Polymer Degradation

What Does Polymer Degradation Mean?

Polymer degradation means **gradual breakdown** of polymers, exposure to various environmental factors like **heat, light, oxygen, etc**. This deterioration can lead to the **loss of desirable properties such as strength and flexibility**.

The term polymer degradation refers to the **processes induced by sunlight, heat and other atmospheric agents** that lead to a **modification** of the polymer structure, which are normally accompanied by a **decrease in the mechanical characteristics of the material.**

Types of polymer degradation

The degradation of polymers usually starts at the outer surface and penetrates gradually into the bulk of the material. The following table shows a summary of the **different types of degradation** depending on the **external agent** acting on the polymer.

External agent	Type of degradation
Sunlight	Photodegradation
Heat	Thermal degradation
Atmospheric agents	Oxidative degradation
Humidity	Hydrolytic degradation
Fungi and microorganisms	Biodegradation
Light + oxygen	Oxidative photodegradation
Heat + oxygen	Thermoxidative degradation
Light + humidity	Photohydrolytic degradation

Degradation Mechanisms

1) Thermal-Oxidative Degradation

It consists of the **attack of the active oxygen** on the polymer. As in thermal degradation, **oxygen causes free radicals** in the polymer. This type of degradation has been **widely studied in polyolefins** and clearly depends on the **O_2 concentration**.

✓ **Initiation:**

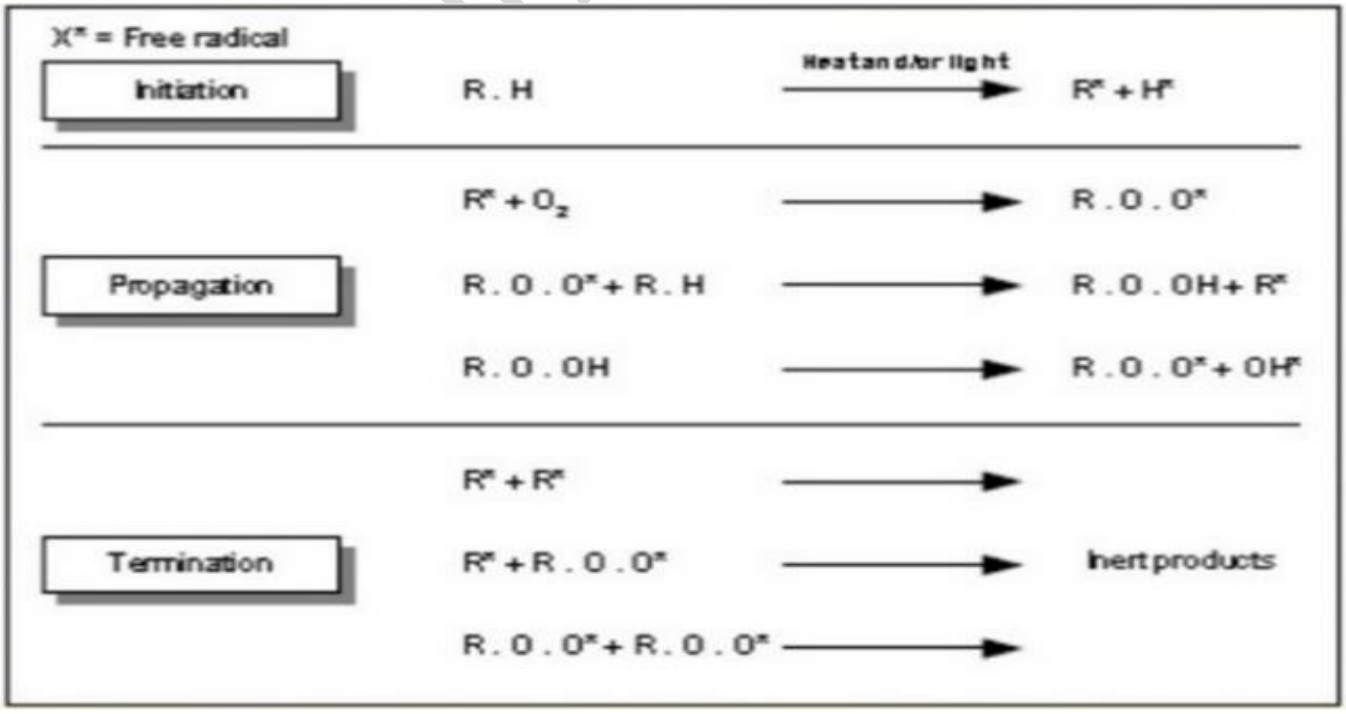
The initiation of thermal degradation involves the loss of a hydrogen atom from the polymer chain (show below as R.H) as a result of energy input from heat or light.
This creates a highly reactive and unstable polymer " free radical" (R*) and a hydrogen atom with an unpaired electron (H*).

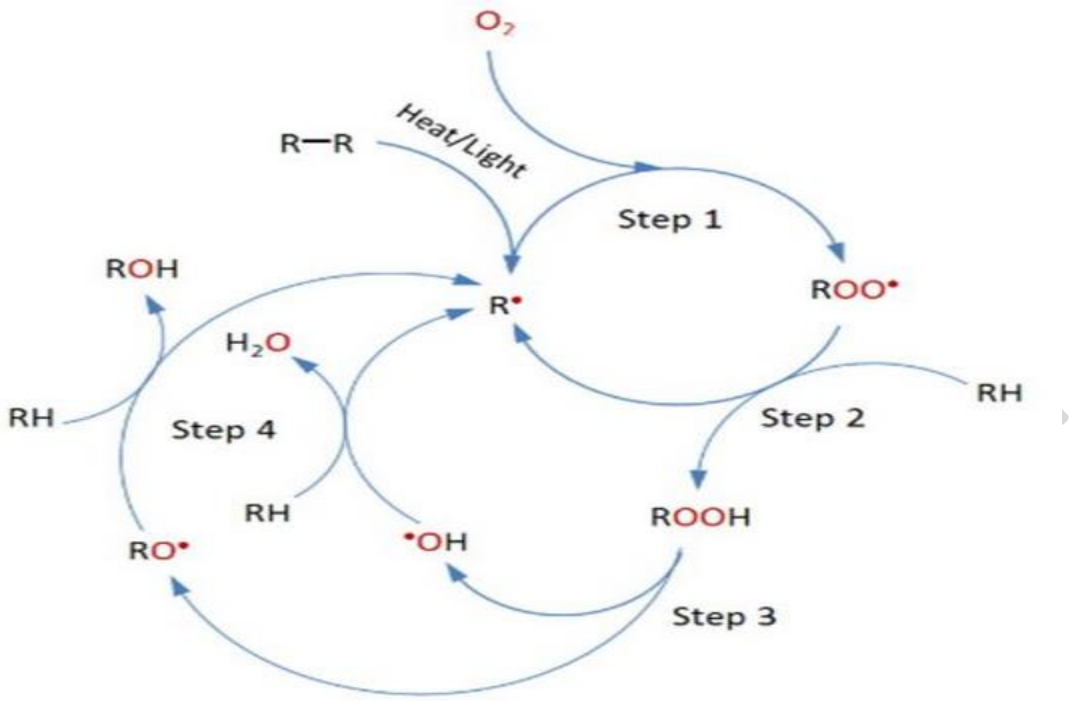
✓ **Propagation:**

The propagation of thermal degradation can involve a variety of reactions and one of these is where the free radical (R*) reacts with an oxygen (O2) molecule to form a peroxy radical (R00*) which can then remove a hydrogen atom from another polymer chain to form a hydroperoxide (ROOH) and so regenerate the free radical (R*). The hydroperoxide can then Split into two new free radicals, (RO*) + (OH*), which Will continue to propagate the reaction to other polymer molecules. The process can therefore accelerate depending on how easy it is to remove the hydrogen from the polymer chain.

✓ **Termination:**

The termination of thermal degradation is achieved by "mopping up" the free radicals to create inert products. This can occur naturally by combining free radicals or it can be assisted by using stabilizers in the plastic.





Mechanism of thermal-oxidative degradation [1]

2) Photodegration

Polymers will change over time when **exposed to UV radiation**. These changes are the result of **light-induced homolytic fission of chemical bonds (photolysis)** and **photo-oxidation**. This process is based on the fact that the **energy of ultraviolet light from sunlight** is greater than the binding energy of the **C-C and C-H molecular bonds** and therefore break the molecular chains, reducing their molecular weight and mechanical properties.

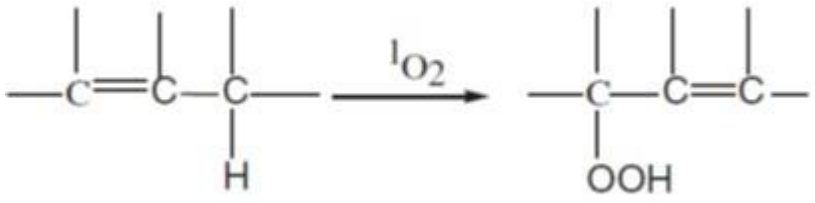
Mechanism of photo-oxidative degradation of polymers

Two mechanisms have been proposed to explain the photooxidation of polymers. One proceeds through **direct reaction of singlet oxygen** with **the substrate** while the other involves the **production of radicals** and subsequent reaction **with oxygen**.

(I)The singlet oxygen mechanism of oxidation

It has been clearly demonstrated that many photosensitized oxidation reactions proceed with participation of oxygen in an electronically excited singlet state. Singlet oxygen exhibits several specific reactions and the one that has been most often invoked in the photooxidation of polymers is the formation of a hydroperoxide

by oxidation of an olefin containing an allylic hydrogen, and which could further decompose and lead to chain scission and formation of a terminal of carbonyl group.



(II)The free radical mechanism of oxidation

The radical mechanism of photooxidation of polymers proceeds through a chain reaction (initiation, propagation and termination steps)

3) Thermal Degradation (High Temperature)

Hemolytic disruption of covalent bonds in the **chain or side groups**, caused by increased temperature. After the link is broken, the reactions that occur depend on the **activity of each radical** (**obviously, the higher the temperature, the greater the degradation**). It also **influences the viscosity of the melt**. Polymer degrades faster if it is **already partially degraded**.

4) Hydrolytic Degradation

When the material comes into contact with an **aqueous medium**, the water **penetrates the polymer** matrix and causes **swelling, rupture** of intermolecular hydrogen bonds, hydration of the molecules and finally the **hydrolysis of unstable bonds.**

5) Biodegradation

This term is applied when **the transformations and deterioration** of the polymer are due to the **action of living organisms**: the process is catalyzed by the action of **fungi, bacteria, etc. and enzymes** secreted by them. When happening in aqueous media, sometimes biodegradation and hydrolytic degradation may occur together.

Some other degradation as follows--

6) Mechanical Degradation, 7) Chemical degradation, 8) Radiolytic degradation, 9) Ozone degradation, 10) Flame degradation, 11) Endothermic degradation etc.