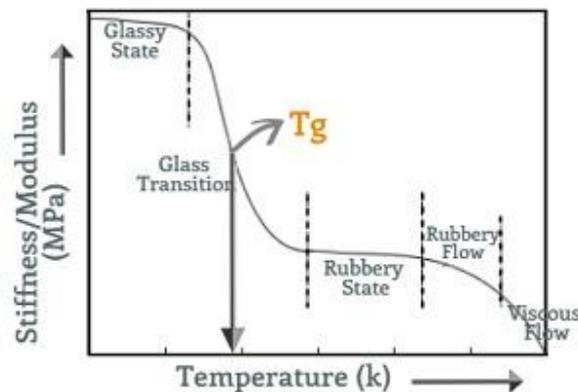


# Glass Transition Temperature

## What does T<sub>g</sub> stand for?

When an amorphous polymer is heated, the temperature at which the polymer structure turns “viscous liquid or rubbery” is called the Glass Transition Temperature, T<sub>g</sub>. It is also defined as a temperature at which **amorphous polymer** takes on characteristic glassy-state properties like brittleness, **stiffness** and rigidity (upon cooling).

This temperature (measured in °C or °F) depends on the chemical structure of the polymer and can therefore be used to identify polymers.



- Amorphous polymers only exhibit a T<sub>g</sub>.
- Crystalline polymers exhibit a T<sub>m</sub> (melt temperature) and typically a T<sub>g</sub> since there is usually an amorphous portion as well (“semi”-crystalline).

The value of T<sub>g</sub> 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.

At T<sub>g</sub>, changes in hardness, volume, percent **elongation to break** and **Young’s modulus** of solids are mainly seen.

Some polymers are used below their T<sub>g</sub> (in glassy state) like polystyrene, **poly(methyl methacrylate)** etc., which are hard and brittle. Their T<sub>g</sub>s are higher than room temperature.

Some polymers are used above their T<sub>g</sub> (in rubbery state), for example, rubber elastomers like polyisoprene, polyisobutylene. They are soft and flexible in nature; their T<sub>g</sub>s are less than room temperature.

### **Applications include:**

Identifying the T<sub>g</sub> of polymers is often used for quality control and research and development. Also, it is an important tool used to **modify physical properties** of polymer molecules.

Further, improvement in handling characters, solubility and reproducibility in dissolution of solids can be achieved by increasing the T<sub>g</sub> of solids.

### ***Check out more on Glass Transition Temperature:***

- » **Glass Transition Temperature Values Table of Several Plastics**
- » **What are Amorphous and Crystalline Polymers**
- » **How to Determine Glass Transition Temperature**
- » **Key difference Between T<sub>g</sub> and Melting Temperature**
- » **Factors Affecting T<sub>g</sub> of any plastic**

### **Amorphous Polymers and Crystalline Polymers**

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.

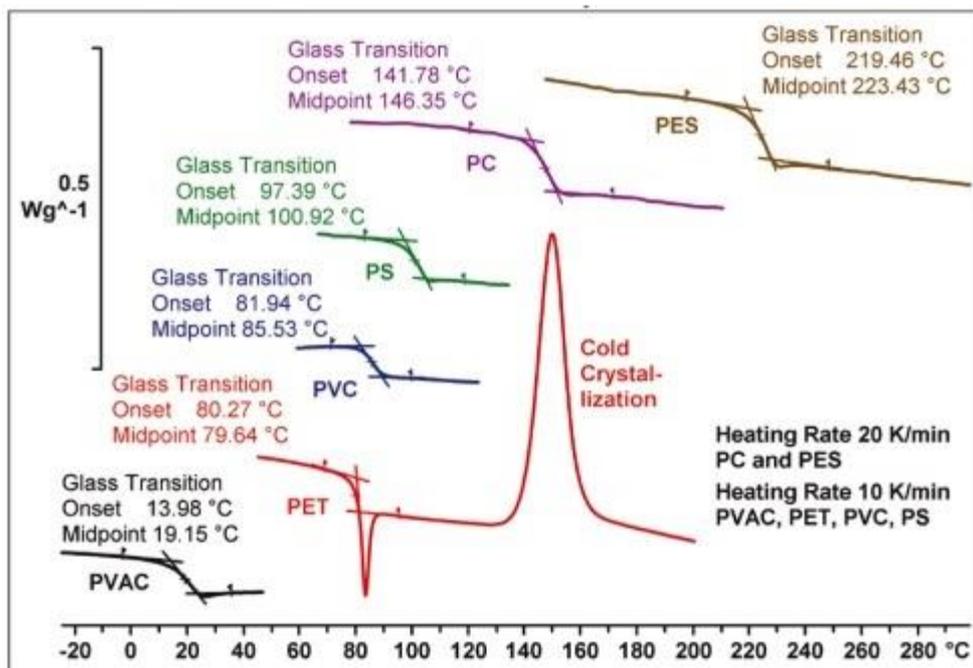
## How to Measure Glass Transition Temperature

The most usual test method to determine Glass Transition Temperature of plastics is **ASTM E1356**. This test method covers the assignment of the glass transition temperatures of materials using **differential scanning calorimetry** or **differential thermal analysis**.

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.

Both methods, DTA and DSC, yield peaks relating to endothermic and exothermic transitions with thermal input and show phase changes or occurrence of reactions.

- In DTA, the difference in temperature between the sample and a reference material is monitored against time or temperature while the temperature rise/fall of the sample, in a specified atmosphere, is programmed.
- In DSC, 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.



**Glass Transition Temp. Measurements of Different Polymers Using DSC**

**(Source: Mettler-Toledo Analytical)**

*Of course there exists several other methods as well to determine  $T_g$ , such as:*

- *Specific heat measurements*
- *Thermo mechanical analysis*
- *Thermal expansion measurement*
- *Micro-heat-transfer measurement*
- *Isothermal compressibility*
- *Heat capacity*

*... but they all are not discussed in detail*

## **Glass Transition Temperature Vs Melting Temperature**

At the molecular level, at  $T_g$ , the chains in amorphous (i.e., disordered) regions of the polymer gain enough thermal energy to begin sliding past one another at a noticeable rate. The temperature where entire chain movement occurs is called the melting point ( $T_m$ ) and is greater than the  $T_g$

1. Glass Transition is a property of the amorphous region while melting is the property of crystalline region
2. Below  $T_g$ , there exists 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  $T_g$ .
3. While, below  $T_m$  it is an ordered crystalline solid which becomes disordered melt above  $T_m$

The operating temperature of polymers is defined by transition temperatures

## **Factors Affecting $T_g$**

### **Chemical Structure**

- **Molecular Weight** – In straight chain polymers, increase in MW leads to decrease in chain end concentration resulting in decreases free volume at end group region – and increase in  $T_g$
- **Molecular Structure** - Insertion of bulky, inflexible side group increases  $T_g$  of material due to decrease in mobility,

- **Chemical cross-linking** - Increase in cross-linking decreases mobility leads to decrease in free volume and increase in  $T_g$
- **Polar groups** - Presence of polar groups increases intermolecular forces; inter chain attraction and cohesion leading to decrease in free volume resulting in increase in  $T_g$ .

### **Addition of Plasticizers**

Addition of plasticizer increases the free volume in polymer structure (Plasticizer gets in between the polymer chains and spaces them apart from each other)

This results in polymer chains 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

### **Water or moisture content**

Increase in moisture content leads formation of hydrogen bonds with polymeric chains increasing the distance between polymeric chains. And, hence increases the free volume and decreases  $T_g$ .

### **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.

### **Pressure and free volume**

Increase in pressure of surrounding leads to decrease in free volume and ultimately high  $T_g$ .

Other factors like branching, alkyl chain length, bond interaction, flexibility of polymer chain, film thickness etc. also have significant impact on glass transition temperature of polymers.

### **Glass Transition Temperature Values of Several Plastics**

Polymer Name	Min Value (°C)	Max Value (°C)
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ABS - Acrylonitrile Butadiene Styrene	90.0	102.0
ABS Flame Retardant	105.0	115.0
ABS High Heat	105.0	115.0
ABS High Impact	95.0	110.0
Amorphous TPI, Moderate Heat, Transparent	247.0	247.0
Amorphous TPI, Moderate Heat, Transparent (Food Contact Approved)	247.0	247.0
Amorphous TPI, Moderate Heat, Transparent (Mold Release grade)	247.0	247.0
Amorphous TPI, Moderate Heat, Transparent (Powder form)	247.0	247.0
CA - Cellulose Acetate	100.0	130.0
CAB - Cellulose Acetate Butyrate	80.0	120.0
Cellulose Diacetate-Pearlescent Films	120.0	120.0
Cellulose Diacetate-Gloss Film	120.0	120.0
Cellulose Diacetate-Integuard Films	113.0	113.0
Cellulose Diacetate-Matt Film	120.0	120.0
Cellulose Diacetate-Window Patch Film (Food Grade)	120.0	120.0
Cellulose Diacetate-Clareflect metallized film	120.0	120.0
Cellulose Diacetate-Colored Films	120.0	120.0
Cellulose Diacetate-Flame retardant Film	162.0	162.0
Cellulose Diacetate-High Slip Film	120.0	120.0
Cellulose Diacetate-Semitone Films	120.0	120.0
CP - Cellulose Propionate	80.0	120.0

COC - Cyclic Olefin Copolymer	136.0	180.0
CPVC - Chlorinated Polyvinyl Chloride	100.0	110.0
EVOH - Ethylene Vinyl Alcohol	15.0	70.0
HDPE - High Density Polyethylene	-110.0	-110.0
HIPS - High Impact Polystyrene	88.0	92.0
HIPS Flame Retardant V0	90.0	90.0
LCP Glass Fiber-reinforced	120.0	120.0
LCP Mineral-filled	120.0	120.0
LDPE - Low Density Polyethylene	-110.0	-110.0
LLDPE - Linear Low Density Polyethylene	-110.0	-110.0
PA 11 - (Polyamide 11) 30% Glass fiber reinforced	35.0	45.0
PA 11, Conductive	35.0	45.0
PA 11, Flexible	35.0	45.0
PA 11, Rigid	35.0	45.0
PA 12 (Polyamide 12), Conductive	35.0	45.0
PA 12, Fiber-reinforced	35.0	45.0
PA 12, Flexible	35.0	45.0
PA 12, Glass Filled	35.0	45.0
PA 12, Rigid	35.0	45.0
PA 46, 30% Glass Fiber	75.0	77.0
PA 6 - Polyamide 6	60.0	60.0
PA 66 - Polyamide 6-6	55.0	58.0
PA 66, 30% Glass Fiber	50.0	60.0
PA 66, 30% Mineral filled	50.0	60.0
PA 66, Impact Modified, 15-30% Glass	50.0	60.0

Fiber		
Polyamide semi-aromatic	115.0	170.0
PAI - Polyamide-Imide	275.0	275.0
PAI, 30% Glass Fiber	275.0	275.0
PAI, Low Friction	275.0	275.0
PAR - Polyarylate	190.0	190.0
PBT - Polybutylene Terephthalate	55.0	65.0
PC (Polycarbonate) 20-40% Glass Fiber	150.0	150.0
PC (Polycarbonate) 20-40% Glass Fiber Flame Retardant	150.0	150.0
PC - Polycarbonate, high heat	160.0	200.0
PCL - Polycaprolactone	-60.0	-60.0
PE - Polyethylene 30% Glass Fiber	-110.0	-110.0
PEEK - Polyetheretherketone	140.0	145.0
PEEK 30% Carbon Fiber-reinforced	140.0	143.0
PEEK 30% Glass Fiber-reinforced	143.0	143.0
PEI - Polyetherimide	215.0	215.0
PEI, 30% Glass Fiber-reinforced	215.0	215.0
PEI, Mineral Filled	215.0	215.0
PESU - Polyethersulfone	210.0	230.0
PESU 10-30% glass fiber	210.0	230.0
PET - Polyethylene Terephthalate	73.0	78.0
PET, 30% Glass Fiber-reinforced	56.0	56.0
PETG - Polyethylene Terephthalate Glycol	79.0	80.0
PFA - Perfluoroalkoxy	90.0	90.0

PGA - Polyglycolides	35.0	40.0
PHB-V (5% valerate) - Poly(hydroxybutyrate - co- valerate)	3.0	5.0
PI - Polyimide	250.0	340.0
PLA, Fiber Melt Spinning	55.0	65.0
PLA, Heat Seal Layer	52.0	58.0
PLA, Injection molding	55.0	60.0
PLA, Spunbond	55.0	60.0
PLA, Stretch blow molded bottles	50.0	60.0
PMMA - Polymethylmethacrylate/Acrylic	90.0	110.0
PMMA (Acrylic) High Heat	100.0	168.0
PMMA (Acrylic) Impact Modified	90.0	110.0
PMP - Polymethylpentene	20.0	30.0
PMP 30% Glass Fiber-reinforced	20.0	30.0
PMP Mineral Filled	20.0	30.0
POM - Polyoxymethylene (Acetal)	-60.0	-50.0
PP - Polypropylene 10-20% Glass Fiber	-20.0	-10.0
PP, 10-40% Mineral Filled	-20.0	-10.0
PP, 10-40% Talc Filled	-20.0	-10.0
PP, 30-40% Glass Fiber-reinforced	-20.0	-10.0
PP (Polypropylene) Copolymer	-20.0	-20.0
PP (Polypropylene) Homopolymer	-10.0	-10.0
PP, Impact Modified	-20.0	-20.0
PPE - Polyphenylene Ether	100.0	210.0
PPE, 30% Glass Fiber-reinforced	100.0	150.0
PPE, Impact Modified	130.0	150.0

PPE, Mineral Filled	100.0	150.0
PPS - Polyphenylene Sulfide	88.0	93.0
PPS, 20-30% Glass Fiber-reinforced	88.0	93.0
PPS, 40% Glass Fiber-reinforced	88.0	93.0
PPS, Conductive	88.0	93.0
PPS, Glass fiber & Mineral-filled	88.0	93.0
PPSU - Polyphenylene Sulfone	220.0	220.0
PS (Polystyrene) 30% glass fiber	90.0	120.0
PS (Polystyrene) Crystal	90.0	90.0
PS, High Heat	90.0	90.0
PSU - Polysulfone	187.0	190.0
PSU, 30% Glass fiber-reinforced	187.0	190.0
PSU Mineral Filled	187.0	190.0
PVC (Polyvinyl Chloride), 20% Glass Fiber-reinforced	60.0	100.0
PVC, Plasticized	-50.0	-5.0
PVC, Plasticized Filled	-50.0	-5.0
PVC Rigid	60.0	100.0
PVDC - Polyvinylidene Chloride	-15.0	-15.0
PVDF - Polyvinylidene Fluoride	-42.0	-25.0
SAN - Styrene Acrylonitrile	100.0	115.0
SAN, 20% Glass Fiber-reinforced	100.0	115.0
SMA - Styrene Maleic Anhydride	110.0	115.0
SMA, 20% Glass Fiber-reinforced	110.0	115.0
SMA, Flame Retardant V0	110.0	115.0
SRP - Self-reinforced Polyphenylene	150.0	168.0