GLASS TRANSITION

Glass transition is the transition of an amorphous substance from its soft and pliable state to a hard and brittle (glassy) state.

- **Glass transition vs. crystallization**
- **Effect of structure factors on glass transition temperature**

Glass transition vs. crystallization

With regards to their molecular structures the Polymers may be either amorphous or crystalline.

When the temperature of a crystalline polymers lowers it undergoes the Crystallization (transformation of the liquid into a solid crystalline phase). In the liquid state the polymer molecules are disordered and can move freely whereas in the crystalline state they are arranged in the pattern according to a crystal lattice.

The crystallization process is reversible: a crystalline polymer may be crystallized and melted again unlimited number of times.

The temperature at which liquid-solid transition of a crystalline polymer occurs is called **freezing point** or **melting point**.

An amorphous polymer stays amorphous at any temperature however the mobility of its molecules changes sharply when the temperature reaches a certain temperature (**glass transition temperature**).

Below the glass transition temperature the molecules can not change freely their position nor configuration despite the fact that they are not arranged in a rigid crystal pattern. The polymer is amorphous in the glassy state but it is hard and relatively brittle. Above the glass transition temperature the molecules become mobile. The polymers in such viscous state (rubbery state) are soft and flexible.

Most polymers are composed of both crystalline and amorphous portions (domains) which behave differently according to their structures: the amorphous domains turns viscous and soft when heated above the glass transition temperature whereas the crystalline parts melt when the temperature reaches the melting point.
The glass transition temperature (**Tg**) of a particular polymer in amorphous state is lower than the melting point (**Tm**) of the polymer in the crystalline state.

Effect of structure factors on glass transition temperature

- **Molecule flexibility**. In the soft (rubbery) state some segments of the polymer chains gain a capability to rotate around the chain axis. Such molecule mobility makes the polymer soft and viscous. The more flexible the polymer molecules the lower the glass transition temperature.

- **Side groups**. Mobility of the polymer molecules depends on their ability to slide along each other. Side groups (pendant groups) prevent the sliding motion and increase the glass transition temperature.

- **Free volume**. Rotational movement of the molecular segments is easier if there is enough free space around the molecule therefore the polymers with larger free volume have lower glass transition temperature. Shrinkage of the free volume caused by an increased pressure applied to the polymer results in a greater glass

transition temperature. One of the methods to lower the glass transition temperature is an addition of a plasticizer molecules of which locate between the polymer chains and provide more free space for their motion.

- **Cross-linking** decreases the molecule mobility and therefore increases the glass transition temperature.

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