

Glass Transition Temperature of Polymers

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 becomes soft and flexible, is known as glass transition temperature (T_g).
- The glass transition is a property of only amorphous portion of a semi-crystalline solid. The crystalline portion remains crystalline during the glass transition.
- The value of T_g depends on the mobility of the polymer chain, and for most synthetic polymers lies between 170 K to 500 K
- The transition from the glass to the rubber-like state is an important feature of polymer behavior, marking a region of dramatic changes in the physical properties, such as hardness and elasticity.

Melting temperature (T_m)

When a polymer is heated beyond T_g , it changes from glassy state to rubbery state. Further heating 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 of the polymer, while the temperature at which the polymer starts flowing is known as its flow temperature.

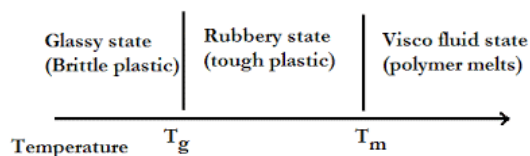


Fig 1: Relation of polymer state and temperature

Effect of temperature on polymer

The hard and brittle state is the glassy state and soft-flexible state is the viscoelastic state. If viscoelastic state of polymer is heated further, the polymer becomes a viscous liquid and can flow. This state is known as viscofluid state.

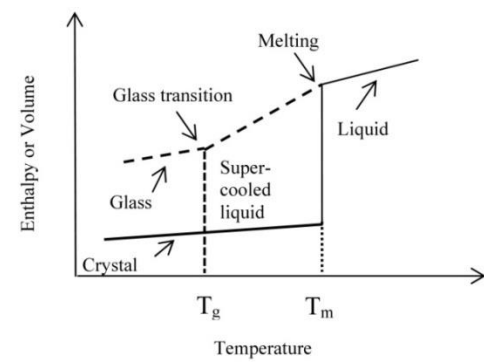


Fig 2: Relation of enthalpy or volume with temperature

- **Below T_g** the molecules in polymer do not move apart and do not have movements within the molecular chains. Therefore, a stress transfer property is lost and polymer below T_g is brittle.
- **Above T_g** the polymers in the viscoelastic state have flexibility or stress transfer properties.
- **Above T_m** , the kinetic energy of the polymer molecules is high enough to cause movement with the chain segments as well to move from one position to another. Therefore, this state has flow character like liquids.

Relation of Structure of Polymer to T_g and T_m

Polymers (plastics, elastomers or rubber) are made up of long chains of molecules and may be amorphous or crystalline. The structure of a polymer is defined in terms of crystallinity. Amorphous polymers have a random molecular structure that does not have a sharp melting point. Instead, amorphous material softens gradually as temperature rises. Amorphous materials are more sensitive to stress failure due to the presence of hydrocarbons, e.g., PC, GPPS, PMMA, PVC, ABS. Crystalline or Semi-crystalline polymers have a highly ordered molecular structure. These do not soften as the temperature rises, but rather have a defined and narrow melting point. This melting point is generally above that of the upper range of amorphous thermoplastics, e.g., Polyolefins, PEEK, PET, POM etc.

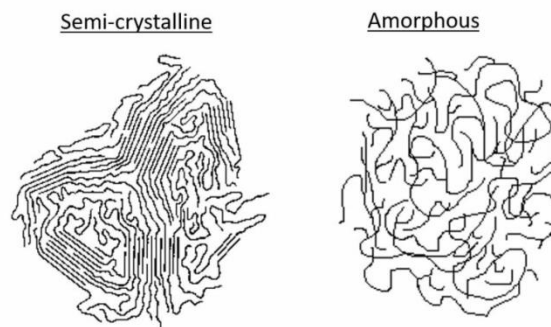


Fig 3: Structure of crystalline and amorphous polymer

Most of the polymers are semi-crystalline in nature that contains both crystalline and amorphous regions in their structures. In the amorphous region of the polymer, at lower temperature, the molecules of the polymer are in, say, frozen state, where the molecules can vibrate slightly but are not able to move significantly. This state is referred as the **glassy state**. In this state, the polymer is brittle, hard and rigid analogous to glass. Hence the name is glassy state. The glassy state is similar to a super cooled liquid where the molecular motion is in the frozen state. The glassy state shows hard, rigid, and brittle nature analogous to a crystalline solid with molecular disorder as a liquid. Now, when the polymer is heated, the polymer chains are able to wiggle around each other, and the polymer becomes soft and flexible similar to rubber. This state is called the **rubbery state**. The temperature at which the glassy state makes a transition to rubbery state is called the **glass transition temperature T_g** . Note that the glass transition occurs only in the amorphous region, and the crystalline region remains unaffected during the glass transition in the semi-crystalline polymer

The glass transition temperature is the property of the amorphous region of the polymer, whereas the crystalline region is characterized by the melting point. In thermodynamics, the transitions are described as first and second order transitions. Glass transition temperature is the **second order transition**, whereas the melting point is the **first order transition** (Fig. 4). The value of glass transition temperature depends on several factors such as molecular weight, measurement method, and the rate of heating or cooling.

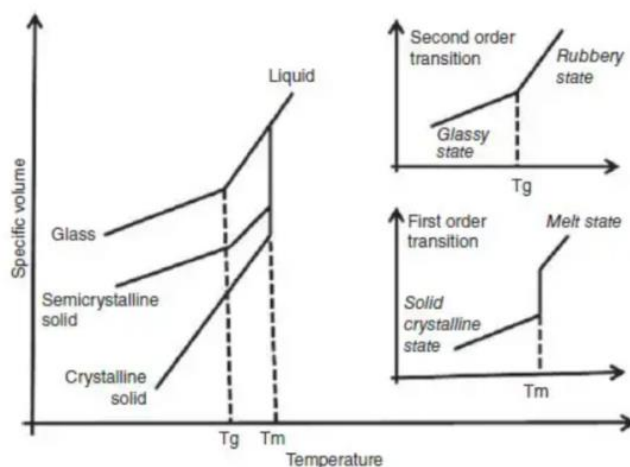


Fig 4: First order and second order transition

The semi-crystalline polymer shows both the transitions corresponding to their crystalline and amorphous regions. Thus, the semi-crystalline polymers have true melting temperatures (T_m) at which the ordered phase turns to disordered phase, whereas the amorphous regions soften over a temperature range known as the glass transition (T_g). **It should be noted that amorphous polymers do not possess the melting point, but all polymers possess the glass transition temperature.**

The polymer melting point T_m is increased if the double bonds, aromatic groups, bulky or large side groups are present in the polymer chain, because they restrict the flexibility of the chain. The branching of chains causes the reduction of melting Point, as defects are produced because of the branching. Crystalline polymers have melting point while amorphous polymers have glass transition temperature and semi-crystalline polymers can have both melting point and glass transition temperature.

Factors affecting glass transition temperature:

Factors affecting glass transition temperature are discussed below:

- 1. Chain flexibility:** Chain flexibility is one of the important factors that affect T_g . Intrinsic chain flexibility is determined by the nature of polymer backbone and groups directly attached to it. Aliphatic C-C and C-O bonds show quite flexibility while introduction of ringed structures causes stiffening of chain. The presence of stiffening groups (like amide, sulfone, carbonyl, p-phenylene etc.) in the polymer chain reduces the flexibility of the chain, causing increase in glass transition temperature. Therefore glass transition temperature of polyethylene terephthalate is higher than their aliphatic counterparts like poly(ethylene adipate) due to the presence of benzene ring.

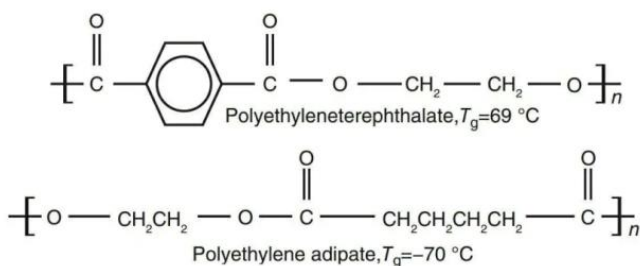


Fig. 5. Presence of benzene in polyethyleneterephthalate makes it stiffer (hence higher T_g) than polyethylene adipate

- 2. Intermolecular interactions:** Segmental rotations are also affected by intermolecular interactions or secondary bonding such as dipole-dipole interaction, induction forces, van der Waals forces and hydrogen bonding, etc. These types of interactions increase the rigidity of polymeric material therefore increase the glass transition temperature. For example, Polyvinyl chloride or PVC ($T_g = 80^\circ\text{C}$) has stronger intermolecular forces than polypropylene ($T_g = -18^\circ\text{C}$) because of the dipole-dipole forces from the C—Cl bond. Nylon-6 also has higher transition point than polyolefin. Polyvinylidene chloride has lower transition point than polyvinylchloride because of the reduction in dipole moment due to symmetry of substitution.
- 3. Polarity and hydrogen bonding:** Polar polymers and those polymers, in which hydrogen bonding is present, have a high T_g . As we know, polar groups or hydrogen bonding increases the intermolecular forces of attraction; inter chain attraction and cohesion leading to the decrease in free volume resulting in increase of T_g .
- 4. Presence of bulky pendant groups:** Bulky group attached to polymer backbone also reduces flexibility of chain backbone therefore polypropylene has higher T_g than polyethylene. Again, polytetrafluoroethylene has higher T_g than polyethylene, as size of fluorine atom is large and it requires the molecule to take zig-zag configuration in which fluorine atoms are tightly packed and chain gets stiffened. In addition, the introduction of double bond also causes stiffening of the chain which may increase the flexibility of adjacent bonds. These factors explain the lower T_g of cis-1,4-polybutadiene in comparison to polyethylene. Also, the presence of bulky pendant group, such as a benzene ring, can restrict rotational freedom leading to higher glass transition temperature. In polystyrene, the presence of benzene ring increases the T_g , but in polypropylene, there is no benzene ring that leads to lower T_g value (Fig. 6).

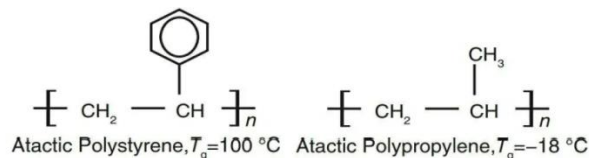


Fig 6. Role of bulky pendant groups in affecting glass transition temperature

- 5. Presence of flexible pendant groups:** The presence of flexible pendant groups, for example, aliphatic chains, limits the packing of the chains and hence increases the rotational motion leading to less T_g value. In polybutylmethacrylate, the presence of large aliphatic chain reduces the T_g value when compared with that of polymethylmethacrylate (Fig. 7).

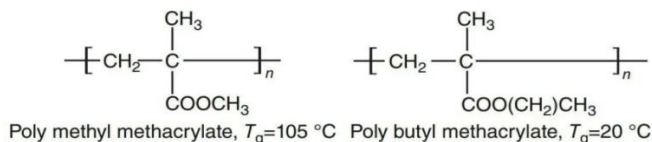


Fig 7: Role of flexible pendant groups in affecting glass transition temperature.

- 6. Molecular weight:** Polymers having low molecular weights have more number of chain ends in comparison of polymers having high molecular weights. Chain ends have less strain and become more active than the chain backbone and cause greater molecular mobility. Therefore increase in molecular weight decreases the glass transition temperature of polymer and it is reasonable to assume that with increase of chain-end concentration, glass transition temperature increases linearly. Thus, we can say that glass transition temperature decreases linearly with increase of molecular weight of polymer.

The molecular weight is related to the glass transition temperature by the **Fox-Flory Equation:**

$$T_g = T_{g,\infty} - \left(\frac{K}{M_n} \right) \quad (\text{Fox-Flory Equation})$$

Where $T_{g,\infty}$ is the glass transition temperature at the molecular weight of infinity, and K is the empirical parameter called Fox–Flory parameter related to the free volume inside the polymer. It is observed that T_g is increased up to the molecular weight of approximately 20,000, and after this limit, the T_g is not affected appreciably.

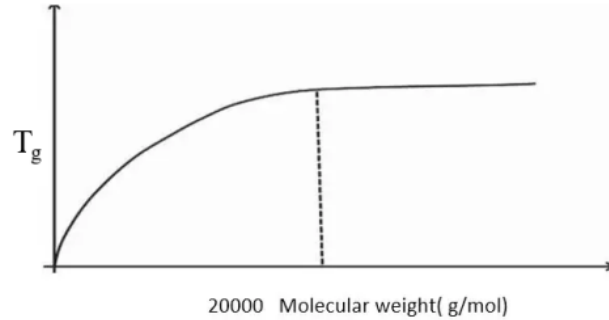


Fig 8: Variation of glass transition temperature with molecular weight

- 7. Co-polymerization:** Random co-polymerization causes disorder and reduces molecular packing therefore glass transition temperature is often reduced on random copolymerization. Glass transition temperature of random copolymer depends on composition of two monomeric components and their individual value of T_g .

The following relation gives the glass transition temperature of a random polymer:

$$1/T_{g(A,B)} = W_A/T_{g(A)} + W_B/T_{g(B)}$$

Where $T_{g(A,B)}$, $T_{g(A)}$ and $T_{g(B)}$ are glass transition temperature of copolymer AB and homopolymer A and B respectively. W_A and W_B are the weight fraction of monomer A and monomer B in the copolymer AB.

Syndiotactic and isotactic polymers have symmetry, so they can be explained as linear polymers. Effect of block co-polymerization will depend on type of block present in the polymer system. In some cases, block-copolymers show two transitions corresponding to each block while in some cases, only single transition is observed and this transition is close to the value predicted by linear relationship. This is because random polymers causes more disorder in polymer system in comparison of block copolymer as there is less contact of dissimilar co-monomer units in block copolymer.

- 8. Cross-linking:** The cross-links between chains restrict rotational motion and thus cross-linking introduces restriction and stiffness in the polymer. Hence, higher cross-linked molecule will show higher T_g than that with lower cross-linked molecule.
- 9. Plasticizer:** Plasticizers are low molecular weight and non-volatile materials added to polymers. Addition of plasticizer increases the free volume in polymer structure as the plasticizer gets in between the polymer chains and spaces them apart from each other. This causes the polymer chains to sliding past each other more easily. As a result, the polymer chains can move around at lower temperatures resulting in decrease in T_g of a polymer.
- 10. Water or moisture content of the polymer:** Increase in water or moisture content leads to the formation of hydrogen bonds with polymeric chains, thereby increasing the distance between polymeric chains. Hence increases the free volume and decreases T_g .
- 11. Effect of entropy and enthalpy:** The value of entropy for amorphous material is higher and low for crystalline material. If value of entropy is high, then value of T_g is also high.

12. Pressure and free volume: Increase in pressure of surrounding leads to decrease in free volume and ultimately high T_g .

Significance of T_g

- Molecular weight- T_g is directly proportional to molecular weight of polymer.
- Cross links - T_g is directly proportional to degree of cross links.
- Flexibility - T_g is inversely proportional to flexibility.
- Plasticizer - T_g is inversely proportional to plasticization.
- Inter molecular force - T_g is directly proportional to intermolecular force.
- Side groups - T_g is directly proportional to number of side groups

Determination of T_g :

The glass transition temperatures of materials can be measured by using various methods. However differential scanning calorimetry (DSC) or differential thermal analysis (DTA) are the two most widely used methods. Sometimes trial and error has to be used to see which technique is best. It is extremely important to know which technique and test parameters were used to determine T_g if comparing back to historical data. Similarly, if testing to a specification or industry standard, the technique and test parameters must be well defined. Even within a test technique, the means of obtaining the T_g can be performed in various ways and the results can vary significantly. The T_g by DSC, TMA or DMA rarely will be the same and can vary by as much as 20°C or more.

a) Differential Scanning Calorimetry (DSC)

This is probably the most traditional and common technique for most polymeric materials. In this method, the difference in heat flow to a sample and to a reference is monitored against time or temperature while the temperature rise/fall of the sample, in a specified atmosphere, is programmed. Simply stated, DSC utilizes a heat flow technique and compares the amount of heat supplied to the test sample and a similarly heated "reference" to determine transition points. T_g is typically calculated by using a half-height technique in the transition region. The heating rate and sample heat history are some of the factors that may affect the test results. Depending on the equipment capability, DSC can be used for a wide range of thermoplastic and thermoset polymers. For materials that have broad T_g 's, DSC may not be sensitive enough to show a large enough transition for calculation purposes. Thus, it determines the thermal properties of the polymer. This test method is applicable to amorphous materials or to partially crystalline materials containing amorphous regions, that are stable and do not undergo decomposition or sublimation in the glass transition region. These materials do not undergo decomposition or sublimation in the glass transition region.

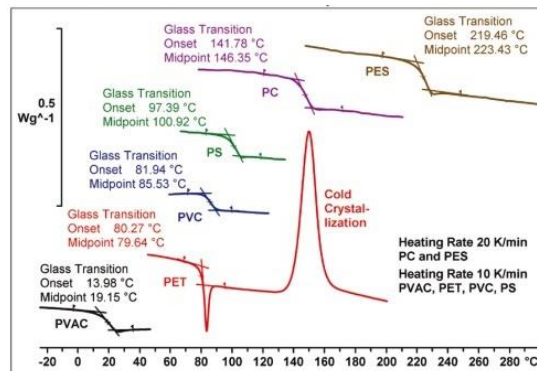


Fig 9. Glass Transition Temperature Measurements of Different Polymers Using DSC

b) Differential Thermal Analysis (DTA): Differential Thermal Analysis (DTA) is a popular thermal analysis technique. It is often employed for measuring T_g of the material. This test method is similar to differential scanning calorimetry (DSC). The technique involves an inert reference material. The material under analysis in DTA undergoes various heating and cooling (thermal) cycles. It determines the temperature difference between the reference and the sample. It maintains the same temperature throughout the heat cycles for reference and sample. This ensures that the testing environment is uniform. Both methods, DTA and DSC, yield peaks relating to endothermic and exothermic transitions with thermal input and show phase changes or occurrence of reactions.

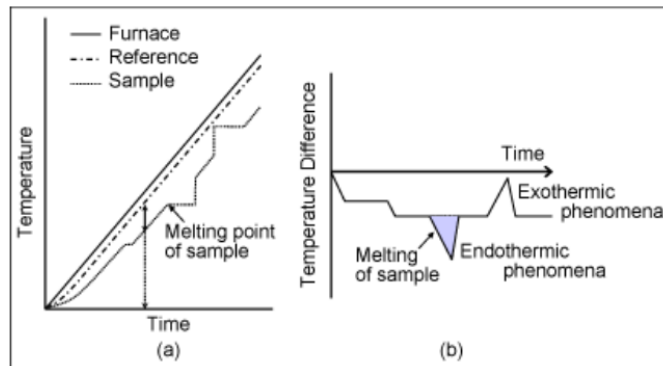


Fig 10. Measurement Principles of DTA

Where Graph (a) Shows the Temperature Change of the Furnace, Reference and Sample against Time
 Graph (b) Shows the Temperature Difference (ΔT) Against Time Detected with the Differential Thermocouple

c) Dynamic Mechanical Analysis (DMA): DMA is probably one of the most sensitive techniques for T_g analysis. DMA measures the response of a material to an applied oscillatory strain (or stress), and how that response varies with temperature, frequency, or both. DMA is able to separate and measure the elastic and viscous components of polymers. How the material responds to the temperature increase can be illustrated by various means on the DMA graph. There are three typical approaches for reporting T_g by DMA. All techniques are viable but may yield different results. Several results may include: 1) Onset of the storage modulus curve; 2) Peak of the loss modulus curve; and/or 3) Peak of the Tan Delta curve. There also are different modes of oscillation used for DMA, such as torsional, single and dual cantilever, tension, compression, three-point bend and compression. Various heating rates, frequencies and strains can be utilized as well. All of these variables can affect the T_g . Compared to DSC, DMA can be 10 to 100 times more sensitive to the changes occurring at the T_g . DMA is useful for polymers with difficult to find T_g 's such as epoxies, polymers with T_g 's well below ambient temperature and highly crosslinked polymers. It is important to note T_g by DMA can vary significantly from one reporting technique to the next.

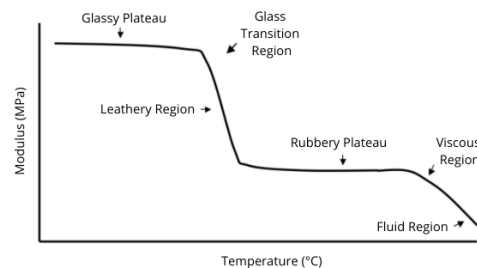


Fig 11. Typical DMA Analysis Graph

d) Thermal Mechanical Analysis (TMA) – TMA is used to measure Coefficient of Thermal Expansion (CTE) of polymers. TMA uses a mechanical approach for measuring T_g . A sensitive probe measures the expansion of the test specimen when heated. Polymers typically expand as temperature is increased. From the expansion curve, a CTE can be calculated over a temperature range. If a material goes through a T_g during a TMA test, the curve shape changes significantly and T_g can be calculated by using an onset technique. Amorphous polymers would typically not utilize the TMA approach because the material would soften to the point where the probe penetrates into the sample. Samples that remain somewhat rigid through T_g would be good candidates for T_g by TMA. The heating rate chosen can affect the T_g .

Question: What is the difference between T_g and T_m ?

Answer: At the molecular level, the chains in amorphous regions of the polymer gain enough thermal energy to begin sliding past one another at a noticeable rate. The temperature where the entire chain movement occurs is called the melting point. It is greater than the T_g .

- Glass Transition is a property of the amorphous region while melting is the property of the crystalline region.
- Below T_g , there exists a disordered amorphous solid where chain motion is frozen and molecules start wiggling around above T_g . The more immobile the chain, the higher the value of T_g .
- While, below T_m it is an ordered crystalline solid which becomes disordered melt above T_m .

Question: Why is it important to identify the T_g of polymers?

Answer: Glass transition temperature is an important property used to change the physical properties of polymers.

- Increasing T_g improves handling characters, solubility, and reproducibility in the dissolution of solids.
- Changes in physical properties such as hardness and elasticity.
- Changes in volume, percent elongation to break, and Young's modulus of solids.
- Used for quality control, research, and development.

Question: What are the examples of polymers with high or low T_g ?

Answer:

Polymers with high T_g :

Some polymers are used below their T_g (in glassy state) like:

- Polystyrene
- Poly(methyl methacrylate)

These polymers are hard and brittle. Their T_g 's are higher than room temperature.

Polymers with low T_g :

Some polymers are used above their T_g (in rubbery state), for example, rubber elastomers like:

- Polyisoprene
- Polyisobutylene

They are soft and flexible in nature. Their T_g 's are less than room temperature.

Question: Which type of polymers undergoes glass transition?

Answer: T_g is the property of amorphous polymers and the amorphous part of a semi-crystalline solid. Thus amorphous polymers like PC, PMMA, PVC, ABS, GPPS etc. undergo glass transition. Whereas purely crystalline polymers like polyolefins, PEEK, PET, POM, etc. do not undergo glass transition.

Question: Why is the determination of glass transition temperature so important?

Answer:

- The determination of glass transition temperature (T_g) is critical for understanding the properties of the material.
- It indicates the temperature at which a substance transforms from a glassy state to a rubbery state or vice versa.
- For practical applications, it is important to realize that the properties of glasses differ significantly from those of other solids.
- The glass transition provides information about molecular dynamics in the supercooled melt.
- It defines the upper temperature limit for the use of solid amorphous materials; for rubbery materials, it is the lower temperature limit.
- Knowledge of the glass transition is also important for optimizing production parameters and the properties of products.
- In addition, the glass transition can be used to identify and compare materials and is therefore important for quality assurance and failure analysis.
- For example, the solubility of glasses is higher than for crystals; this influences the biological activity of pharmaceutical substances.