Crystallization, melting & glass transition phenomena in polymers.

~~Crystallization is the pro~~ These are important wrt the design & processing of polymeric materials.

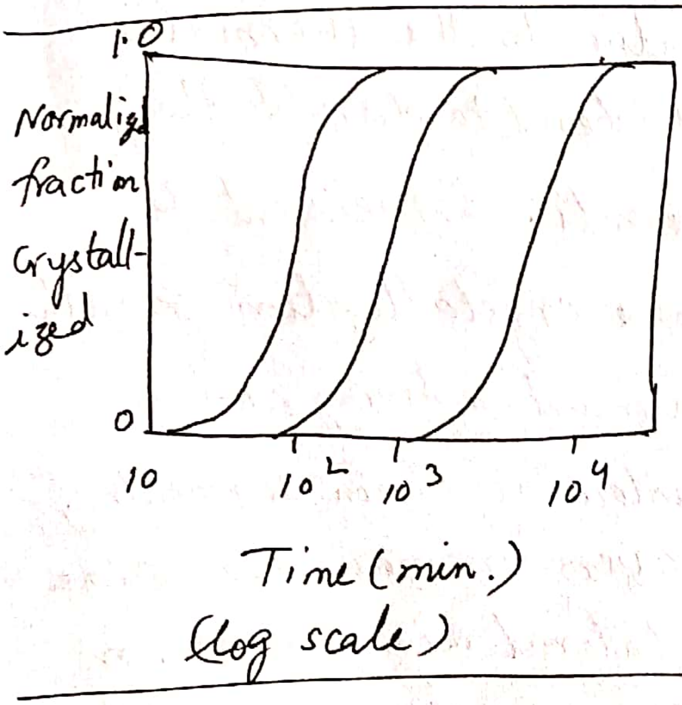
crystalline region experiences melting & crystallization
non crystalline region passes through glass transition.

Crystallization of molten polymers →
— occurs by nucleation and growth processes.
— Upon cooling through the melting temperature, nuclei form wherein small regions of the tangled and random molecules become ordered and aligned in the manner of ~~th~~ chain-folded layers.
At temperatures in excess of the ~~m~~ melting temp. these nuclei are unstable due to the thermal atomic vibrations ~~th~~ that tend to disrupt the ordered molecular arrangements. Subsequent to nucleation and during the crystallization growth stage, nuclei grow by the continued ordering and allignment of additional molecular chain segments; that is the chain folded layers remain the same thickness, but increase in lateral dimensions, or for spherulitic structures, there is an increase in spherulite radius.

The time dependence of crystallization is the same as for many solid-state transformations i.e. a sigmoidal shaped curve results when fraction transformation (i.e. fraction crystallized) is plotted vs the log of time (at constant temp.). Such a ~~potot~~ plot is presented in fig. for the crystallization of ~~P~~ Poly propylene at 3 temperatures. Mathematically, fraction crystallized y is a function of time 't' according to the Avrami eqn

$$y = 1-\exp(-kt^{n})$$

where k and n are time independent constants, whose ~~x~~ values depend on the crystallizing system.



Plot of normalized fraction crystallized vs the log of time for PP at constant temp.s of 140°C, 150°C and 160°C

Normally, the extent of crystallization is measured by specimen volume changes ~~on~~ since there will be a difference ~~be~~ in volume for liquid and crystallized phases. Rate of crystallization is equal to the reciprocal of time required for crystallization to proceed to 50% completion. This rate is dependent on crystallization temperature and also on the molecular weight of the polymer, rate decreases with increasing molecular weight.

For P.P. the attainment of 100% crystallinity is not possible. Therefore, the vertical axis is scaled as "normalized fraction crystallized". ~~The~~ A value of 1.0 for this parameter corresponds to the highest level of crystallization that is achieved during the tests, which, in reality, is less than complete crystallization.

14.11 Melting

The melting of a polymer crystal → transformation of a solid material (ordered structure of aligned molecular chains,) to a viscous liquid (highly random structure).

This phenomenon occurs, upon heating at T_m

✱ Melting of polymer – distinctive features (wrt metal/ceramic)

① melting takes place over a range of temperatures.

② melting behaviour depends on the history of the specimen in particular the temperature at which it crystallized;

③ The thickness of chain folded lamellae will depend on crystallization temperature; the thicker the lamellae, the higher the melting temperature.

④ Impurities in the polymer and imperfections in the crystals ~~th~~ also decrease the melting temperature.

⑤ The apparent melting behaviour is a function of the rate of heating; increasing this rate results in an elevation of the melting temperature.

Heat treatments can produce structural and property alterations.

An increase in lamellar thickness may be induced by annealing just below the Tm. Annealing also raises the Tm by decreasing the vacancies and other imperfections in polymer crystals and increasing crystallite thickness.

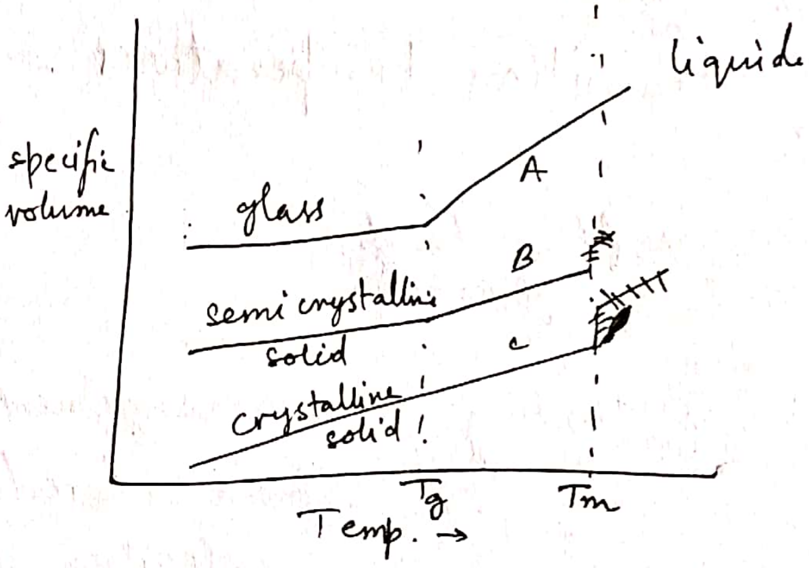
14.12 The Glass transition

The glass transition occurs in amorphous (or glassy) and semi crystalline polymers and is due to a reduction of motion of large segments of molecular chains with decreasing temperature.

14.13 Melting & Tg

Specific volume vs temp.

upon cooling from the liquid melt, for totally amorphous (curve A) semicrystalline (curve B) and crystalline (curve C) polymers.



- crystalline → discontinuous change ~~at~~ at Tm.

Amorphous → slight decrease in slope " Tg

semicrystalline → Intermediate behaviour.

Material.	Tg (°C)	Tm (°C)
LD PE	−110	115
Polytetrafluoroethylene	−97	327
HDPE	−90	137
PP	−18	175
Nylon 6,6	57	265
PET (polyester)	69	265
PVC	87	212
PS	100	240
Polycarbonate	150	265.

14.14 Factors that influence melting and glass transition temperatures.

Melting temp.

Melting – rearrangement of the molecules from ordered to disordered molecular states.

① Chain stiffness – It is controlled by the ease of rotation about the chemical bonds along the chain.

- The presence of doble bonds and aromatic groups in the polymer backbone lowers chain flexibility and causes an increase in Tm.

- Bulky or large side groups restrict molecular rotation and raise Tm.

eg. PP (175°C) has a higher Tm than PE.

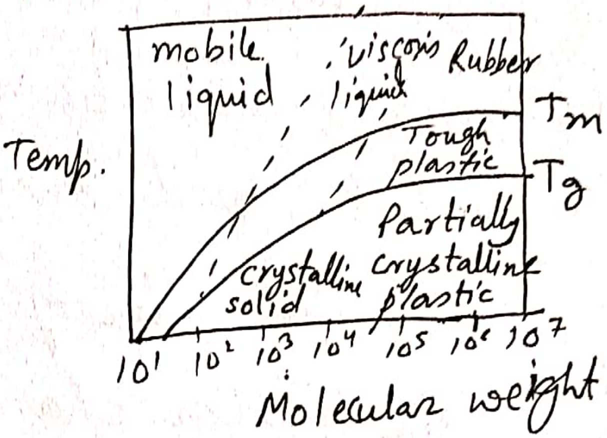
the CH_3 methyl side group for PP is larger than H group of PE.

T_m PP = 175°C T_m PVC = 212°C

② Molecular weight

At relatively low molecular weights increasing $\bar{M}$ or chain length raises Tm.

Dependence of polymer properties as well as melting and glass transition temperatures on molecular weight.



~~Ther~~ Every polymer ~~*~~ is composed of molecules having a variety of molecular wts. Therefore, the melting is over a range of temperatures & Tms.

The ~~=~~ Tm near the higher ends of the ranges is reported in the tables.

③ Degree of branching.

Introduction of side branches introduces defects into the crystalline material and lowers the melting temperature. HDPE being a predominantly linear polymer, has a higher Tm (137°C) than ~~k~~ LDPE (115°C) which has some branching.

T_g

Heat through T_g, the amorphous solid polymer transforms from a rigid to a rubbery state. Correspondingly ~~mo~~ virtually frozen molecules ~~above~~ below T_g begin to experience rotation and translation motions above T_g..

Thus the value of T_g will depend on molecular characteristics that affect chain stiffness.

① Bulky side groups :-

	T_g
PP	−18°C
PS	100°C

② Polar groups

	T_g
PVC	87°C
PP	−18°C

③ Double bonds and aromatic groups in the backbone, which tend to stiffen the polymer chain.

Increasing the molecular weight also tends to raise the T_g. A small amount of branching will tend to lower T_g. High density of branching reduces mobility and hence T_g ↑. Crosslinking elevates T_g. High density crosslinking → polymers might not experience T_g.

Normally T_g lies between 0.5 & 0.8 T_m. (K)

Homopolymer → not possible to independently vary both T_g & T_m.

Copolymer → greater degree of control over these two parameters.

Callister

Polymer types

Classification depends on end use.

Plastic — if cross-linked & used above T_g = Elastomer.

Fiber — used as plastic if not drawn into fibers.

Plastics — Materials that have some structural rigidity under load, and are used in general purpose applications.

e.g. PE, PP, PVC, PS, epoxy, phenolic, PE.

- rigid / brittle or flexible
- crystallinity (any degree of)
- molecular structure & configuration (linear, branched, isotactic, etc)
- thermoplastic / thermosetting

→ Linear or branched polymers must be used below their T_g (if amorphous) or below their T_m (if semicrystalline), or must be crosslinked enough to maintain their shape.

PS & PMMA are good for applications requiring optical transparency.
~~is critical applications~~

Trade names, Characteristics and Typical Applications for a number of plastic materials

Material type	Trade names	Major Applications Characteristics	Typical Applications
		Thermoplastics	
ABS Acrylonitrile butadiene styrene	Abson	Outstanding strength and toughness, resistant to heat distortion; good electrical properties, flammable and soluble in some organic solvents.	Refrigerator linings, lawn and garden equipment, toys, highway safety devices
Acrylics poly (methyl methacrylate)	Acrylite Lucite	Outstanding light transmission & resistance to weathering, only fair mechanical properties	Lenses, transparent aircraft enclosures, drafting equipment, outdoor signs.
Fluoro carbons PTFE or TFE	Teflon	Chemically inert in almost all environments, excellent electrical properties, low coefficient of friction, may be used to 260°C, relatively weak & poor cold-flow properties.	Anticorrosive seals, chemical pipes and valves, bearings, anti-adhesive coatings, high temperature electronic parts.

Material type	Trade Name	Major application characteristics	Typical applications
Polyamides (nylons)	Nylon	Good mechanical strength, abrasion resistance, and toughness low coefficient of friction, absorbs water & some other liquids	Bearings, gears, cams, bushings, handles, and jacketing for wires & cables.
Poly Carbonates	Calibre Lexan	Dimensionally stable, low water absorption, transparent, very good impact resistance and ductility; chemical resistance not outstanding	safety helmets, lenses, light globes, base for photographic film.
Poly ethylene	Alathon Rigiden	chemically resistant and electrically insulating, tough and relatively low coefficient of friction, low strength and poor resistance to weathering	Flexible bottles, toys, tumblers, battery parts, ice trays, film wrapping materials.

Material type	Trade name	Materia Major ~~applications~~ characteristics	Typical Applications
PP	Herculon	Resistance to heat distortion; excellent electrical properties & fatigue strength, chemically inert, relatively inexpensive poor resistance to UV light	Sterilizable bottles, packaging film, cabinets, luggage.
PS	Carinex	~~Et~~Excellent electrical properties and optical clarity, good thermal and dimensional stability relatively inexpensive	Wall tile, battery cases, toys, indoor lighting panels, appliance housings.
Vinyls	Darvic	Good low-cost, general purpose materials, ordinarily rigid, but many be made flexible with plasticizers, often copolymerized Susceptible to heat distortion	~~A~~ Floor coverings, pipe, electrical wire insulation, garden hose, phonograph records
2D ↑ Polyester PET	Calanar Petra	One of the toughest of plastic films, excellent fatigue & tear strength, and resistance to humidity.	Magnetic recording tapes, clothing automotive tyre cords, beverage containers

acids, greases, oils & solvents.

Thermosetting

Epoxies	Araldite	Excellent combination of mechanical properties & corrosion resistance; dimensionally stable, good adhesion, relatively inexpensive, good electrical properties.	Electrical moldings, sinks, adhesives, protective coatings, used with fiberglass laminates
Phenolics	Bakelite	Excellent thermal stability to over 150 °C, may be compounded with a large number of resins fillers etc inexpensive.	Motor housings, telephones auto distributors, electrical fixtures.
3D network ↑ **Polyesters** ↓ structure decides whether thermoplastic or thermoset	Acropol	Excellent electrical properties and low cost can be formulated for room- or high-temperature ~~ete~~ use, often fiber reinforced.	Helmets fiberglass boats, auto body components, chairs, fans.

Elastomers.

~~The characteristics~~

Important synthetic elastomer' = SBR used in

- automobile tires
- reinforced with carbon black.
- NBR – resistant to degradation and swelling
- Silicone rubber → alternating Si & O atoms $-\!\left(\overset{R}{\underset{R'}{Si}}-O\right)_n$

Chemical type	Trade (Common names)	Elongation (%)	Useful temp. range (°C)	Major application characteristics	Typical applications
Natural poly-isoprene.	Natural rubber (NR)	500-760	-60 to 120	Excellent physical properties, good resistance to cutting, gouging and abrasion, low heat, ozone, and oil resistance good electrical properties.	Pneumatic tires & tubes, heel and soles gaskets.
Styrene butadiene ~~rubber~~ copolymer	GRS Buna-S SBR	450-500	-60 to 120	Good physical properties excellent abrasion resistance, not oil ozone, or weather resistant, electrical	Same as natural rubber

				properties good but not outstanding	~~Gasoline, c~~
Acrylonitrile butadiene copolymer	Buna A nitrile NBR	400-600	-50 to 150	Excellent resistance to vegetable, animal & petroleum oils, poor low temperature properties electrical properties not outstanding	Gasoline, chemical & oil hose, seals and O rings heels & soles.
Chloroprene	Neoprene CR	100-800	-50 to 105	Excellent ozone, heat and weathering resistance, good oil resistance, excellent flame resistance, not as good ~~as~~ in electrical applications as natural rubber	Wire & cable, chemical, tank linings, belts, hoses, seals & gaskets.
Polysiloxane	Silicone VMQ	100-800	-115 to 315	Excellent resistance to high & low temperatures, Low strength, excellent electrical properties	High & low temp. insulation, seals, diaphragms tubing for food & medical uses.

Silicone elastomers - flexible upto -90°C, stable upto 250°C, resistant to weathering & lubricating oils, hence useful in ~~engi~~ automobile engine compartments. Bio-compatible hence used in medical applications — blood tubing. vulcanize at room temp. (RTV rubber)

Fibers.

- can be drawn
  - 100:1::L:D
- Textile — woven/knit ⇒ cloth/fabric
- Aramid fiber ⇒ composite material.
- deformation types → in use → stretch, twist, shear, abrade
- ∴ need high UTS (over a relatively wide temp. range) and a high mod. of elasticity as well as abrasion resistance.
- Properties governed by chemistry of the polymer chains and also by the fiber drawing process.
- The molecular wt of fiber materials should be relatively high or the molten material will be too weak and will break during the drawing process. Also, because the tensile strength increases with degree of crystallinity, the structure and configuration of the chains should allow the production of a highly crystalline polymer.
- Linear & unbranched chains are required, that are symmetrical & have regular repeat units. Polar groups in the polymer also improve the fiber forming properties by increasing both crystallinity & the intermolecular forces between the chains. Convenience in washing and maintaining

clothing depends primarily on the thermal properties of the fiber ~~pl~~ polymer, that is, its melting & glass transition temperatures.

Fiber polymers should be chemically stable in a variety of environments like : acids, bases, bleaches, dry cleaning solvents & sunlight. In addition they ~~sto~~ must be relatively non inflammable & amenable to drying.

Miscellaneous applications

I **Coatings =** Applied for the following functions

① to protect from environmental corrosion or deterioration
② to improve appearance.
③ to provide electrical insulation.

Many ingredients in coatings are polymers (majority organic). Organic coatings :- paint, varnish, ~~&~~ enamel, lacquer, and shellac.

Latexes are ~~a~~ common coatings.

Latex = stable suspension of ~~many~~ small insoluble polymer particles ~~in~~ dispersed in water. These materials release low quanitities of volatile organic compound emissions. VOC react with atmosphere to produce smog.

Hence Latexes are preferred.

II Adhesive

Adhesive is used to bond surfaces of 2 solids or adherends, mechanically or chemically.

Mechanical bond – actual penetration of adhesive into surface pores or crevices

Chemical bonding involves intermolecular forces between adhesive & adherend.

– bonding ~~cont~~ can be covalent &/or van der Waals.

– polar groups in adhesives increase " " "bonding

New adhesives based on synthetic polymers :–

polyurethanes, polysiloxanes (silicones), epoxies, polyimides, acrylics, and ~~rup~~ rubber materials.

Choice of adhesive depends on

① materials to be bonded & their porosities.

② the required adhesive properties (i.e. whether the bond is to be temporary or permanent;

③ maximum / minimum exposure temperatures

④ Processing conditions

Except pressure sensitive adhesives, the adhesives material is applied as a low viscosity liquid – cover evenly & completely the adherend – allow for maximum bonding interactions – actual joint forms after curing (liquid to solid transition) — through either a physical process (crystallization, solvent evaporation) or a chemical process (polymerization [add, condense], ~~or~~ vulcanization) — characterization ~~of joint strength~~ - sound joint should have high shear, peel & fracture strengths.

Adhesive bonding has advantages over riveting, bolting, welding, etc :—

- lighter weight
- ability to join dissimiliar materials
- " " " thin components
- ~~Low~~ better fatigue resistance
- lower manufacturing costs.
- ~~fast pr~~ choice for high processing speed manufacturing.

Drawbacks :—

- service temp. limitation.
- max. temp. possible for continuous use for some ~~pol~~ new polymers is 300 °C.

Applications :- Aerospace, automotive, construction, packaging, household goods.

Pressure sensitive adhesives or self adhesive.

eg. self-stick tapes, labels & postage stamps.

These contain polymer tackifying resins; during detachment of the two bonding surfaces, small fibrils form that are attached to the surfaces & tend

to hold them together. tacky = sticky
eg. acrylics, Styrenic block copolymers & natural rubber, are used.

III Films

- 0.025 to 0.125 mm thin films are popular.
- used as bags for packaging food products and other merchandise, as textile products, etc.
- Imp. Characteristics = low density, a high degree of flexibility, high tensile and tear strengths, resistance to attack by moisture & other chemicals, low permeability to gases like water vapour.
- eg. PE, PP, cellophane, Cellulose acetate

IV Foams

Foams – plastic materials that contain a relatively high volume %age of small poses and trapped gas bubbles.

- can be thermoplastic or thermoset.
- PU, rubber, PS, PVC, etc
- used as cushions in auto sector, furniture packaging, thermal insulation, etc.
- A blowing agent is incorporated into the batch of material; it decomposes to release a gas on heating; Gas bubbles ~~a fill the~~ are generated throughout the material which solidifies on cooling; producing a sponge.

~~Ano~~

Another method ~~is~~ involves dissolution of an inert gas into a molten polymer under high pressure. When the pressure is rapidly reduced the gas comes out of solution. Bubbles are formed. As the solid cools ~~the~~ pores are obtained