner diameter of the cavity varies from 500 to 800 pm.

Crystal structure analysis has demonstrated that all glucopyranose units in the torus-like ring possess the thermodynamically favoured chair conformation because all substituents are in the equatorial position. As a consequence of the 4C1 conformation of the glucopyranose units, all secondary hydroxyl groups are situated on one of the two edges of the ring, whereas all the primary ones are placed on the other edge. All secondary hydroxyl groups are situated on the larger side of the two edges of the ring, whereas all the primary ones are placed on the smaller side of the ring. These hydroxyl groups ensure good water solubility. The cavity is lined by the hydrogen atoms of C3, by the glycosidic oxygen bridges and hydrogen atoms of C5. The nonbonding electron pairs of the glycosidic oxygen bridges are directed toward the inside of the cavity producing a high electron density there and because of this the inner side of the cavity has some Lewis base characteristics. The C-2-OH group of one glucopyranose unit can form a hydrogen bond with the C-3-OH group of the adjacent glucopyranose unit. In the cyclodextrin molecule, a complete secondary belt is formed by these H bonds, therefore the β-cyclodextrin has a rather rigid structure. Because of this arrangement, the interior of the toroids is not hydrophobic but considerably less hydrophilic than the aqueous environment and thus able to host hydrophobic molecules. Cyclodextrins behave more or less like rigid compounds with two degrees of freedom, rotation at the glucosidic links C4-O4 and C1-O4 and rotations at the O6 primary hydroxyl groups at the C5-C6 band.

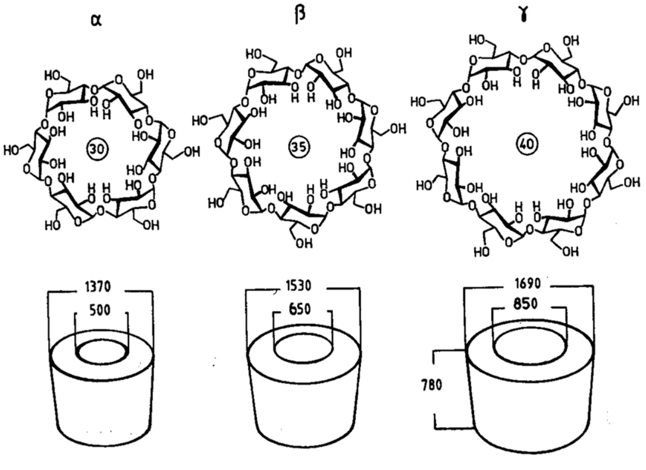


Fig. 1. Structure and dimensions of α-, β- and γ-cyclodextrin

The intramolecular hydrogen bond formation is probably the explanation for the observation that β-cyclodextrin has the lowest water solubility of alls. The hydrogen-bond belt is incomplete in the α-cyclodextrin molecule, because one glucopyranose unit is in a distorted position. Consequently, instead of the six possible hydrogen-bonds, only four can be established fully. γ-Cyclodextrin is a noncoplanar with more flexible structure; therefore, it is the most soluble of the three cyclodextrins. Fig. 2 shows a sketch of the characteristic structural features of cyclodextrins. On the side where the secondary hydroxyl groups are situated, the diameter of the cavity is larger than on the side with the primary hydroxyls, since free rotation of the primary hydroxyls reduces the effective diameter of the cavity (Connors, 1997).

2.2 Toxicological considerations

Since fabrics are in direct contact with human skin, toxic specification of cyclodextrins have been studied (Martin Del Valle, 2004; Dajstjerdi & Montazer, 2010). Since year 2000, β-cyclodextrin has been introduced as a food additive in Germany. With respect to OECD experiments, this compounds has shown no allergic impact.

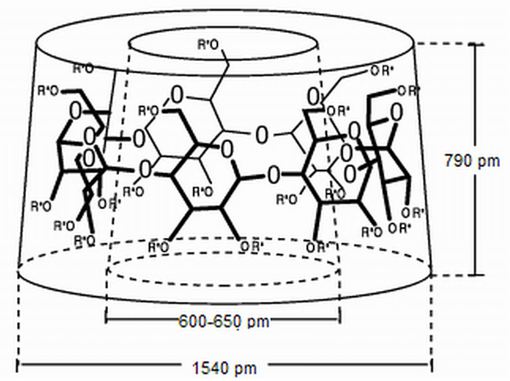


Fig. 2. Structural features of β-cyclodextrin

In general, the natural cyclodextrins and their hydrophilic derivatives are only able to permeate lypophilic biological membranes, such as the eye cornea, with considerable difficulty. All toxicity studies have demonstrated that orally administered cyclodextrins are practically non-toxic, due to lack of absorption from the gastrointestinal tract. The main properties of β-cyclodextrin (β-CD), the most important cyclodextrin in textile application are: less irritating than α-cyclodextrin after i.m. injection, binds cholesterol, small amount (1-2%) is adsorbed in the upper intestinal tract, no metabolism in the upper intestinal tract, metabolised by bacteria in caecum and colon, LD50 oral rat > 5000 mg/kg, LD50 i.v., rat: between 450 – 790 mg/kg, however, application of high doses may be harmful and is not recommended.

2.3 Inclusion complex formation

The most notable feature of cyclodextrins is their ability to form solid inclusion complexes (“host–guest” complexes) with a very wide range of solid, liquid and gaseous compounds by a molecular complexation.

In these complexes a guest molecule is held within the cavity of the cyclodextrin host molecule. Complex formation is a dimensional fit between host cavity and guest molecule. The lipophilic cavity of cyclodextrin molecules provides a microenvironment into which appropriately sized non-polar moieties can enter to form inclusion complexes. No covalent bonds are broken or formed during formation of the inclusion complex. The main driving force of complex formation is the release of enthalpy-rich water molecules from the cavity. The water molecules located inside the cavity cannot satisfy their hydrogen bonding potentials and therefore are of higher enthalpy. The energy of the system is lowered when these enthalpy–rich water molecules are replaced by suitable guest molecules which are less polar than water. In an aqueous solution, the slightly apolar cyclodextrin cavity is occupied by water molecules which are energetically unfavoured, and therefore can be readily substituted by appropriate "guest molecules" which are less polar than water. This apolar–apolar association decreases the cyclodextrin ring strain resulting in a more stable lower energy state. The dissolved cyclodextrin is the "host" molecule, and the "driving force" of the complex formation is the substitution of the high-enthalpy water molecules by an appropriate "guest" molecule.

The binding of guest molecules within the host cyclodextrin is not fixed or permanent but rather is a dynamic equilibrium. Binding strength depends on how well the 'host–guest' complex fits together and on specific local interactions between surface atoms. Complexes can be formed either in solution or in the crystalline state and water is typically the solvent of choice. Inclusion complexation can be accomplished in a co-solvent system and in the presence of any non-aqueous solvent (Martin Del Valle, 2004). Generally, one guest molecule is included in one cyclodextrin molecule, although in the case of some low molecular weight molecules, more than one guest molecule may fit into the cavity, and in the case of some high molecular weight molecules, more than one cyclodextrin molecule may bind to the guest. In principle, only a portion of the molecule must fit into the cavity to form a complex. Cyclodextrin inclusion is a stoichiometric molecular phenomenon in which usual only one guest molecule interacts with the cavity of the cyclodextrin molecules to become entrapped. 1:1 complex is the simplest and most frequent case. However, 2:1, 1:2, 2:2, or even more complicated associations, and higher order equilibrium exist almost always simultaneously.

Inclusion in cyclodextrins has a profound effect on the physical and chemical properties of guest molecules as they are temporarily locked or caged within the host cavity (Martin Del Valle, 2004).

These properties are:

- solubility enhancement of highly insoluble guests,
- stabilisation of labile guests against the degradative effects of oxidation, visible or UV light and heat,
- control of volatility and sublimation,
- physical isolation of incompatible compounds,
- chromatographic separations,
- taste modification by masking off flavours, unpleasant odours
- controlled release of drugs and flavours
- removal of dyes and auxiliaries from dyeing effluents
- retarding effect in dyeing and finishing baths
- protection of dyes from undesired aggregation and adsorption.

Therefore, cyclodextrins are used in food, pharmaceuticals, cosmetics, environment protection, bioconversion, packing and the textile industry.

The ring structure of cyclodextrins allows them to act as hosts and form inclusion compounds with various small molecules. Such complexes can be formed in solution, in the solid state, as well as when cyclodextrins are linked to a solid surface where they can act as permanent or temporary hosts to those small molecules that provide certain desirable attributes such as adsorption of dyestuff molecules, fragrances or antimicrobial agents. This "molecular encapsulation" is already widely utilized in many industrial products, technologies, and analytical methods.

3. Cyclodextrins in textile applications

3.1 Cyclodextrins in textile dyeing processes

Cyclodextrins can be considered as a new class of auxiliary substances for the textile industry. Cyclodextrins can be used for textile application because of their natural origin and their biodegradability. There are no published studies about the influence of cyclodextrin/dye complexations on human skin, but we can use some studies from the field of cosmetics (Förster et al., 2009). Skin is a heterogeneous membrane; lipophilic on its surface and hydrophilic in its deeper layers. The stratum corneum is a highly resistant barrier which limits the penetration of drugs into the skin because its structure contributes to its function both as a barrier to water loss and as a barrier against the external environment. The skin's barrier function is therefore important in considering both the transdermal delivery of drugs and in making a risk assessment following dermal exposure to chemicals and dyestuffs. The major challenge for dermal or transdermal delivery is to "tune" the vehicle in which the drug is entrapped in order to reach its target site i.e. the skin surface, the skin compartments or the systemic circulation. The study of the stratum corneum structure is essential for understanding the barrier function of the skin. There are numerous formulation parameters and formulation systems which influence the penetration of active compounds. Here is one example: in cosmetic applications complexation has improved the photostability of sunscreens (Scalia et al., 1998; Scalia et al., 1999) but its influence on skin penetration behaviour is a compromise. There is an increasing effect due to better solubility (Vollmer et al., 1994; Legendre et al., 1995) but a decreasing effect resulting from using molecules with large relative molar masses (equivalent to more than 1000 Da) (Sarveiya et al., 2004; Simeoni et al., 2004; Williams et al., 1998). A recent trend is the use of modified cyclodextrin molecules. The most commonly used is hydroxypropyl-β-cyclodextrin (HP-β-CD). It is able to form hydrophilic inclusion complexes with many lipophilic compounds in aqueous solution, which can enhance the aqueous solubility of lipophilic drugs without changing their intrinsic abilities to permeate lipophilic membranes. An interesting example is sunscreen delivery onto a skin surface. Simeoni et al. have investigated the penetration of oxybenzone, a lipophilic sunscreen agent, on human skin, from HP-β-CD and from SBE-β-CD, a sulfobutylether-β-cyclodextrin (Simeoni et al., 2004; Simeoni et al., 2006). The authors showed that SBE-β-CD had the greater solubilizing activity on oxybenzone, a highly lipophilic sunscreen, (a 1049-fold increase) when compared with the use of HP-β-CD (a 540-fold increase). The sunscreen penetration to the deeper living layers of the skin was remarkably decreased (1.0% and 2.0% of applied dose for epidermis and dermis respectively) compared with the unbound OMC (octyl methoxycinnamate) formulation used as control and with OMC loaded HP-β-CD (~5%). This result is interesting because modified cyclodextrin carrier can promote the solubilising and photostabilising properties of sunscreen agents while staying on top of the skin where they are intended to act (Simeoni et al., 2006). Even with modified complexes, conflicting results have been found in the literature concerning their effect to promote or decrease skin penetration of drugs. But there still remain the problems of their molar mass and their limited capacity to penetrate into the skin (Cal & Centkowska, 2008). In the review by Förster and co-workers (Förster et al., 2009) the newest examples have been given and discussed. But their conclusion is that the effects of various systems on the skin still cannot be completely explained. One of the main problems is the molar mass of active components (»guests«) and their limited capacity to penetrate into the skin.

Further, for the textile use it is very important that chemical oxygen demand of cyclodextrins in the waste-water is lower or at least similar to the usual textile auxiliaries; while the chemical oxygen demand for polyester is about 2020 mg/g, for a fatty alcohol polyglycol ether is 1930 mg/g and for β-cyclodextrin is 1060 mg/g (Szejtli, 2003; Knittel et al., 1992).

Cyclodextrins play on important role in textile scientific research area and should play a significant role in the textile industry as well to remove or substitute various auxiliaries or to prepare textile materials containing molecular capsules which can immobilize perfumes, trap unpleasant smells, antimicrobial reagents and flame retardants. A rather new idea of using cyclodextrins in textile industry is the preparation of textile filters containing cyclodextrins for separate filtration/adsorption of POPs (persistent organic pollutants) from waste water.

As cyclodextrins can incorporate into their cavity different dyes, they should be able to act as retarders in a dyeing process. Variables which could be changed during the finishing process, dyeing, printing or washing to achieve the desired properties of the finished goods are besides the efficient pretreatment of the textile material, pH, temperature and addition of electrolytes, the addition of different auxiliaries. Various auxiliary products are used in wet finishing processes, especially in dyeing and washing. One of the dyeing auxiliary products are levelling agent. Levelling agents help to achieve uniform dyeing by slowing down the dye exhaustion or by dispersing the dye taken by the fibre in a uniform way. They can be classified into two groups: agents having affinity to the dye and agents having affinity to the fibre. Agents having affinity to the dyes slow down the dyeing process by forming complexs with the dyes. The complex compound moves slower compared to the dye itself; at higher temperature the dye is released and it can be fixed to the fibre. Application of cyclodextrins as levelling agents having affinity to dyestuffs has been investigated in research work about dyeing of cellulose fibres with direct dyes by using an exhaust method (Cireli & Yardakul, 2006) where β-cyclodextrin was tested as a dye complexing agent. β- cyclodextrins as a dye retardant in the dyeing of PAN fibres with cationic dyes was studied (Voncina et al., 2007); further it was reported that some azo disperse dyes formed inclusion complexes with α-, β- and γ-cyclodextrins (Shibusawa et al., 1998). Improvement of colour uniformity was achieved when PA 66 and microfiber PP 6 in the presence of cyclodextrin were dyed (Savarino et al., 1999; Savarino et al., 2000). The effect of β-cyclodextrin as an additive in the dyeing of polyester with disperse dyes was studied (Carpignano et al., 2010). It is reported that cyclodextrins can form inclusion complexes with some suphonated azo dyes (Zhang et al., 2006).

Cireli with co-workers used β-cyclodextrin and eight different direct dyestuffs with known chemical structures. After a certain period of time of exhaust dyeing, a dynamic equilibrium between the dye and β-cyclodextrin was established thus the amount of the dyestuff adsorbed by the fibres does not increase even though the dyeing procedure continued. In this research it is shown that the use of β-cyclodextrin as a levelling reagent is limited according to the size of the dyestuffs applied and according to the substituents on the dyestuff molecules which can hinder or enable the inclusion formation (Cireli & Yardakul, 2006).

Cationic dyes have very low migration power on polyacrylonitrile (PAN) fibres due to their high substantivity and rapid uptake over a small temperature range above the T_g of the fibre. Colour levelness can be improved by the use of different retarding reagents. In our past research work (Voncina et al., 2007) β-cyclodextrin was investigated as a retarding agent in the dyeing of PAN fibres with cationic dyes. The retarding effect of β-cyclodextrin was compared to that of a commercial product based on a quaternary ammonium compound (N-tetra-alkyl ammonium methyl sulphate) Tinegal MR New by Ciba. The cationic dye, C.I. Basic Blue 41, is schematically presented in Fig. 3.

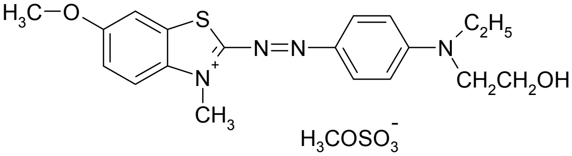


Fig. 3. Structure of C.I. Basic Blue 41

Quality dyeing was obtained and the values of bath exhaustion were significantly improved when β-cyclodextrin was used as a retarding reagent compared to the cationic retarding reagent based on the quaternary ammonium compound (Fig. 4).

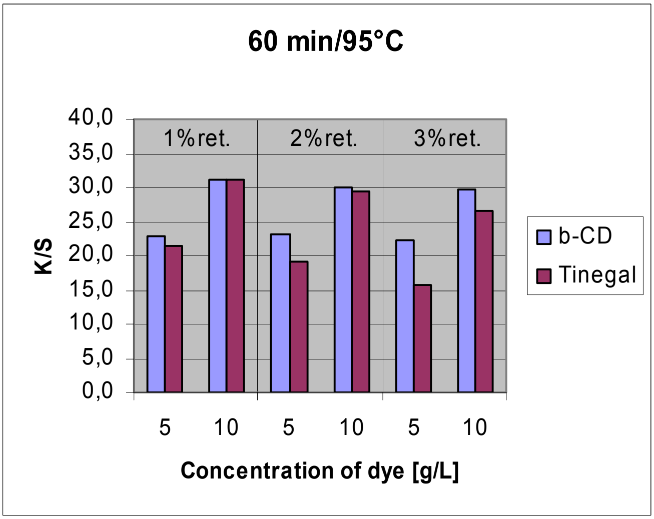


Fig. 4. K/S values of PAN fabrics dyed with different concentrations of dye (5 and 10 g/l) and retarding reagents: β-cyclodextrin and commercial reagent (1, 2 and 3%); dyeing procedure: 60 minutes at 95 °C

Significant improvement of colour levelness (Fig. 5) and some improvements in colour depth have been found when PAN fibres were dyed in the presence of β-cyclodextrin compared to dyeing in the presents of commercial retarding reagent. These improvements are more significant when higher concentrations of the dye and β-cyclodextrin were used. Research work shows that in a water solution a complex between β-cyclodextrin and the dye is formed at elevated temperatures. The β-cyclodextrin/dye complex with the increased molecular weight does not diffuse within the fibre and has low substantivity for the textile substrate. Because the complex formation is a dynamic equilibrium, the dye can easily be released and adsorbed on the textile substrate during the dyeing procedure. This indicates that the mechanism of retarding when using β-cyclodextrin is the formation of a dye/β-cyclodextrin complex (Fig. 6). This complex would slow down the rapid uptake of the dye by the fibre.

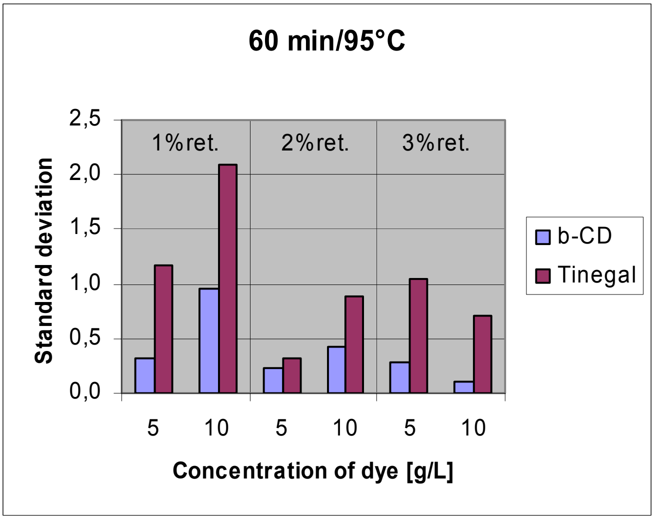


Fig. 5. Standard deviation of the mean K/S values of PAN fabrics dyed with different concentrations of dye (5 and 10 g/l) and retarding reagents: β-cyclodextrin and commercial reagent (1, 2 and 3%); dyeing procedure: 60 minutes at 95°C

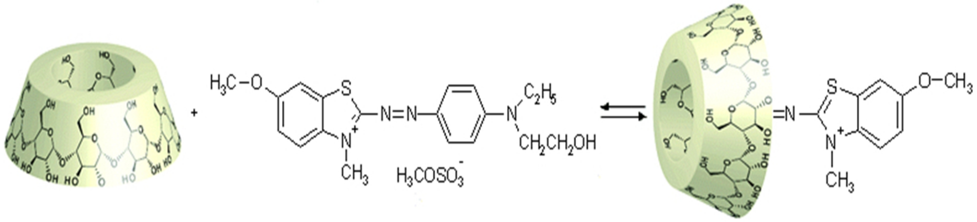
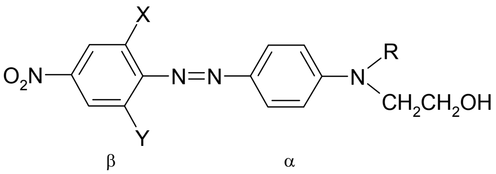


Fig. 6. Formation of a dye/β-cyclodextrin complex-retarding mechanism when using β-cyclodextrin

Changes in the sorption isotherms of six azo disperse dyes (4-amino-4′-nitroazobenzene derivatives) on hydrophobic secondary cellulose acetate filament yarn on addition of α-, β- and γ-cyclodextrins were measured at elevated temperature (Shibusawa et al. 1998). Structures of used dyes are presented in Fig. 7.

The formation constant and the stoichiometry of the dye-cyclodextrin complex formation were obtained by analyzing the changes in the isotherms. It was shown that most of the analysed dyes form 1:1 complexes with cyclodextrins when their maximum cross section area (actually, cross section of β-phenyl ring) is comparable to or smaller than the cyclodextrin cavity diameter. Azo dyes with electron withdrawing groups form 2:2 complexes with γ-cyclodextrin. Computer simulation presented in the paper showed that β- and γ-cyclodextrin are effective as retarders in the dyeing procedure when using relatively small molecules of disperse dyestuffs.



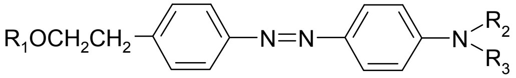
Designation	X	Y	R	Maximum cross section size of β-phenyl ring (pm)
Dye 1	H	H	CH_2CH_3	675
Dye 2	H	H	CH_2CH_2OH	675
Dye 3	Cl	Cl	CH_3	904
Dye 4	Cl	Cl	CH_2CH_2OH	904
Dye 5	NO_2	H	CH_2CH_2OH	858
Dye 6	NO_2	Br	CH_2CH_2OH	989

Fig. 7. Structures of six azo disperse dyes (4-amino-4’-nitroazobenzene derivatives)

Savarino with co-workers (Savarino et al., 1999; Savarino et al., 2000) studied the possibilities of using cyclodextrins as a dye complexing agent in dyeing of polyamide fibres with acid dyes. They reported that β- and γ-cyclodextrins may form inclusion complexes with dye molecules, but only the latter has been proven effective for controlling dyeing uniformity. Further they prepared a series of seven azo disperse dyes with variable hydrophobic chain lengths and hydrophilic substituents. Fig. 8 show the dyes structures. The interaction between dyes and polyamide fibres were studied by recording the dyeing isotherms; the influence of cyclodextrins (β-cyclodextrin and methyl-β-cyclodextrin) addition on colour yield and colour uniformity of dyed polyamide fibres was tested. They found out that the presence of cyclodextrins gives the positive effects on the quality of polyamide dyeing with disperse dyes. The quality of the dyeing depends on the type of cyclodextrin and on the size and hydrophilic properties of the analysed dyes.

The same group prepared 12 azo disperse dyes of a dialkylaminoazobenzene series and studied their complexation with β-cyclodextrin in the solid state by using TGA and DTA analysis and in dye bath by means of solubility isotherms (Savarino et al., 2004). Dye structures are presented in Fig. 9. For comparison purposes they dyed polyamide fibres with prepared solid complexes of the dyes with β-cyclodextrin by means of milling. They found out that the presence of β-cyclodextrin in the dyeing baths (irrespective if solid dye/β-cyclodextrin complexes were added to the bath or complexes were formed in the baths during the dying procedure) systematically increases dye solubility due to complex formation; dyeing tests evidenced a positive effect on colour uniformity and intensity in present of β-cyclodextrin both when added as free additive or when added as a complex.

The Savarino group synthesized the dialkylaminoazobenzene series of dyes with various substituents and used them in the dyeing of polyester (Carpignano et al., 2010); β-cyclodextrin was explored as an additive in the dyeing as a substitute for a commercial surfactant commonly used. The aim was reducing the environmental impact of the exhausted baths.



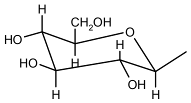
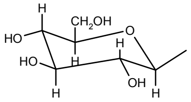
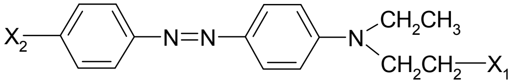
Designation	R_1	R_2	R_3
Dye 1	H	CH_3	CH_3
Dye 2	H	C_2H_5	C_2H_5
Dye 3	H	C_2H_5	C_4H_9
Dye 4	H	C_2H_5	C_8H_{17}
Dye 5	H	C_2H_5	$C_{12}H_{25}$
Dye 6		C_2H_5	C_2H_5
Dye 7		C_2H_5	C_8H_{17}

Fig. 8. Azo disperse dyes (Savarino et al., 2000)



Designation	X_1	X_2
Dye 1	H	H
Dye 2	H	CH_3O
Dye 3	H	CN
Dye 4	H	NO_2
Dye 5	CN	H
Dye 6	CN	CH_3O
Dye 7	CN	CN
Dye 8	CN	NO_2
Dye 9	OH	H
Dye 10	OH	CH_3O
Dye 11	OH	CN
Dye 12	OH	NO_2

Fig. 9. Azo disperse dyes of dialkylaminoazobenzene series (Savarino et al., 2004)

From the literature about the use of cyclodextrins in textile dyeing it is evident that one of the main reasons that determines if a complex is formed or not is the size of the dye molecule. The Savarino group used the chromometric approach where a small group of dyes were selected as a "training set" to be representative of a larger series of dyes with similar structures. The training set of dyes was used for dyeing of polyester fabrics. The properties of the dyed samples were evaluated to assess the ability of β-cyclodextrin to be used as a substitute for synthetic surfactants. The interactions of dyes with β-cyclodextrin were studied by the solubility isotherm method. It was shown that the equilibrium concentration was reached after *ca*. 10 h and it was found to be a function of β-cyclodextrin concentration. The relationship between the dye and β-cyclodextrin was observed to be generally linear. The solubility isotherms differ according to the dyes which were used for complex formation; for certain dyes data can be well fitted by a straight line with a slope value smaller than one indicating that only one complex type is present in the solution and that the dye/β-cyclodextrin stoichiometry is either 1:1 or 1:n, where $n>1$, in contrast to some other dyes relationship between the dye and β-cyclodextrin was presented by a second-order polynomial equation. However, solubility isotherms indicate that the complexation between all dyes and β-cyclodextrin increases the dye solubility. Further the effect of β-cyclodextrin in comparison with commercial surfactants in polyester dyeing was evaluated; colour uniformity, fastness to light and washing and bath exhaustion were evaluated. The colour difference values (ΔE) between dyed and un-dyed fabrics correspond to the colour intensity qualitatively corresponded to dye uptake. The standard deviation $\sigma_{\Delta E}$ was used as a measure of dyeing uniformity. Their research showed that dyeing uniformity results are generally higher in the presence of surfactants than in the absence of additive. Dyeing uniformity did not increase when dye/β-cyclodextrin in a molar ratio 1:1 was used. Better results were obtained with dye/β-cyclodextrin in a molar ratio 1:2. Washing and rubbing fastness values measured at 60 °C were generally higher and were shown to be independent from bath composition and dye structure. Light fastness values showed that the composition of the dye bath did not affect the light fastness, on other hand, light fastness showed a large variation along the set of dyes. When the presence of β-cyclodextrin in polyester dyeing was studied two main advantages were brought up: the presence of biodegradable substances in exhausted dyeing baths and the use of additives obtained from renewable sources.

Cyclodextrins can not be used only as a dye carrier for improving the exhaustion or levelness of dyed materials, but they can also be used for encapsulation of dyes and other active substances (Zhang et al., 2006). Zhang and co-workers reported the successful encapsulation of various sulphonated azo dyes which are widely used as colouring agents in foodstuffs, cosmetic and others by using different cyclodextrins.

3.2 Cyclodextrins in polyfunctionalization of textiles

Various auxiliary products are used in wet finishing processes, previously we discussed auxiliaries which form inclusion complexes with dyes during the dyeing processes, however auxiliaries which bond on fibre surfaces before adding the dyestuff can have an influence on the dye uptake; thus more homogenous dispersion onto fibre and more efficient penetration into the fibre can be achieved. Covalent bonding of cyclodextrins onto textile fibres was firstly patented in 1980 by Szejtli (Szejtli et al., 1980) where it is reported to bond cyclodextrin via epichlorhydrin onto alkali-swollen cellulose fibers. According to the references the most promising approach to bond cyclodextrin onto textile fibres is the modification of cyclodextrins with trichlorotriazines to prepare monochlorotriazinyl-cyclodextrin (Reuscher et al., 1996; Grechin et al., 2007). An article prepared by Ibrahim and co-workers (Ibrahim et al., 2007) reports new trials for improving the UV protective properties of cotton/wool and viscose/wool blends via incorporating certain reactive additives, such as reactive monochlorotriazinyl-β-cyclodextrin, in the easy care finishing formulations, followed by subsequent treatment with copper-acetate or post-dyeing with different classes of dyestuffs (acid, basic, direct and reactive). The post-dyeing of the blends was carried out at pH 3, at a 1:20 material to liquor ratio by conventional procedures in a Laundrometer with 3%owf. The dyed fabrics were rinsed and washed at 50 °C for 15 min in the presence of 1g/L of nonionic wetting agent, rinsed again and air dried. They found out that post-dyeing of the prefinished textile blends results in a significant increase in the UPF (UV-protection factor) values as a direct consequence of a remarkable reduction in UV radiation transmission through the plain weave fabric.

Very effective bonding of cyclodextrins on cellulose fibres can be achieved by a high-performance resin finish (Ostertag, 2002) or with non-formaldehyde reagents such as polycarboxylic acids (Voncina & Le Marechal, 2005; Martel et al., 2002b) which can covalently esterify hydroxyl groups of cellulose and cyclodextrins and link both moieties together. The same linking/crosslinking reagents can be used in the treating of different synthetic fibres. Polyester fibres were modified by β-cyclodextrin using citric acid (Martel et al., 2002a), in our laboratories (Voncina et al., 2009), 1,2,3,4-butane tetracarboxylic acid was used as a linker. Within our current research we study the influence of β-cyclodextrin on PET/cotton blend dyeing with disperse dye. Fig. 10 schematically presents Disperse Brown 1 dye.

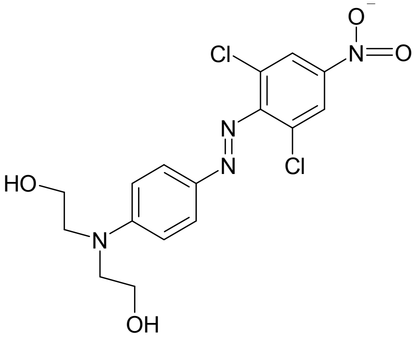


Fig. 10. Disperse Brown 1 (Terasil Braun 3R)

Fig. 11 graphically presents K/S values of PET/cotton blend pre-treated with β-cyclodextrin and Disperse Brown 1 (sample A), untreated PET/cotton blend dyed with the same dye (sample B) and C presents sample dyed with the addition of β-cyclodextrin into the exhausting dye bath. From colour measurements it is possible to conclude that pre-treatment of PET/cotton blend with β-cyclodextrin (sample A) increases the disperse dye uptake slightly; the addition of β-cyclodextrin into exhausting dye bath increases the dye uptake as well; a possible explanation could be that β-cyclodextrin/disperse dye complexation enhances the solubility of the dye.

El Ghoul and co-workers (El Ghoul et al., 2007; El Ghoul et al., 2010) reported that polyamide and polypropylene fabric were treated with cyclodextrins via crosslinking reaction which was carried out using the pad-dry-cure process. Dyeability of cyclodextrin modified polypropylene fibres was enhanced when using three dyes belonging to different classes (disperse, acid and reactive dyes), using the exhaustion dyeing method. Formation of inclusion complexes between the dyes and β-cyclodextrin bonded onto polypropilene fibres increase the exhausting rate of the dyes from the dyeing baths. The observed enhancement of dye uptake was due to the encapsulation of dyes in the β-cyclodextrin cavities on one hand and due to other interactions (ionic and hydrogen bonding) or even covalent bonding with the poly-citric acid/β-cyclodextrin network in the case of reactive dye on the other hand. Various possible interactions between the reactive dye and fibres functionalized with β-cyclodextrin are illustrated in Fig. 12. It was observed that the dyeing level depends on the modification rate of polypropylene fibres with cyclodextrin.

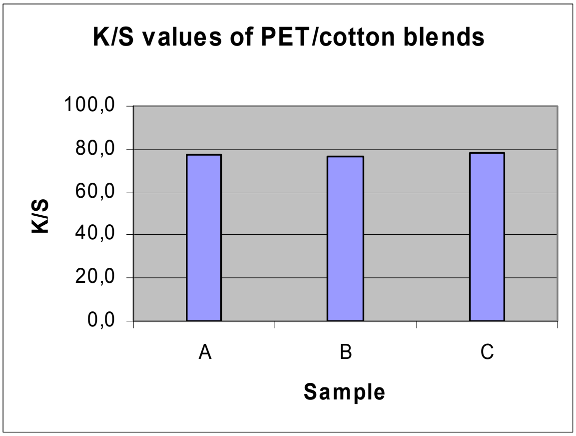


Fig. 11. K/S values of pre-treated PET/cotton blends dyed with Disperse Brown 1 (sample A), K/S values of samples dyed with the same dye (sample B) and K/S values of samples dyed with the addition of β-cyclodextrin into exhausting dye bath (sample C)

A novel technique for preparation of β-cyclodextrin-grafted chitosan was carried out by reacting β-cyclodextrin citrate with chitosan (El-Tahlawy et al., 2006).

4. Cyclodextrins in textile waste water treatments

The world production of dyes is estimated to be over 10 000 tonnes per year. Treatment of wastewater containing dyes is one of the most important ecological problems because the effluents containing the dyes are not only highly coloured, but also toxic to aquatic life. Textile effluents are highly variable in composition. They are generally characterized by high concentrations of colour, COD, BOD, TOC and dissolved solids. Wool and polyamide are dyed with the acid chrome dyes using the mordant dyeing technique causing the additional contamination of the effluents by high contents of chromium. Acid chrome dyes are the class of dyes that are at the same time most widely used in Eastern Europe and most difficult to eliminate. Due to the low biodegradability of dyes, conventional biological wastewater treatment is not very efficient.

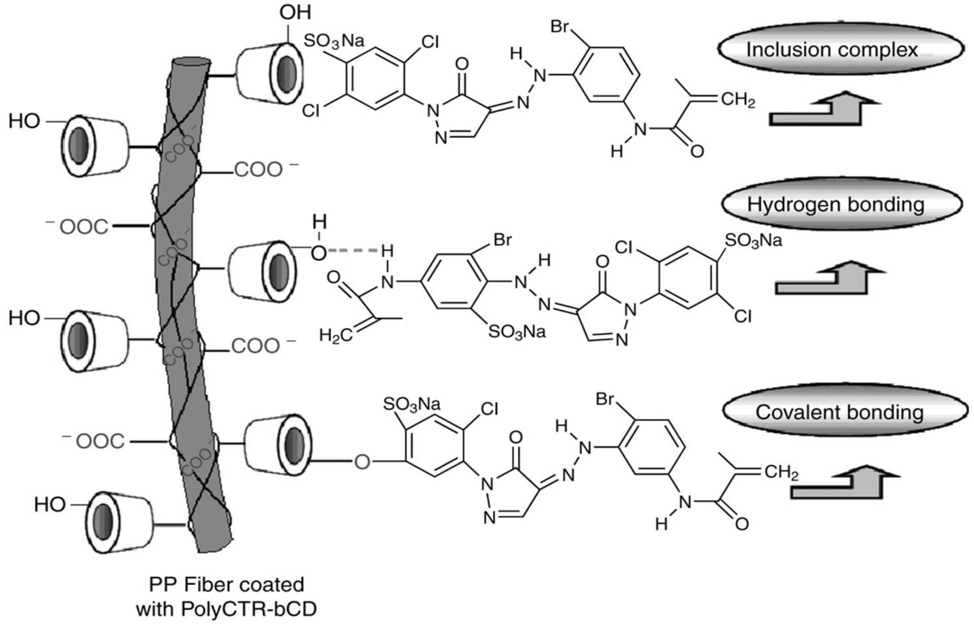


Fig. 12. Different interactions between the reactive dye Yellow Lanasol 4G and polypropilene fibres modified with β-cyclodextrin

Coagulation and adsorption onto various supports are the most frequently used physical methods. Due to interactions of ionic dyes with oppositely charged ionic surfactants, the extraction of ion pairs can also be used to remove dyes from aqueous streams. However, solvent extraction is not very useful as the concentrations of dyes present are usually low and the aqueous stream can be contaminated with diluents. Chemical methods such as oxidation and chlorination are more effective.

As a result of continuous water recycling, several groups of substances such as salts, organic micro pollutants, microorganisms, etc., are concentrated in the water loop and may cause water quality problems as well as health risks. The research is now focused also on the reduction/elimination of toxic organic pollutants like degradation products of dyestuffs and auxiliaries (phenols, aromatic amines, formaldehyde, persistent organic pollutants (POPs) etc), which can be formed also during the waste water treatment inside the factory or present in low concentrations in used chemicals or basic materials.

Basically, cytotoxicity of typical azo dyes may be relatively low, but the toxicity of related aromatic amine intermediates is very likely still significantly high due to their carcinogenicity or mutagenicity. Azo compounds like textile dyes can be reduced to amines through co-metabolism and the aid of azoreductases during decolourization treatments (Haug et al., 1991). As aromatic amines are difficult to be removed via traditional wastewater treatment and inevitably tend to be persistent, the toxicity evaluation of these amines will be apparently crucial to operation success or failure in dye decolourization and biodegradation afterwards. Aniline, the simplest and one of the most important aromatic amines, being used as a precursor to more complex chemicals, is toxic by inhalation, absorption through the skin or swallowing. To remove dyes and toxic micro pollutants several separation techniques, based on filtration, adsorption, and extraction could be applied.

The source of POPs in textile materials and textile effluents could be pesticides for cotton and other materials based on pentachlorophenol, known to be contaminated with dioxins; chloranyl based dyestuffs; textile processes using chlorinated chemicals contaminated with POPs; highly alkaline finishing media; brominated flame retardants and also the waste water after treatment with AOPs (e.g. irradiation with powerful UV lamp in the presence of accelerating agents like H_2O_2, NaOCl, Fenton's regent, etc). Concentrations of POPs in waste water and even on textile material after different finishing processes can be between 100 g/L to 20μg/L. Apart from above mentioned POPs, phenol, and formaldehyde forming compounds and various aromatic amines (as the by-products and decomposition products of textile dyestuffs) present the most problematic pollutants in textile waste water.

Nowadays the membrane methods of separation are widespread as a method of wastewater treatment. The choice of the most suitable membrane process from a technical–economic point of view is very important. Having high dye retention, reverse osmosis (RO) and nanofiltration (NF) can be used for the treatment of dye waters from the textile industry. But industries are somehow reluctant to adopt highly energy-consuming RO and NF processes. Furthermore, NF/RO membranes have a lot more serious issues related to membrane fouling caused by colloids deposition, inorganic precipitation, and biological growth. Biofouling or biological fouling is the undesirable accumulation of microorganisms, plants, algae, and or animals on wetted structures.

Novel nano-porous polymers or nanosponges can be prepared for removal of organic pollutants from waste water. The polymeric «nanosponge» materials are not durable (usually they are in gel form), so they must be impregnated onto the pore structure of either a ceramic or some other porous surfaces. (Salipira et al., 2007). This technology is very specific for the target pollutant, it is very expensive and the removal of the adsorbed pollutant from the nanosponge is not possible. Usually the nano-porous polymers do not have high mechanical strength (Allabashi et al., 2007).

Textile materials are very important as filter materials. The cost of textile materials is acceptable (polyester, viscose), they have a sufficient mechanical strength; the pore size, especially the macro-pore size can vary, it depends on the type of textile (the density of non-woven material) and on the diameter of fibres. Textile materials can be further modified to prepare filtration materials with additional adsorption.

The amount of aromatic organic pollutants (phenols, aniline, formaldehyde and others) can be reduced from dyeing wastewater by using cyclodextrins which can be immobilized on a water insoluble organic support. The new concept for modification of textile substrates is based on permanent fixation of supramolecular compounds - cyclodextrins on the material surface and thus imparts new functionality to the fabric (Mamba et al., 2007; Mhlanga et al., 2007).

The guest molecules could be various organic molecules and some metal ions as well. The formed assembly of nanocapsules on textile materials (Fig. 13) acts as selective filtration/adsorption media for various pollutants. Cyclodextrin covalently bonded onto a textile support will form inclusion complexes with organic toxic pollutants by »host-guest« mechanism. After the filtration process, the organic support with cyclodextrin containing organic compounds can be incinerated.

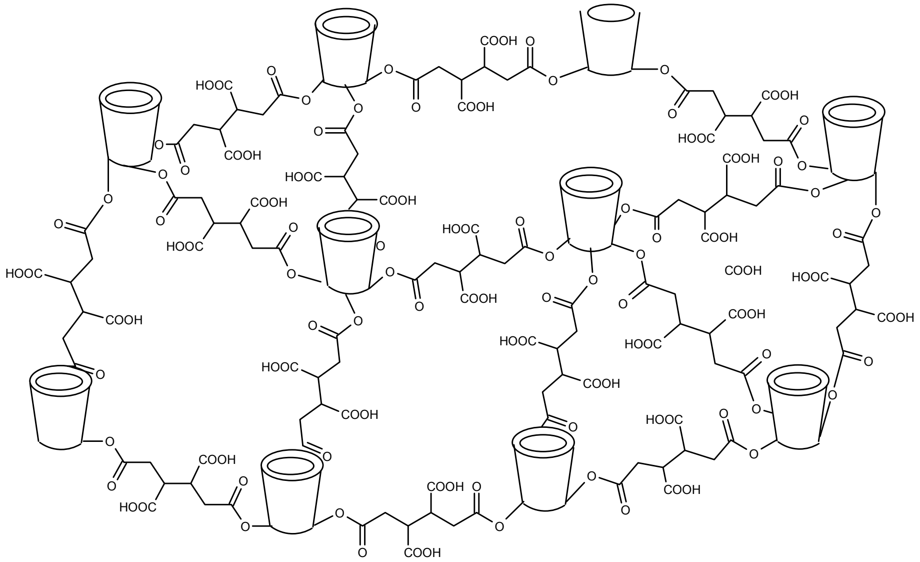


Fig. 13. Assembly of molecular capsules

5. Conclusion

Cyclodextrins have the ability to form inclusion complexes with a large number of organic molecules; this property enables them to be used in a variety of different textile applications. As cyclodextrins can incorporate into their cavities different dyes, they could be used as auxiliaries in dyeing process. Regardless the mechanisms of cyclodextrins actions, if there is a competition for sites on the fibre between dyes and cyclodextrins; or cyclodextrins slow down the dyes migration by forming complexes with the dyes molecules which are released slowly to the fibre, cyclodextrins can act as levelling or retardant reagents in various textile fibre (cotton, polyester, polyamide, polypropylene, polyacrylonitrile) dyeing.

In general, quality dyeing can be obtained and bath exhaustion can be improved when cyclodextrins are used as an additive (levelling reagent or retarding reagent) compared to commercially available auxiliaries; further improvement of colour levelness and some improvements in colour depth have been found when textile fibres were dyed in the presents of cyclodextrins. One of the main criteria for the complex inclusion is the size of cyclodextrins cavity and the size of the dyestuff molecules. The use of cyclodextrins in textile dyeing can not only improve the quality of the dyeing, but it can reduce the environmental impact of the exhausted baths. Further, covalently bonded cyclodextrins on textile support form inclusion complexes with organic pollutants. The adsorbed pollutants will be converted into water and carbon dioxide by the incineration.

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