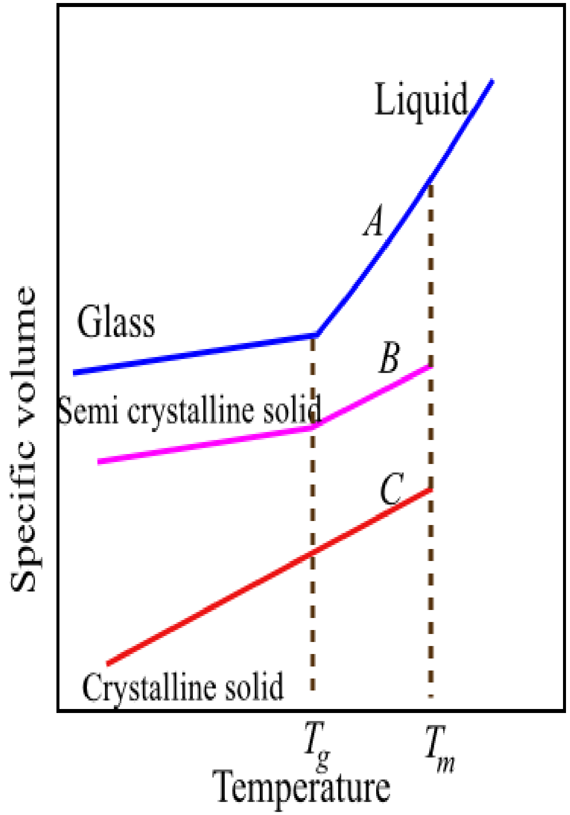
Physical and chemical properties of polymers

Glass transition temperature (Tg)

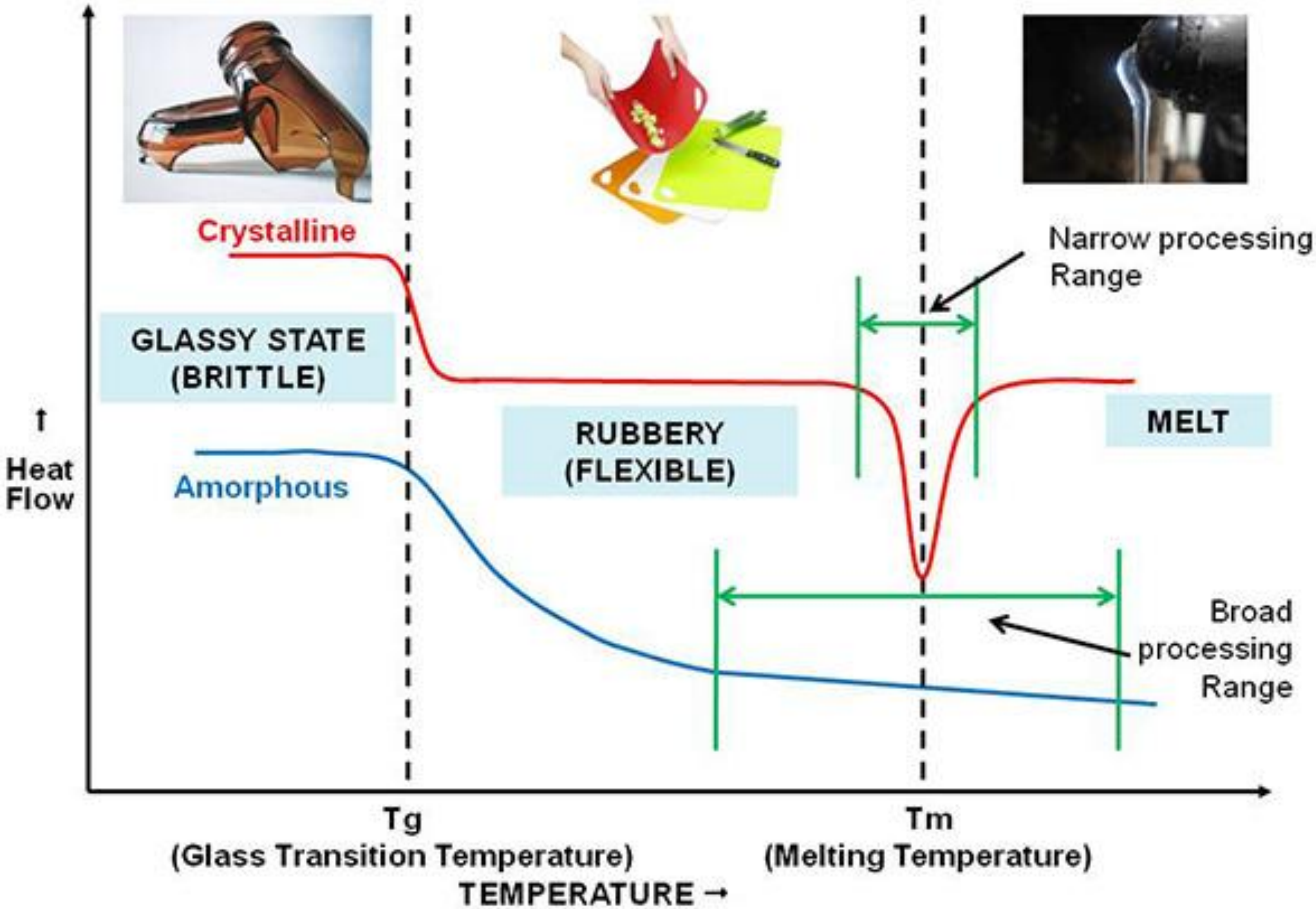
- The glass transition temperature, often called T_g, is an important property when considering polymers for a particular end-use. Glass transition temperature is the temperature, below which the physical properties of plastics change to those of a glassy or crystalline state. Above T_g they behave like rubbery materials. Below the T_g a plastic's molecules have relatively little mobility. T_g is usually applicable to wholly or partially amorphous plastics. A plastic's properties can be dramatically different above and below its T_g. The value of the glass transition temperature depends on the strain rate and cooling or heating rate, so there cannot be an exact value for T_g.
- The glass transition temperature is the temperature range where the polymer substrate changes from a rigid glassy material to a soft (not melted) material, and is usually measured in terms of the stiffness, or modulus.*

Introduction to Plastics, Sina Ebnesajjad, in Chemical Resistance of Engineering Thermoplastics, 2016



Tg and Tm temperatures of some polymers

Polymer	Tg(°C)	Te(°C)
polyethylene	-115	95-140
Polypropylene Atactic isotactic	 -20 -10	 75 160
Polystyrene	100	240
Polyacrylonitrile	85	317
Polyvinyl chloride	81	285
PET	69-80	270
Nylon 6,6	57	267



http://fimmtech.com/knowledgebase/polymers-and-plastics/

- ***The free volume*** of a polymer is defined as "the volume that is not occupied by the polymer molecules" in the total volume of a polymer.

- Tg of a polymer can be defined by using this free volume term.
- In general, it was observed that a polymer can bend and twist (softens) when its free volume reaches to 2.5% of its total volume.

- Thus, it can be said that the T***g*** of a polymer is the temperature when a polymer reaches to its free volume of 2.5%.

- ***Maximum usage temperature*** is the temperature where a polymeric material loses its properties and functionality.
- The polymers can preserve their rigid structure up to 75% times of their Tg’s. E.g. İf a polymer has a Tg of 100oC, then it can be used as a rigid solid at 75oC.
- If a polymer is heated up to the high temperatures, first, the lowest covalent bonds are broken and the polymer starts to decompose. ***Thermal Decomposition Temperature***, is the temperature where the polymer starts to decompose.
- The polymers decompose before reaching to their boiling temperatures since the energy that is required for the vaporization of a polymer is always higher than that of bond energy of chemical bonds in the polymer structure.

- Thermoplastics>>>> The decomposition starts before the melting
- Thermosettings>>>> The decomposition starts at the solid state.

polymer	Max.Usage Temp (^oC)	Thermal Decomp.Temp. (oC)
polytetrafloroethylene	250	500-550
Polycarbonate	125	325-400
Nylon 6	105	300-350
Polyethylene	80	340-440
polyvinylchloride	60	200-300
??	Fill in the blanks	Fill in the blanks
??	Fill in the blanks	Fill in the blanks

Effect of environmental conditions on the polymers

The parameters that can affect the property/usability of the polymers can be listed below:

-Atmospheric conditions (uv-lights, humidity, temperature, climate, and etc.)

-Liquids (organic/inorganic solvents, acids, alkali, and etc.)

Swelling/Solubility of a Polymer

Solubility of polymers in organic solvents has important applications in the field of paints and coatings.

In the polimer-liquid systems with similar chemical natures (such as polar, non-polar), the secondary interactions exist between polymer chains and liquid molecules. As a result of these interactions, if the lineer or branched polymers are exposed to liquids for a sufficient of time, the polymers are dissolved in the liquids by diffusing in the molecular level ,as expected.

E.g. Non-polar benzene, toluene, and ethyl benzene can dissolve polystyrene.

The dissolution can take part into two stages: first, the solvent molecule swells and gels the polymer by the diffusion into polymer lattices then the gel disperses into the solvent by giving a solution .

How about cross-linked polymers?

The physical nature of the polymer will also have an effect, especially for liquids that cause appreciable swelling. In order to be absorbed into a polymer, there must be sufficient space or chain flexibility to accommodate a liquid molecule.

Therefore, amorphous polymers above their T_g will swell more easily than those below their T_g, and crystalline blocks generally show very little absorption.

For a liquid molecule to be stable when dissolved in a polymer, the overall interaction (free) energy change must be negative.

$\Delta G = \Delta H - T.\Delta S$ $\Delta G < 0$, spontaneously soluble

This is made up from an entropy term, which always favors mixing and increases as the temperature increases, and an enthalpy term, which depends on the chemical interactions.

The dissolution of a polymer;

- Chain branching,
- Cross-links,
- Cristallinity,
- The polarity of main chains/side chains,
- Molecular weight.

? Homework: comment on each parameter. Justify the reasons.