Degree of Crystallinity

The degree of crystallinity of the polymer is defined as the fraction of the sample which is crystalline. OR,

Degree of crystallinity is quantity which provides a measure of how much crystalline material is present in a given polymer sample.

It can be either expressed in terms of the mass fraction or the volume fraction. The degree of crystallinity by a volume fraction is given by

$$Xm = Va - V / Va - Vc$$

Where,

X_m = Degree of crystallinity by mass

V = Specific volume of the sample

V_a = Specific volume of fully amorphous polymer

Vc = Specific volume of fully crystalline polymer

Factors Influence Crystallinity

(i) Molecular Weight: With increase in molecular weight of a polymer, % crystallinity increases due to the large number of entanglements of chain which impose restriction for unlimited growth of a crystallite.

(ii) Symmetry of the repeating unit: Symmetrical repeat unit structure like $-CH_2-$ facilitates the formation of crystallites. Random copolymers do not crystallize because there is no regularity of the repeat unit. Geometrical regularity is also desired in a polymer for it to show crystallinity. For example, only the configurationally regular forms of polyproplylene can crystallize but atactic polypropylene is amorphous.

(iii) Chain Branching: High density polypropylene has almost perfectly linear structure and therefore it can be obtained in a highly crystalline state (80-85% crystallinity) with high melting point (133-135^{0}C). Low density polyethylene has number of short chain (ethyl and butyl) and long chain branches. So, it can not be obtained in a highly crystalline state (55% crystalline) and melting point is also low (110-115^{0}C).

(iv) Cross Linking: A polymer with high cross-linked density is devoid of crystallinity because the presence of a dense array of cross-links effectively eliminate crystallinity.

Affect of Crystallinity on Properties of Polymer

With increase in % crystallinity-

(i) Strength and stiffness of polymer increases but brittleness also increases.

(ii) Solubility and permeability of polymer decreases

(iii) Density and melting point of polymer decreases

(iv) Opacity of the polymer also increases.

Crystallinity of Polymer

The structure of a polymer is described in terms of crystallinity. Usually most of the polymers are in **amorphous in nature or semi-crystalline**. All of we know that a **crystalline solid has a sharp melting point** and **amorphous do not have a sharp melting point.**

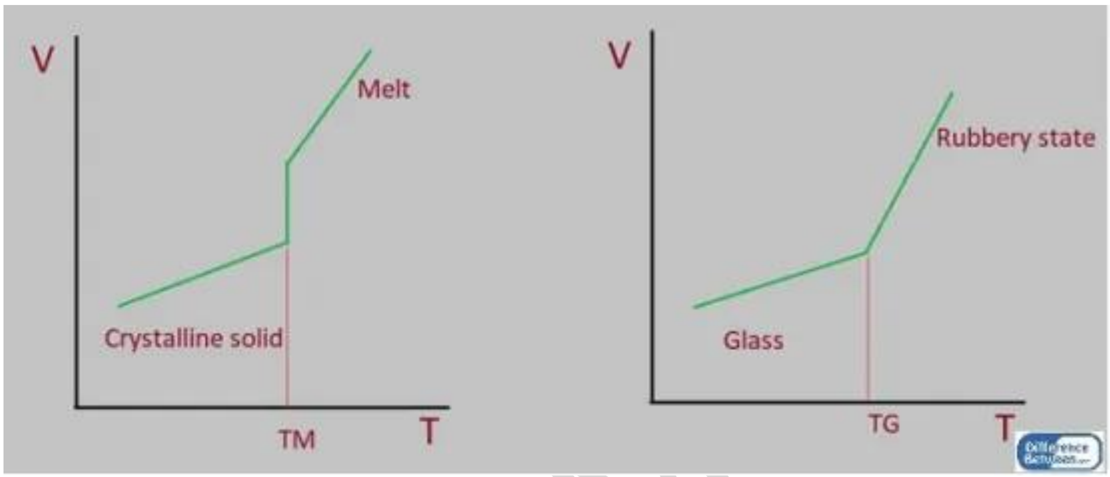
Crystalline solids have a **definite shape** with **orderly arranged ions, molecules or atoms in a three-dimensional pattern** often termed **crystal lattice** with a uniform **inter- molecular force**.

Amorphous solids are the **shapeless, disordered, and irregular arrangement** of the constituent particles of a solid. Their **inter-molecular forces are not the same, nor are the distances between the particles**.

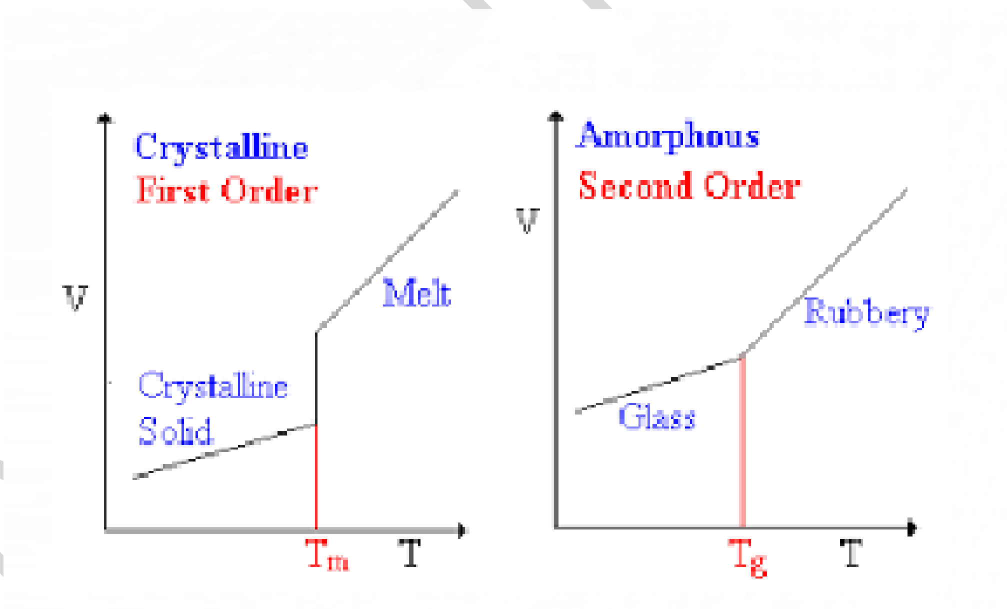
Polymeric material usually contains some crystalline part and some amorphous part.

Glass Transition Temperature

When **plastic or rubber is cooled up** to certain temperature, it becomes so **hard and brittle** that it **breaks into pieces** on application of stress. The **temperature below** which the polymer **becomes hard, brittle and glassy** and above which it is **soft and flexible**, is known as **glass transition temperature (Tg).**



Comparison of TG and TM



Melting Temperature

When a polymer is **heated beyond Tg**, it passes from **glassy state to rubbery state**. Further heating much above, causes melting of the polymer and it starts flowing. The temperature **below which the polymer is in rubbery state** and **above which it is a liquid** is called **melting temperature (Tm)** of the polymer.

Differences between Tg & Tm

Glass transition temperature is the temperature at which a hard glassy state of an amorphous material is converted to a rubbery state	Melting temperature is the temperature at which a solid material is converted into its liquid form
Describes the transition of a glass state into a rubber state	Describes the transition of a solid phase into a liquid phase (phase transition)
Can be observed in amorphous and semi-crystalline compounds	Can be observed in crystalline substances
Depends mainly on the chemical structure of the substance	Depends mainly on the chemical bonding of molecules in the substance and the external pressure

Differences between Tg & Tm Polymers

	TG Polymers	TM Polymers
DEFINITION	TG of polymers or TG Polymers is the glass transition temperature.	TM of polymers or TM Polymers is the melting temperature.
CONVERSION	Glassy state into a rubbery state.	Solid crystalline state into solid amorphous state.
PHASE OF MATTER	Changes from solid to semi-solid or rubbery phase.	Changes from a solid phase to another solid phase; thus, no change of phase of matter.
TYPE OF POLYMERS	For amorphous and semi-crystalline polymers.	For crystalline and semi-crystalline polymers.
APPLICABLE CATEGORIES	Mainly for thermosetting polymers.	Mainly for thermoplastic polymers mainly.
ABOVE THE TEMPERATURE	Polymer has rubbery state and thus less rigid and not brittle.	Polymer has crystalline regions.
BELOW THE TEMPERATURE	Polymer has glassy state, thus, rigid and brittle.	Polymer has amorphous regions.