



Polymers

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Introduction

- Many biological materials are built of polymers (e.g., bone, wood) BUT only in the last 100 years we have learned how to make polymers
- Nowadays, industries that make polymers and polymer composites enjoy a faster growth rate than other branches of materials (metals & ceramics)
- Design with polymers requires special strategies as their properties can change substantially with time and temperature (especially around room temperature)



Introduction

- Polymers properties are very diverse, however common features of all polymers include:
 - long molecules (polymer chains) with a covalently bonded backbone of carbon atoms
 - polymer chains are bonded together by weak “secondary bonds” (van der Waals and hydrogen bonds) or by weak bonds + strong covalent cross-links
 - secondary bonds have a melting point close to room temperature (T_{room}) \rightarrow polymers may show large creep already at T_{room}

\rightarrow design and materials selection with polymers involves considerations much different from metals and ceramics



Material Data

Polymer	Density (Mg m ⁻³)	Youngs Modulus (20 °C 100 s) (GN m ⁻²)	Tensile Strength (MN m ⁻²)	Fracture Toughness (20 °C) (MN m ^{-3/2})	Glass Temperature T _G (K)	Softening Temperature T _s (K)	Specific Heat (J Kg ⁻¹ K ⁻¹)	Thermal Conductivity (Wm ⁻¹ K ⁻¹)	Thermal Coefficient (MK ⁻¹)
<i>Thermoplastics</i>									
Polyethylene, PE (low density)	0.91–0.94	0.15–0.24	7–17	1–2	270	355	2250	0.35	160–190
Polyethylene, PE (high density)	0.95–0.98	0.55–1.0	20–37	2–5	300	390	2100	0.52	150–300
Polypropylene, PP	0.91	1.2–1.7	50–70	3.5	253	310	1900	0.2	100–300
Polytetrafluoroethylene, PTFE	2.2	0.35	17–28	–	–	395	1050	0.25	70–100
Polystyrene, PS	1.1	3.0–3.3	35–68	2	370	370	1350–1500	0.1–0.15	70–100
Polyvinyl chloride, PVC (unplasticized)	1.4	2.4–3.0	40–60	2.4	350	370	–	0.15	50–70
Polymethylmethacrylate, PMMA	1.2	3.3	80–90	1	378	400	1500	0.2	54–72
Nylons	1.15	2–3.5	60–110	3–5	340	350–420	1900	0.2–0.25	80–95
<i>Resins or thermosets</i>									
Epoxies	1.2–1.4	2.1–5.5	40–85	0.6–1.0	380	400–440	1700–2000	0.2–0.5	55–90
Polyesters	1.1–1.4	1.3–4.5	45–85	0.5	340	420–440	1200–2400	0.2–0.24	50–100
Phenolformaldehyde	1.27	8	35–55	–	–	370–550	1500–1700	0.12–0.24	26–60
<i>Elastomers (rubbers)</i>									
Polyisoprene	0.91	0.002–0.1	≈ 10	–	220	≈ 350	≈ 2500	≈ 0.15	≈ 600
Polybutadiene	1.5	0.004–0.1	–	–	171	≈ 350	≈ 2500	≈ 0.15	≈ 600
Polychloroprene	0.94	≈ 0.01	–	–	200	≈ 350	≈ 2500	≈ 0.15	≈ 600
<i>Natural polymers</i>									
Cellulose fibers	1.5	25–40	≈ 1000	–	–	–	–	–	–
Lignin	1.4	2.0	–	–	–	–	–	–	–
Protein	1.2–1.4	–	–	–	–	–	–	–	–

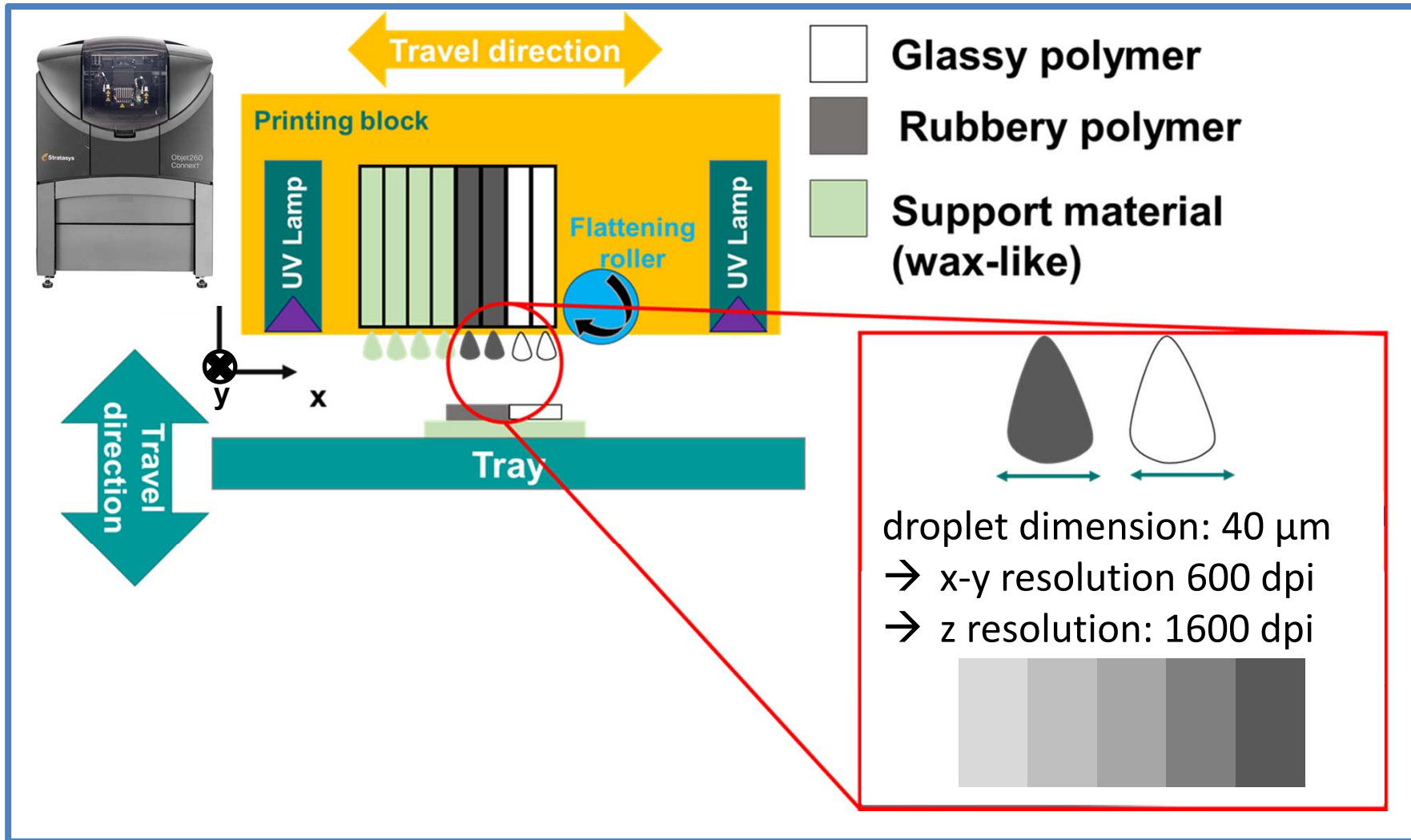


Material Data: Recommendations

- If properties of metals (e.g. stainless steel) differ very little from two different manufacturers this is NOT true for polymers (e.g. polyethylene)
- Many factors have a big influence on the behavior of polymers (e.g., distribution of molecular lengths, polymerization, mechanical processing, additives)
- Data from books are only *approximate*
 - accurate data requires to use manufacturer datasheet or (even better) to perform own tests (e.g. 3D polymer printing)



3D Polymer Printer: Objet Connex260 www.stratasys.com





Material Data: Recommendations

- Polymers bonding: “primary” (covalent) bonds + “secondary” (van der Waals and hydrogen) bonds
- At glass temperature T_G the secondary bonds melt → strong decreases in Young’s modulus (e.g. from 3 GPa for $T < T_G$ to 3 MPa for $T > T_G$)
- In many polymers T_G is only slightly higher than room temperature T_{room}
 - at T_{room} a large fraction of secondary bonds is already melted and under load the remaining secondary bonds creep
 - decrease in modulus $E_{1000 h}(20\text{ }^\circ\text{C}) = \frac{1}{3} E_{100 s}(20\text{ }^\circ\text{C})$
- Tensile strength is a large fraction of elastic modulus: $\sigma_y = \frac{E}{20}$
 - design based on yield gives large deflections without damage (car bumpers, plastic bottles)



Material Data: Recommendations

- For many polymers T_G is near to T_{room} :
 - @ T_{room} polymers are fairly tough, but if $T < T_G$, K_C (fracture toughness) can drop significantly



Material Data: **Recommendations**

Design with polymers requires special attention to:

- **Time-dependent effects**
- **Large elastic deformations**
- **Effects of temperature (even close to room temperature)**



Generic Polymers

Thermoplastics

- Polyethylene is the most common thermoplastics
- They are often linear polymers, i.e. the chains are not cross-linked but may branch
- They soften and flow like a viscous liquid when heated (after the melting of secondary bonds), allowing to be formed
- They are made by adding together (polymerizing) subunits (monomers) to form long chains



Generic Polymers: Thermoplastics

Table 23.1 Generic Thermoplastics

Thermoplastic	Composition	Uses
Polyethylene, PE	$\left(\begin{array}{c} \text{H} \\ \\ -\text{C}- \\ \\ \text{H} \end{array} \right)_n$ <p>Partly crystalline.</p>	Tubing, film, bottles, cups, electrical insulation, packaging.
Polypropylene, PP	$\left(\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C}- & -\text{C}- \\ & \\ \text{H} & \text{CH}_3 \end{array} \right)_n$ <p>Partly crystalline.</p>	Same uses as PE, but lighter, stiffer, more resistant to sunlight. CH₃ → methyl group
Polytetrafluoroethylene, PTFE	$\left(\begin{array}{c} \text{F} \\ \\ -\text{C}- \\ \\ \text{F} \end{array} \right)_n$ <p>Partly crystalline.</p>	Teflon. Good, high-temperature polymer with very low friction and adhesion characteristics. Nonstick saucepans, bearings, seals.



Generic Polymers: Thermoplastics

Table 23.1 Generic Thermoplastics

Thermoplastic	Composition	Uses
Polystyrene, PS	$\left(\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{C}_6\text{H}_5 \end{array} \right)_n$ <p><u>Amorphous.</u></p>	Cheap molded objects. Toughened with butadiene to make high-impact polystyrene (HIPS). Foamed with CO ₂ to make common packaging. C₆H₅ → phenyl group
Polyvinylchloride, PVC	$\left(\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{Cl} \end{array} \right)_n$ <p><u>Amorphous.</u></p>	Architectural uses (window frames, etc.). Plasticized to make artificial leather, hoses, clothing.
Polymethylmethacrylate, PMMA Plexiglas	$\left(\begin{array}{cc} \text{H} & \text{CH}_3 \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{COOCH}_3 \end{array} \right)_n$ <p><u>Amorphous.</u></p>	Perspex, lucite. Transparent sheet and moldings. Aircraft windows, laminated windscreens.
Nylon 66	$(-\text{C}_6\text{H}_{11}\text{NO}-)_n$ Partly crystalline when drawn.	Textiles, rope, moldings.



Generic Polymers

Thermosets (or resins)

- Epoxy is the most famous thermosets
- They are made by mixing two components: a resin and a hardener (either at room temperature or on heating)
- They are heavily cross-linked (also called network polymers)
- The cross-links form during polymerization so the structure is almost always amorphous
- On re-heating the secondary bonds melt and the modulus drops but the crosslinks prevent viscous flow → no hot-working
- Further heating causes decomposition



Generic Polymers: Thermosets

Table 23.2 Generic Thermosets or Resins

Thermoset	Composition	Uses
Epoxy	$\left(\begin{array}{c} \text{CH}_3 \\ \\ -\text{O}-\text{C}_6\text{H}_4-\text{C}-\text{C}_6\text{H}_4-\text{O}-\text{CH}_2-\text{CH}-\text{CH}_2- \\ \\ \text{CH}_3 \end{array} \begin{array}{c} \text{OH} \\ \\ \text{CH} \\ \\ \text{CH}_2 \end{array} \right)_n$ <p>Amorphous.</p>	Fiberglass, adhesives. Expensive.
Polyester	$\left(\begin{array}{c} \text{O} \qquad \qquad \text{O} \qquad \qquad \text{CH}_2\text{OH} \\ \qquad \qquad \quad \qquad \qquad \\ -\text{C}-\text{(CH}_2\text{)}_m-\text{C}-\text{O}-\text{C}- \\ \qquad \qquad \qquad \qquad \qquad \qquad \\ \qquad \qquad \qquad \qquad \qquad \qquad \text{CH}_2\text{OH} \end{array} \right)_n$ <p>Amorphous.</p>	Fiberglass, laminates. Cheaper than epoxy.
Phenolformaldehyde phenolic resins	$\left(\begin{array}{c} \text{OH} \\ \\ -\text{C}_6\text{H}_2-\text{CH}_2- \\ \\ \text{CH}_2 \end{array} \right)_n$ <p>Amorphous.</p>	Bakelite, Tufnol, Formica. Rather brittle. low electrical conductivity



Generic Polymers

Elastomers (or rubbers)

- They are almost linear polymers with occasional cross-links
- At room temperature all the secondary bonds have already melted
- The cross-links provide a memory of the material so that it returns to its original shape on unloading



Generic Polymers: Rubbers

Table 23.3 Generic Elastomers (Rubbers)

Elastomer	Composition	Uses
Polyisoprene	$\left(\begin{array}{cccc} \text{H} & & & \text{H} \\ & & & \\ -\text{C} & - & \text{C} = & \text{C} - & \text{C}- \\ & & & \\ \text{H} & \text{H} & \text{CH}_3 & \text{H} \end{array} \right)_n$ <p><u>Amorphous except at high strains.</u></p>	Natural rubber.
Polybutadiene	$\left(\begin{array}{cccc} \text{H} & & & \text{H} \\ & & & \\ -\text{C} & - & \text{C} = & \text{C} - & \text{C}- \\ & & & \\ \text{H} & \text{H} & \text{H} & \text{H} \end{array} \right)_n$ <p><u>Amorphous except at high strains.</u></p>	Synthetic rubber, car tires.
Polychloroprene	$\left(\begin{array}{cccc} \text{H} & & & \text{H} \\ & & & \\ -\text{C} & - & \text{C} = & \text{C} - & \text{C}- \\ & & & \\ \text{H} & \text{H} & \text{Cl} & \text{H} \end{array} \right)_n$ <p><u>Amorphous except at high strains.</u></p>	Neoprene. An oil-resistant rubber used for seals. collagen

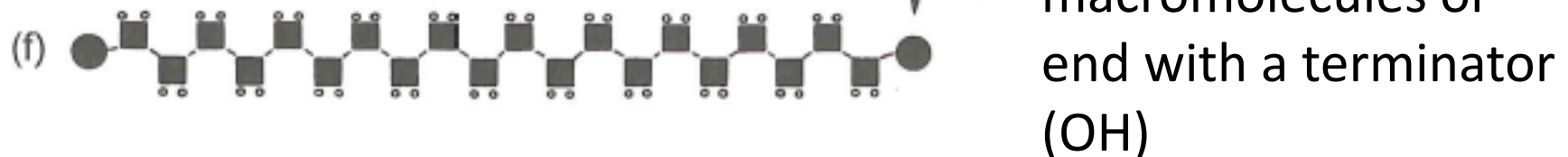
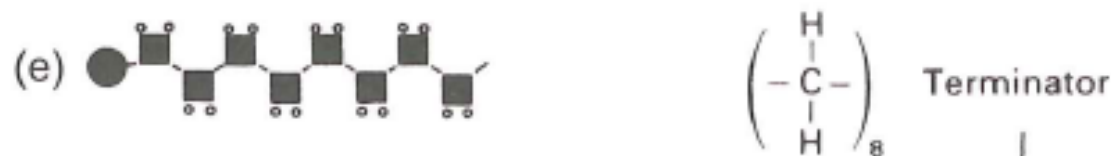
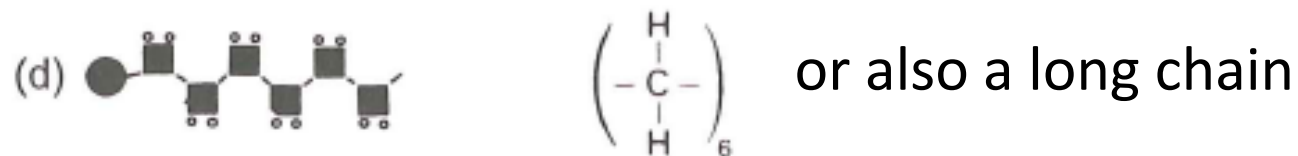
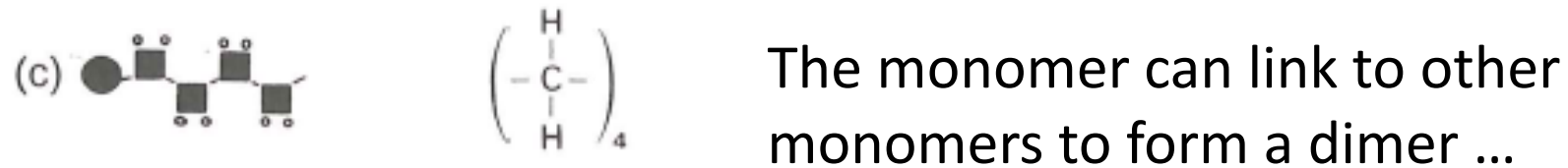
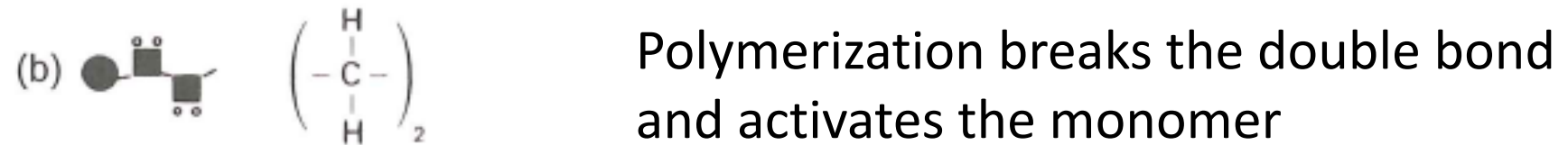


Generic Polymers: Natural Polymers

Table 23.4 Generic Natural Polymers

Natural Polymer	Composition	Uses
Cellulose	$(-C_6H_9O_6-)_n$ Crystalline.	Framework of all plant life, as the main structural component in cell walls.
Lignin	Amorphous.	The other main component in cell walls of all plant life.
Protein	$\left(\begin{array}{c} \boxed{R} \\ \\ -NH - C - C \\ \quad \\ H \quad O \end{array} \right)_n$ \boxed{R} is a radical. Partly crystalline.	Gelatin, wool, silk.

Molecular Length

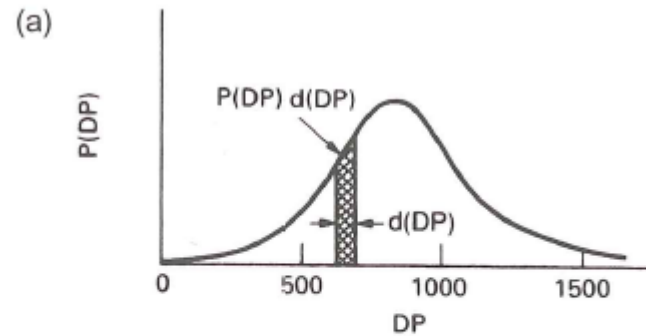




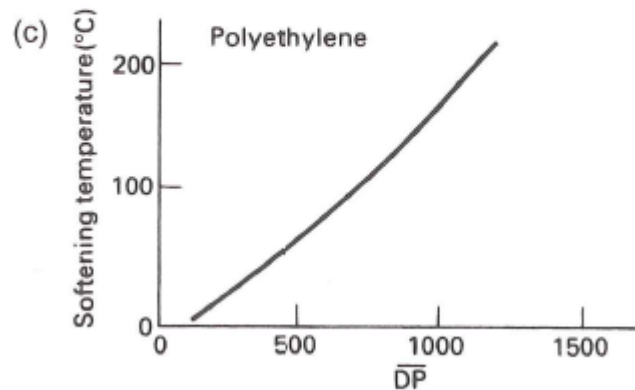
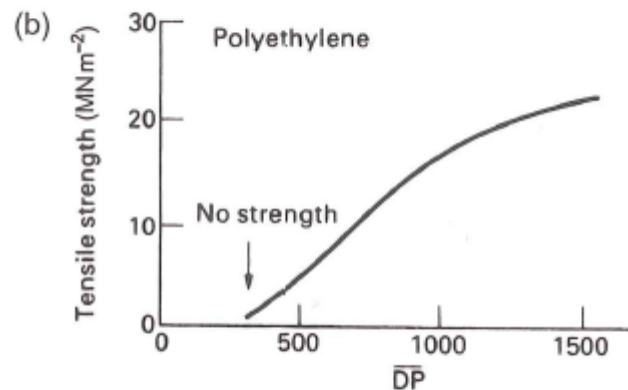
Molecular Length & Weight

- Degree of Polymerization (DP): number of monomer units in the chain
- To have a solid polymer with “useful” mechanical properties the DP must be at least 500
- Commercial polymers have DP: 10^3 - 10^5
- Molecular Weight (MW):
 - DP x molecular weight of the monomer (ethylene monomer C_2H_4 has molecular weight of 28; average DP of polyethylene is 10^4 → average MW=280.000)
- In all commercial polymers there is a range of DP and thus of molecular length and weight

Molecular Length & Weight



$$\overline{DP} = \int_0^{\infty} DP P(DP) d(DP)$$



Polymeric materials based on the same repeating monomer do not have a unique set of properties:

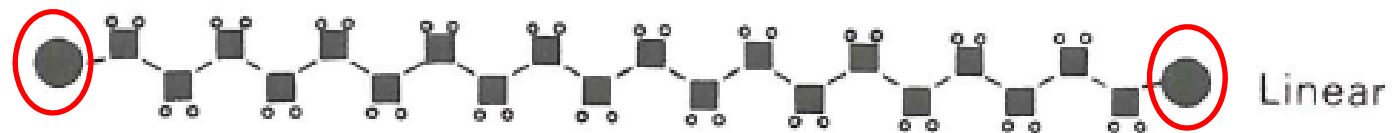
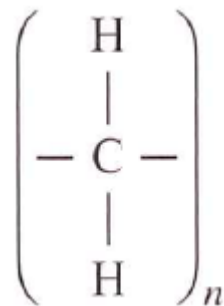
→ there are many polyethylene and their properties strongly depend on the average DP



Molecular Architecture

Thermoplastics

- Largest class of engineering polymers
- Linear molecules **not cross-linked** → soften when heated
- The simplest linear-chain polymer is polyethylene





Molecular Architecture

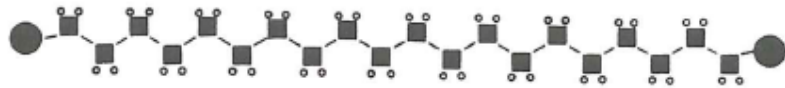
Thermoplastics

- By replacing one H with a side-group R (radical) we have the *vinyl* group of polymers $[-C-H=CH_2]$:
 - R = Cl \rightarrow polyvinyl chloride
 - R = CH₃ \rightarrow polypropylene
 - R = C₆H₅ \rightarrow polystyrene
- The radical gives **asymmetry** to the chain \rightarrow different ways the monomers can be attached to form a chain

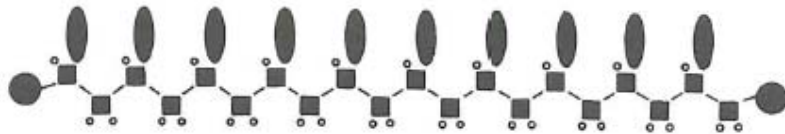


Molecular Architecture

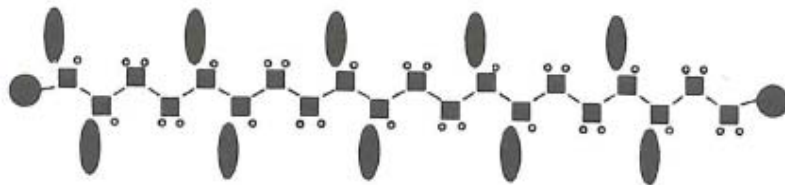
Thermoplastics



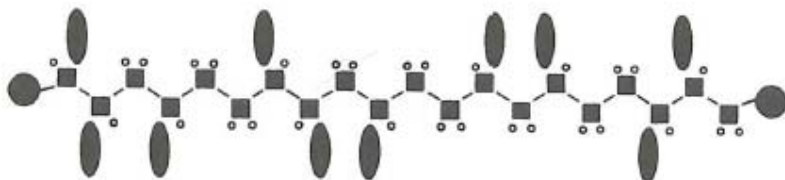
Linear (PE)



Isotactic: the side-groups are all on the same side



Syndiotactic: the side-groups alternate regularly



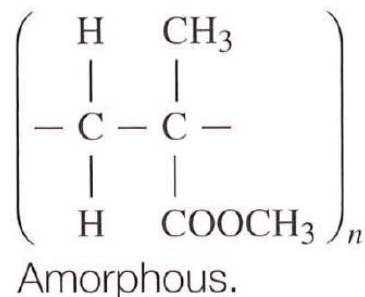
Atactic: the side-groups alternate irregularly



Molecular Architecture

Thermoplastics

- Tacticity influences properties:
 - regular molecules can form crystals whereas irregular molecules (atactic) cannot
 - isotactic molecules carry a net electric dipole and can be electroactive (e.g. piezoelectric effects)
- If two H are replaced \rightarrow *vinylidene* group



- R1 = CH₃ (methyl) & R2 = COOCH₃ (ester)
 \rightarrow PMMA or Plexiglass
- increased difficulty to get regular arrangements
 \rightarrow most of them are amorphous



Molecular Architecture

Thermosets

- Based on large polyfunctional monomers
- Form random three-dimensional networks with several (covalent) cross-links
- Do not melt when heated
- Do not easily dissolve in solvents
- Cannot be formed after polymerization
- Chemical more stable and mechanically stiffer than thermoplastics
- Used as adhesive, coating and matrix for composites



Molecular Architecture

Elastomers

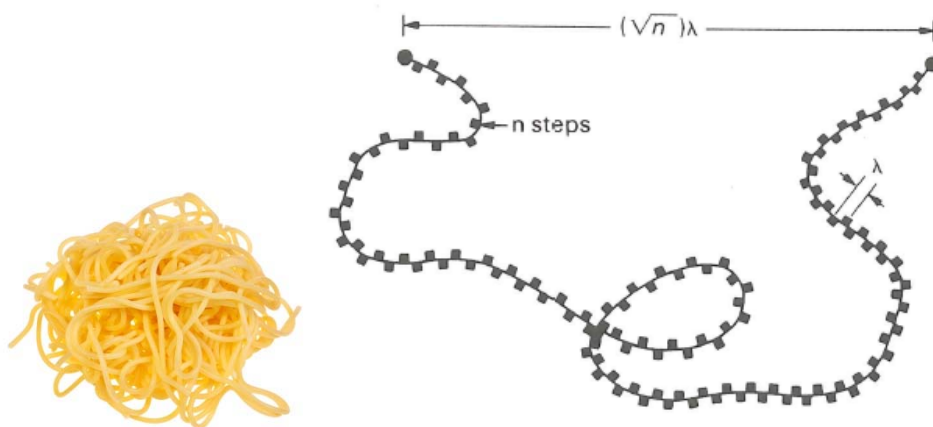
- Linear polymers with a few cross-links
(1 every 100 or more monomers)
e.g., DP 500 → less than 5 cross links !!!
- Glass temperature (T_g) well below room temperature (at room temperature the secondary bonds have melted)



Molecular Packing and Glass Transition

- Due to the rotational degrees of freedom of the C-C backbone, a free polymer molecule is never straight but it can spiral, twist, ...
- This is particularly the case when a linear polymer melts (e.g. during forming)

→ spaghetti-like tangle



The average end-to-end distance is described by the random walk model of a polymer with n units of length λ : $\sqrt{n}\lambda$

Large strain (400%) are needed to straighten out the molecule



Molecular Packing and Glass Transition

- When the polymer melt is cooled the spaghetti-tangle may freeze without rearranging:



Amorphous structure

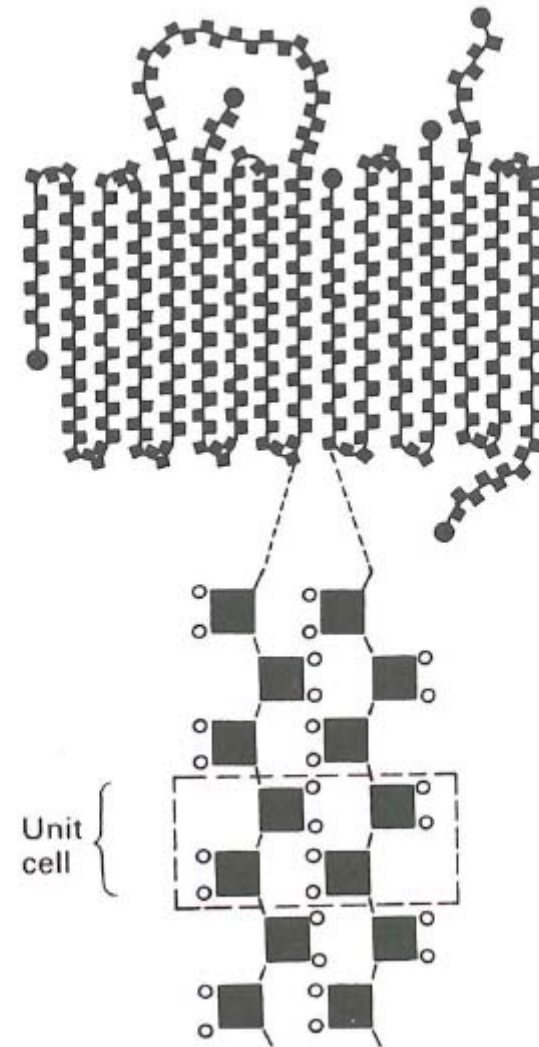
- During cooling molecules can move and may line-up (depending on their architecture and secondary bonds) → they can form *crystallites*



Molecular Packing and Glass Transition

Polymer crystals

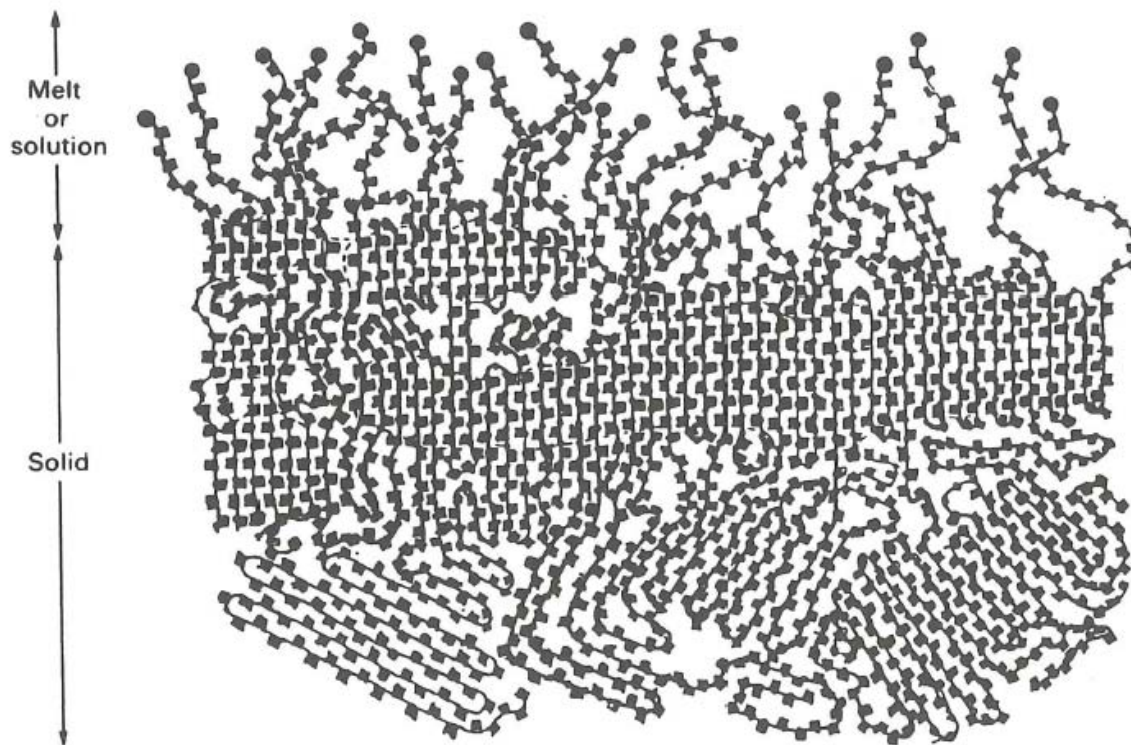
- Linear chain molecules with no side-groups or branches can crystallize (e.g. high density polyethylene)
- On cooling secondary bonds tend to pull the molecules together into parallel bundles → *chain folded* crystals
- In general, crystallinity is not as high as in metals but it is high enough to diffract X-rays and to allow the definition of a unit cell



Molecular Packing and Glass Transition

Polymer crystals

- Even the most crystalline molecules (high density PE) is only 80% crystal



crystalline parts
separated by amorphous
(or glassy) regions



Mechanical Properties



Introduction

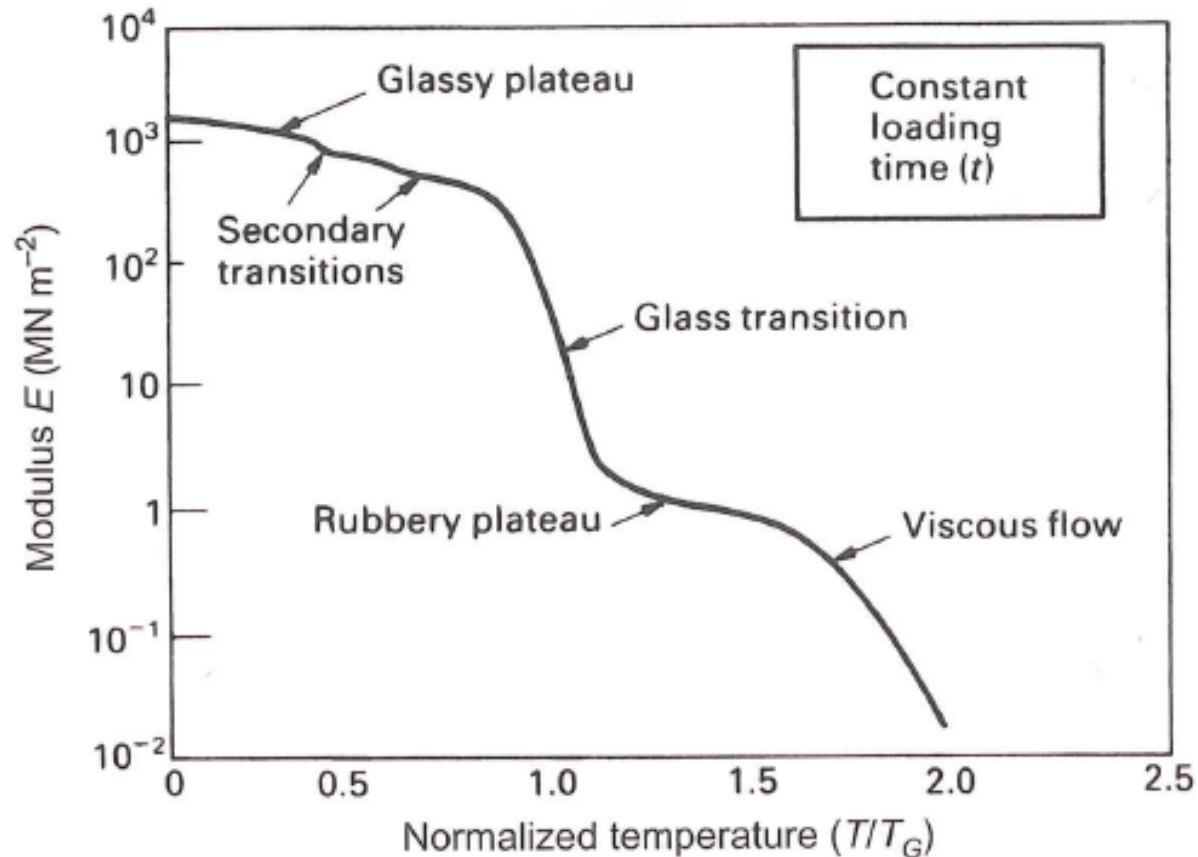
- Large spectrum of mechanical properties (brittle-elastic, plastic, viscoelastic, rubbery and viscous) within a quite “small” temperature range:

[-20 °C → +200 °C]

- While metals and ceramics have a constant stiffness and strength at room temperature, this is **not true** for polymers
- Mechanical state of a polymer mainly depends on **molecular weight** and **temperature** - how close is T to T_G
- Polymer mechanical properties are often plotted against **T/T_G**



Introduction



PMMA: $T_{\text{room}} = 0.75 T_G$
polyethylene: $T_{\text{room}} = 1 T_G$
polyisoprene: $T_{\text{room}} = 1.5 T_G$

general behavior of Young's modulus as a function of temperature for a linear (amorphous) polymer for a fixed loading time



Time and Temperature Dependent Stiffness

- When a polymer is loaded by a constant force, it deflects by an amount that increases with **time t** and **temperature T**

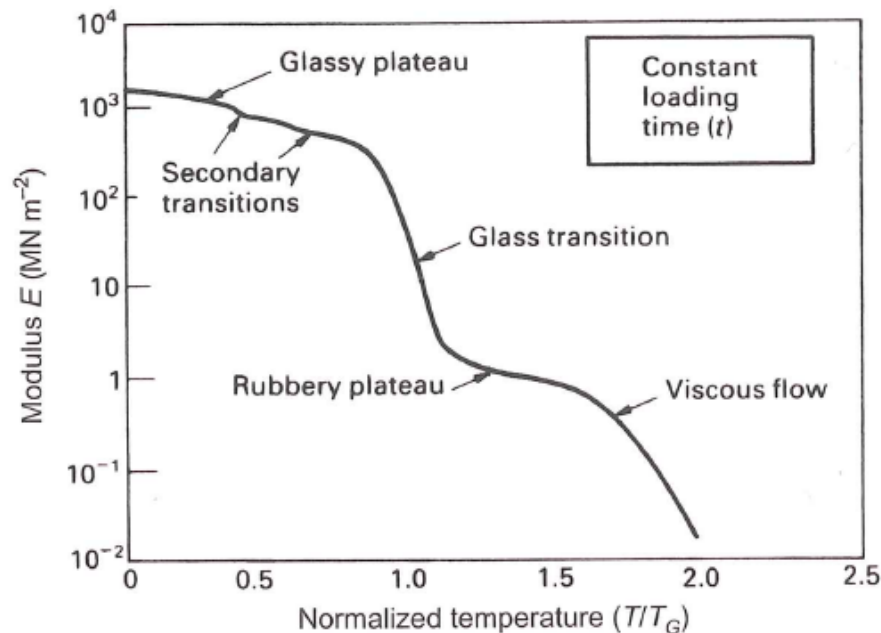
$$E(t, T) = \frac{\sigma}{\varepsilon(t, T)}$$

- The Young's modulus of a polymer can change up to a factor of 10^3 when the temperature is changed, even around room temperature



Time and Temperature Dependent Stiffness

- Behaviour of linear amorphous polymer (PMMA)

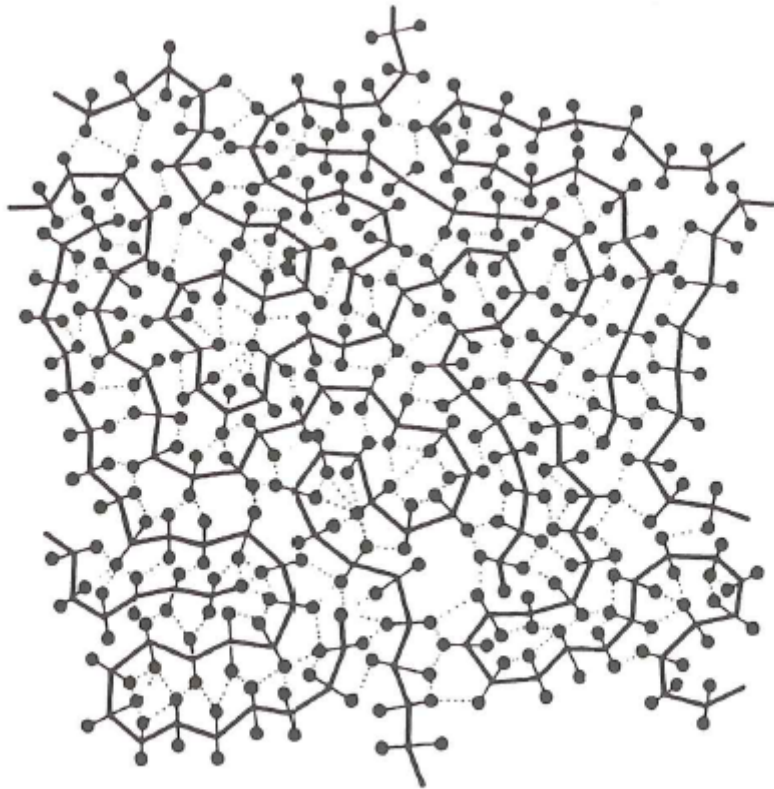


- Glassy regime: large modulus (3 GPa)
- Glass-transition regime: steep drop in modulus (3 GPa \rightarrow 3 MPa)
- Rubbery regime: low modulus (3 MPa)
- Viscous regime: the polymer starts to flow
- Decomposition regime: chemical breakdown starts



Time and Temperature Dependent Stiffness

Glassy regime and secondary relaxation



linear amorphous polymer with strong covalent bonds and weak secondary bonds

Glassy modulus is due to bond stretching and the modulus of the polymer is an “average” of the stiffness of its bonds:

$$E = \left\{ \frac{f}{E_1} + \frac{(1-f)}{E_2} \right\}^{-1}$$

f : fraction of covalent bonds

$f = 1$ (polymer is completely cross-linked) $\rightarrow E \sim 10^3$ GPa (diamond)

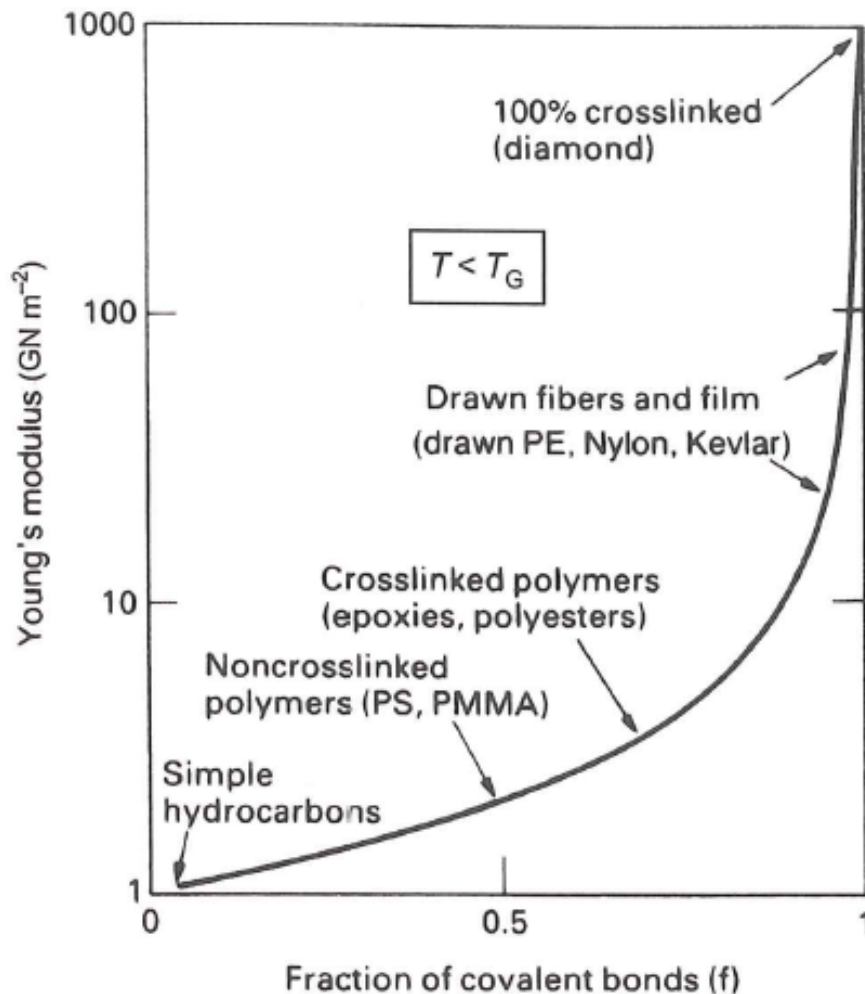
$f = 0$ (no cross-links) $\rightarrow E \sim 1$ GPa (simple hydrocarbon like paraffin)

$$E = \left\{ \frac{f}{10^3} + \frac{(1-f)}{1} \right\}^{-1}$$



Time and Temperature Dependent Stiffness

Glassy regime and secondary relaxation



$$E = \left\{ \frac{f}{10^3} + \frac{(1-f)}{1} \right\}^{-1}$$

Non-crosslinked random linear polymer ($f = 0.5$) → glassy modulus of 3 GPa

heavy cross-linked polymers ($f = 0.75$) → glassy modulus of 8 GPa

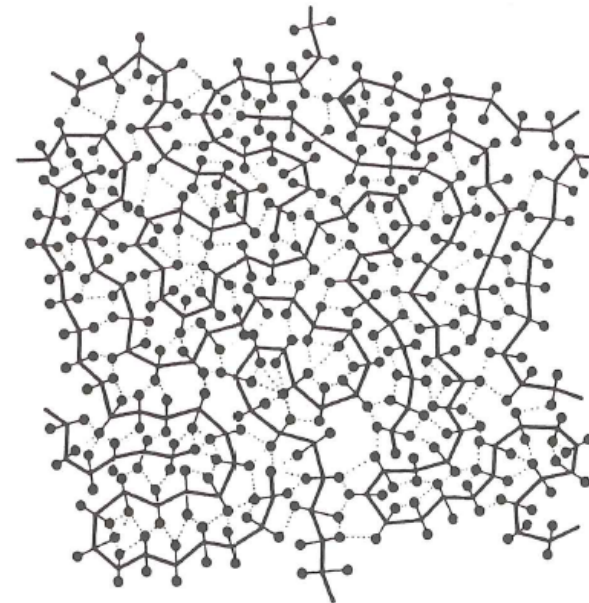
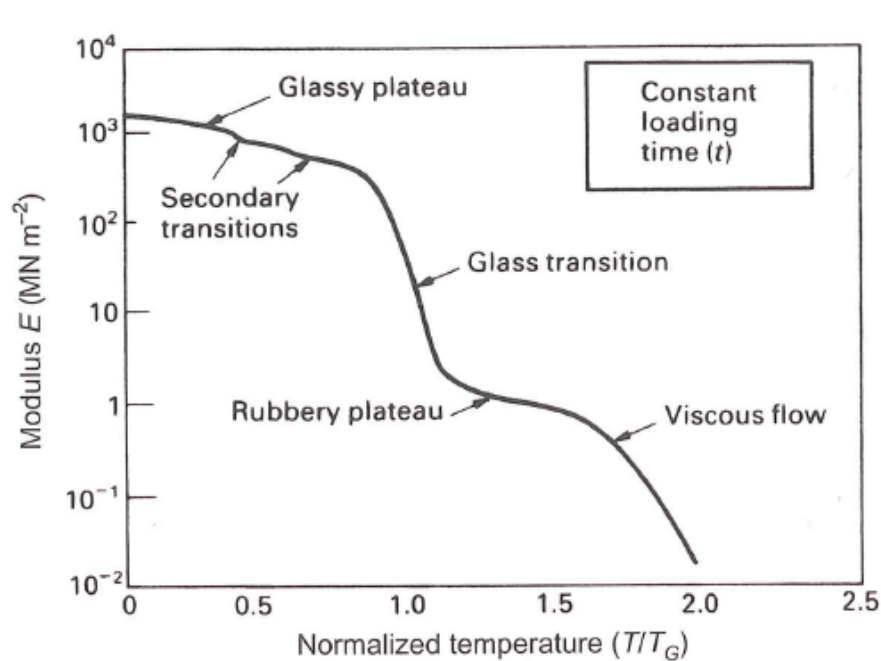
drawn polymers have chains lined-up along the drawing direction (i.e. anisotropic) → $f = 0.98$ in drawing direction → glassy modulus of **100 GPa** (only in drawing direction!)

ORIENTATION STRENGTHENING



Time and Temperature Dependent Stiffness

Glassy regime and secondary relaxation

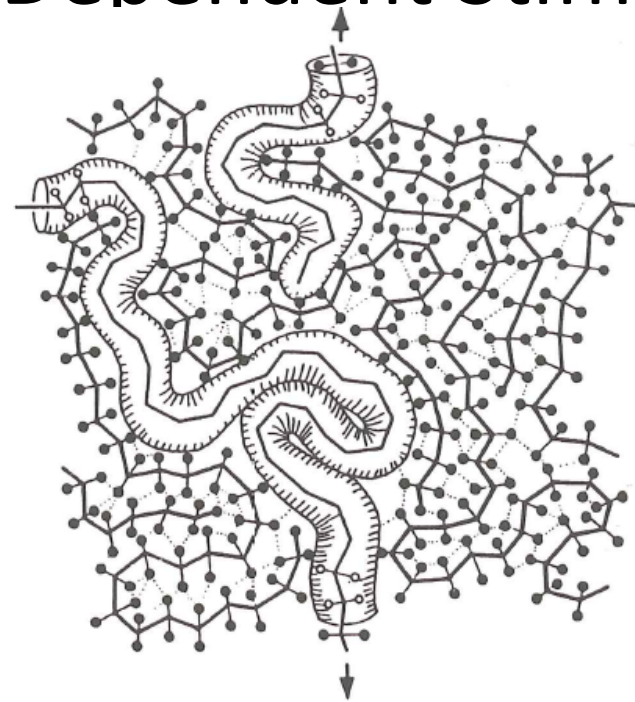
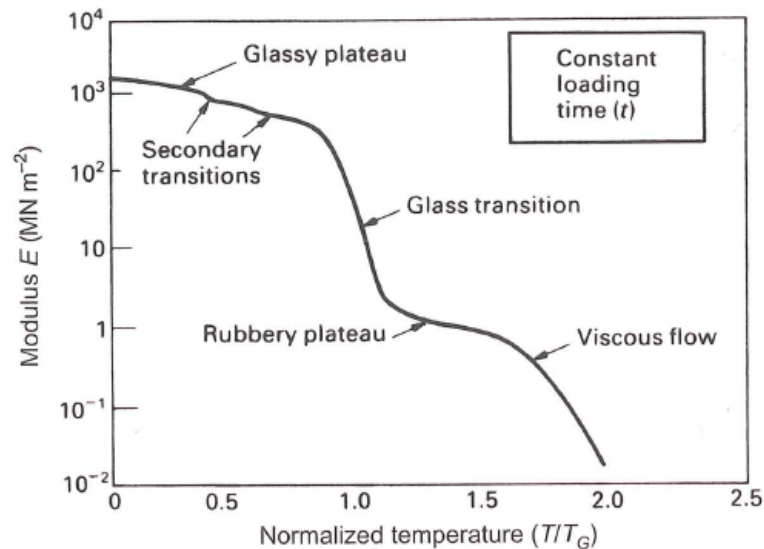


Secondary relaxation: in principle, the glassy modulus (due to bond-stretching) should not depend too much on temperature; however due to the packing of molecules, there are some “loose site” in the structure that can be occupied by side groups or chain segments by increasing temperature. Such rearrangements may cause an “extra” strain which can decrease the glassy modulus by a factor of 2



Time and Temperature Dependent Stiffness

Glass or viscoelastic transition



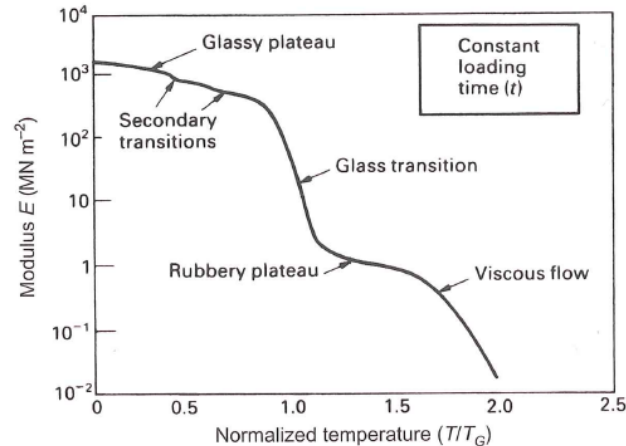
$T \uparrow$: secondary bonds melt and modulus drop considerably

Consider each polymer chain as contained in a “tube” made up by the surrounding molecules: when loaded at T_g each molecule can move in a snake-like manner (reptate) in the tube. Further increasing T , polymer expand giving extra free volume and allowing more regions to slide

As there are still non-sliding parts, on unloading the elastic regions pull the polymer back to its original shape (contrasted by reverse viscous sliding \rightarrow it takes time!)

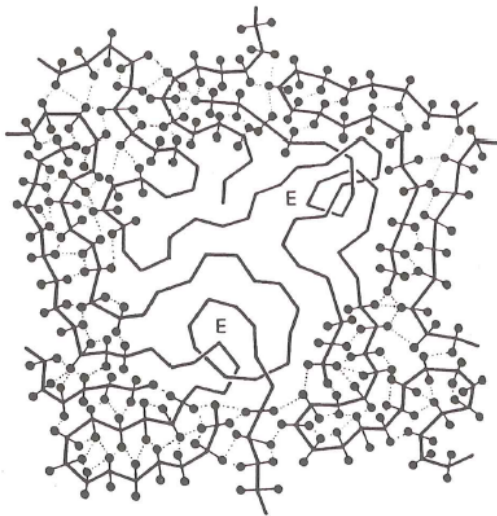
Time and Temperature Dependent Stiffness

Rubbery behavior and elastomers



For $T > T_G$ (up to $1.5 \times T_G$) there can be two different behaviors for amorphous polymers depending on the average degree of polymerization (\overline{DP}):

- $\overline{DP} < 10^3$ (polymer with short chains) \rightarrow molecular flow is easier and easier, elastic modulus decreases \rightarrow viscous flow
- $\overline{DP} > 10^4$ (polymer with longer chains) \rightarrow there is a rubbery state before viscous flow

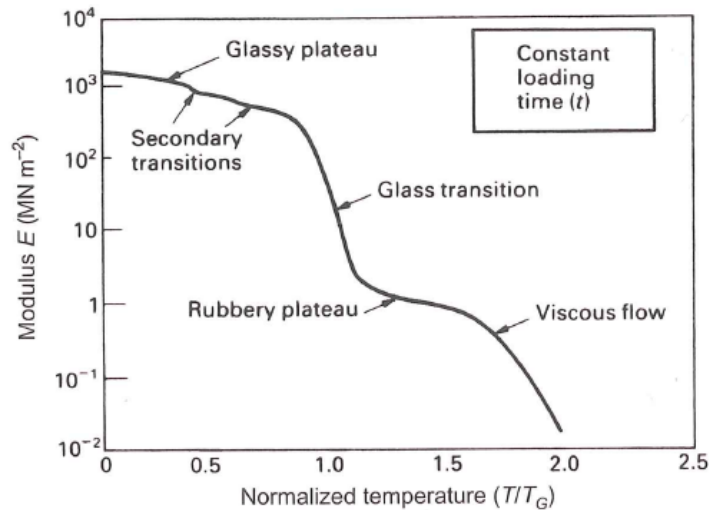


long molecules form entanglements (E): points where the molecules become knotted together
 on loading the molecules reptate except at entanglements (gives a shape memory)
 rubbery modulus is 1/1000 of glassy modulus
 strong rubbery behavior ($\epsilon > 300\%$ completely recoverable) can be obtained by replacing entanglements with cross-links (1 every few hundreds monomer) as they do not melt



Time and Temperature Dependent Stiffness

Viscous flow



At higher T ($>1.5 T_G$) the secondary bonds are melt completely and there is slip event at entanglements \rightarrow linear polymers become viscous liquids (this is the regime in which thermoplastics are molded)

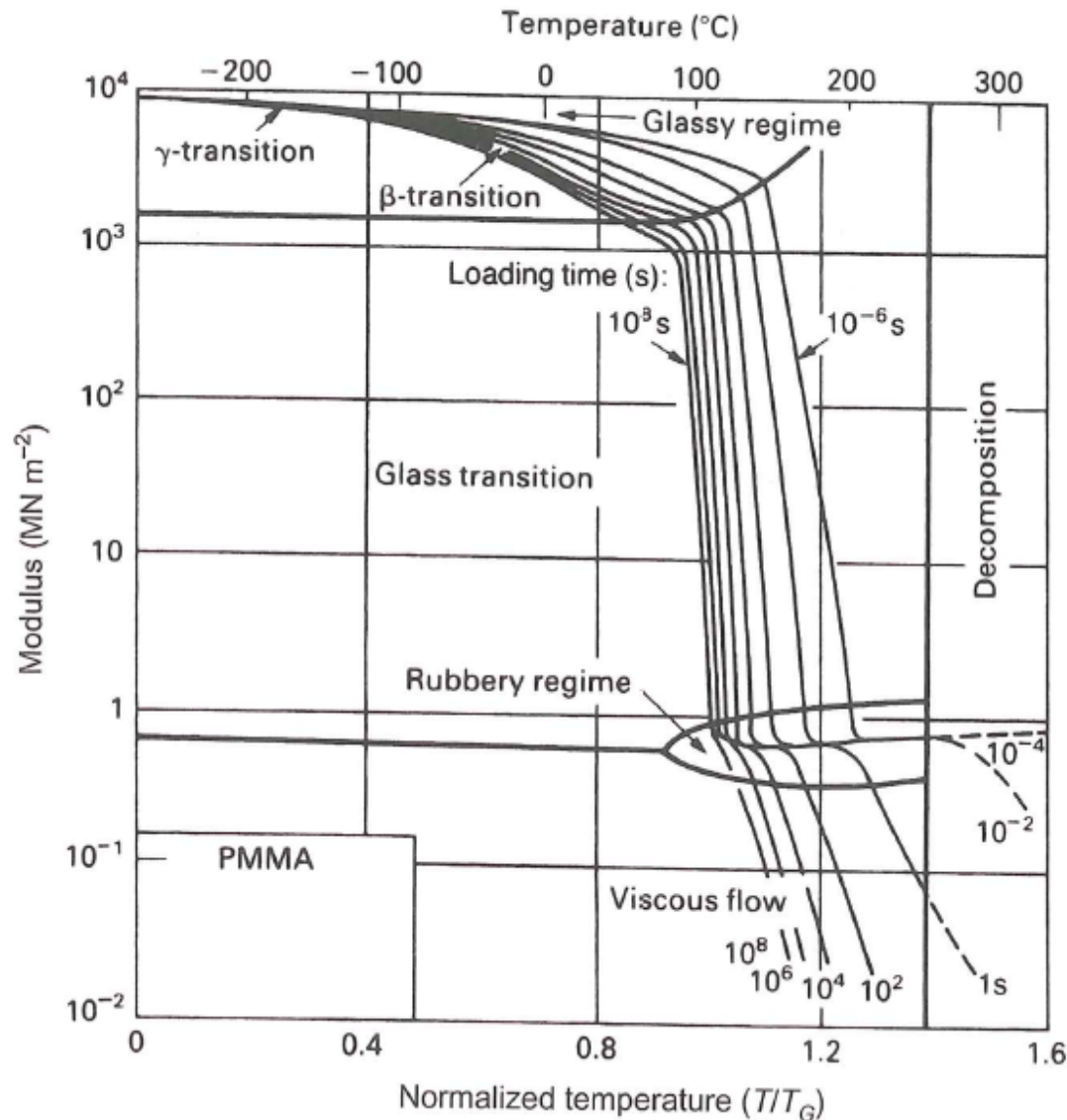
Viscosity is defined (and usually measured) in shear (shear stress σ_s which produces a shear rate $\dot{\gamma}$):

$$\eta = \frac{\sigma_s}{\dot{\gamma}} \quad \text{Poise} = 10 \text{ Pa} \times \text{s}$$

Polymers are formed at a viscosity: 10^4 - 10^6 poise (they can be blown and molded)



Time and Temperature Dependent Stiffness



modulus diagram

for PMMA (**typical linear amorphous polymer**)

→ summarizes temperature and time dependence of Young's modulus for "small-strain" behavior of an amorphous polymer

T range: 0 K up to 1.6 T_G
time range: 10⁻⁶ s to 10⁸ s

5 regions

drop in modulus (/2 glassy and /100 rubbery) for longer loading time



Time and Temperature Dependent Stiffness modulus diagram

influence of cross-links

modulus diagram for polyisoprene (rubber)

Increase crosslink density:

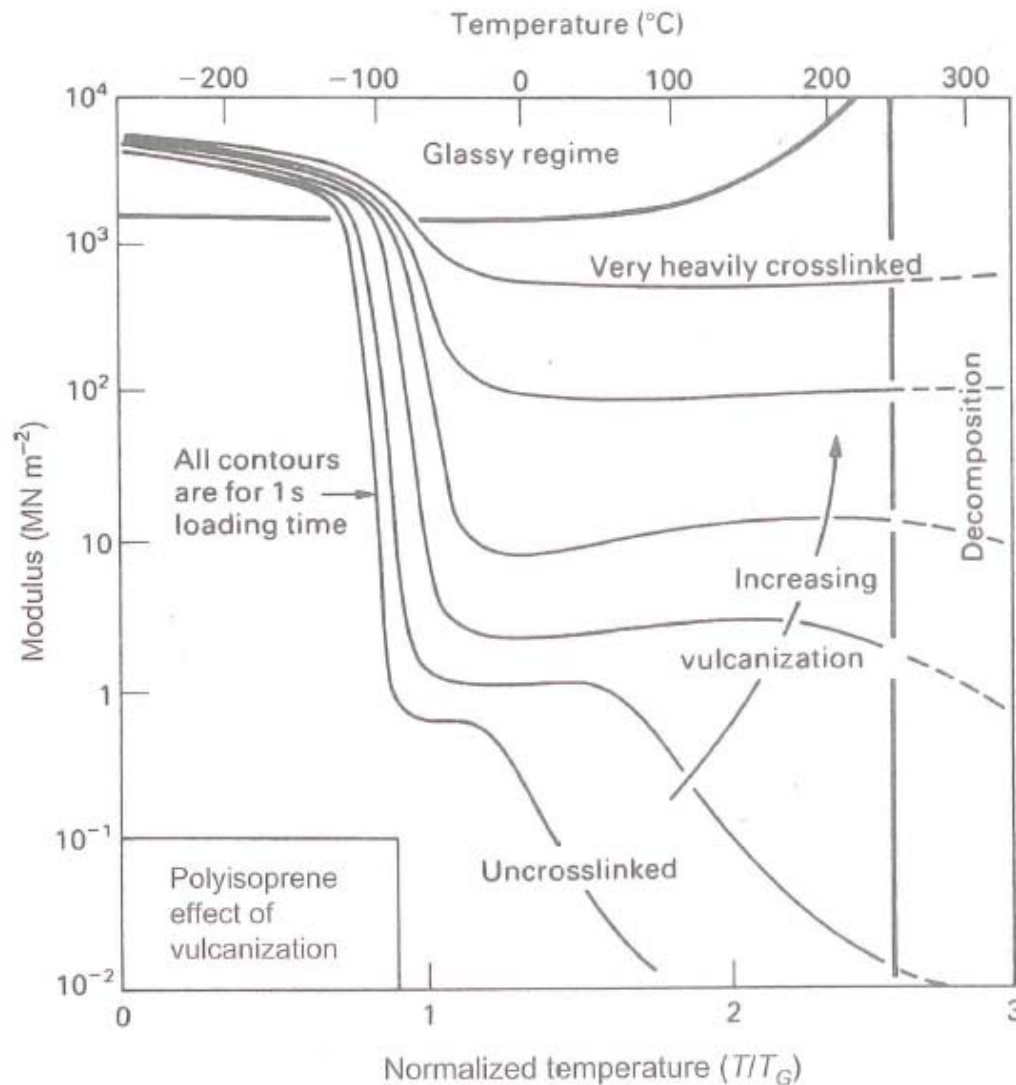
→ contours of the modulus diagram are pushed up (decrease modulus drop)

→ rubbery plateau is extended.

Crystallization increases the modulus too:

→ crystalline regions are stiffer than amorphous because of the highly dense packing

→ does not suppress melting. Crystalline polymers (high density PE) can still be molded (cross-linked polymers cannot)





Strength & Failure

- Strength: stress at which “something” starts to happen giving a permanent shape change (plastic flow or propagation of a brittle crack)
- There are at least 5 processes that can induce **failure** (i.e. limit strength) in polymers
 - 1) **Brittle fracture** (like in ordinary glass)
 - 2) **Cold drawing**: the drawing-out of molecules in solid-state, giving large shape changes
 - 3) **Shear banding**: giving slip bands like in metals
 - 4) **Crazing**: a kind of microcracking associated with local cold drawing
 - 5) **Viscous flow**: when the secondary bonds have melted ($T > 1.5 T_G$)

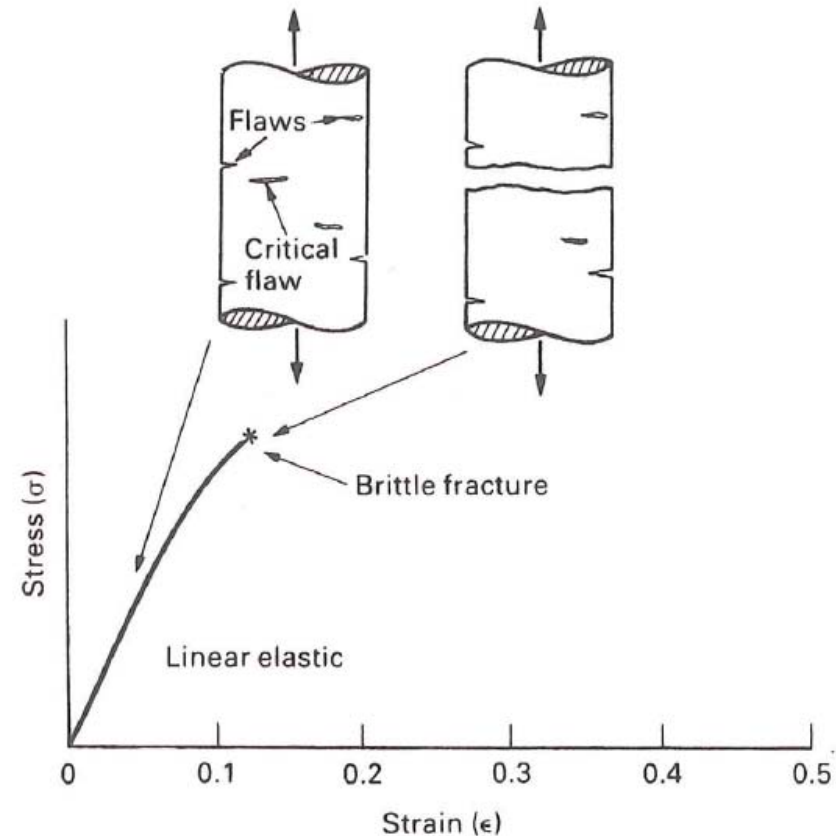
Strength & Failure: Tension

Brittle Fracture

- $T < 0.75 T_G \rightarrow$ polymers are brittle
- In the presence of a small defect (size c)

$$\sigma \sim \frac{K_C}{\sqrt{\pi c}}$$

- K_C : fracture toughness
($1 \text{ MNm}^{-3/2}$)

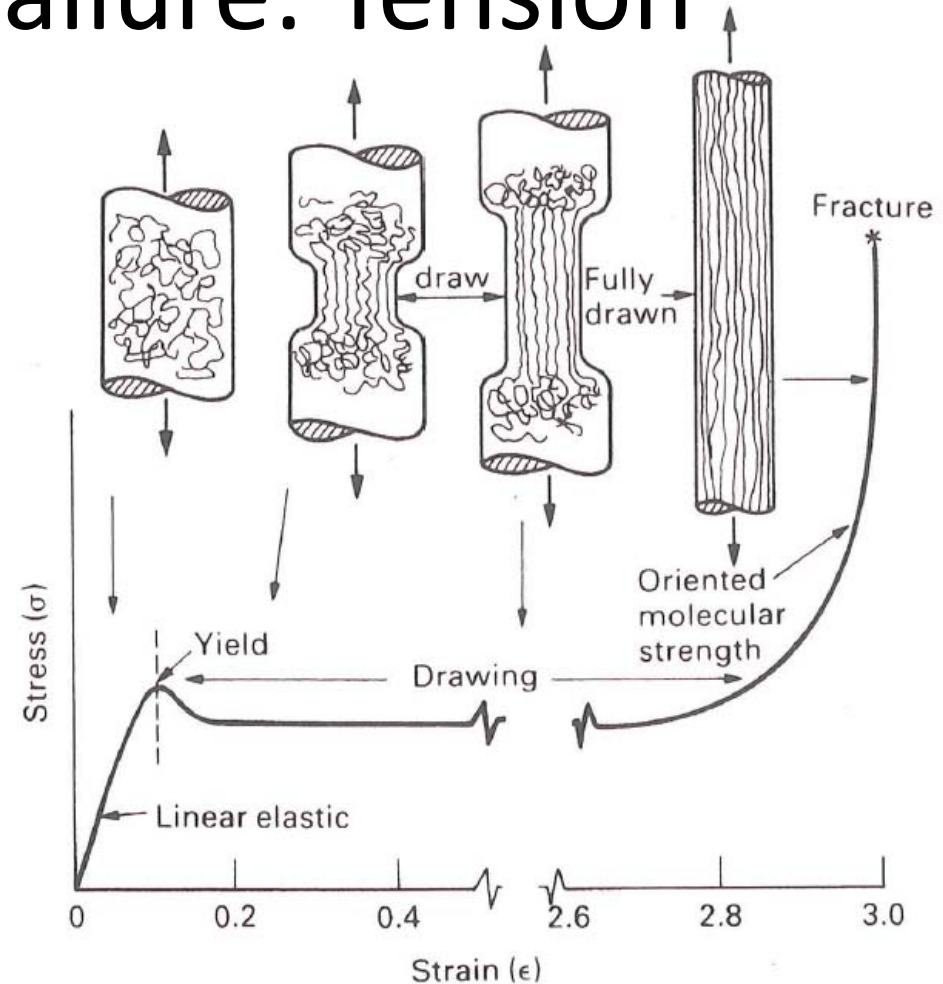


Below $0.75 T_G$ polymers are low-toughness materials and anything that concentrate stresses (e.g., cracks, notches, sharp changes of section) is **dangerous**

Strength & Failure: Tension

Cold drawing

- $T \sim T_G$
- $\epsilon < 0.1$ linear elastic
- $\epsilon = 0.1$ yield
- $0.1 < \epsilon < 2.8$ drawing:
 - chains unfold, draw out from the amorphous tangle, straighten and align
 - formation of a neck which spreads in the entire sample
- $\epsilon > 2.8$ drawing is complete and rapid rise of σ till fracture



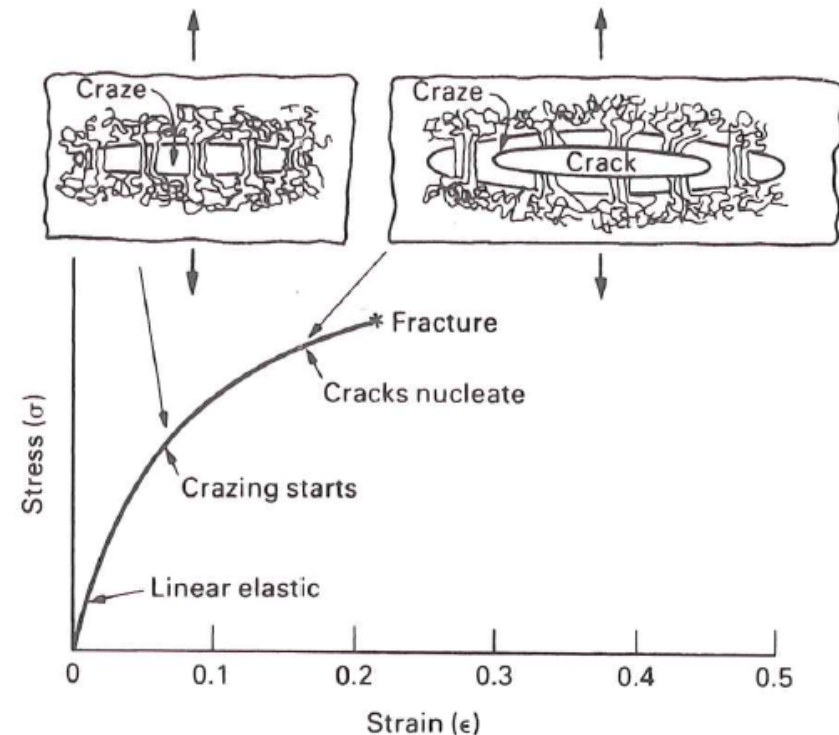
Example of polyethylene (typical behavior of a linear polymer)

Drawing gives a material which is much stiffer and stronger in drawing direction

Strength & Failure: Tension

Crazing

- $T \sim [0.75 T_G - T_G]$
- Crazing is a combination of localized cracking and drawing
- Molecules are drawn out but on a much smaller scale
- Small damaged regions appears (craze) and the drawn material forms ligaments bridging the crazes (stabilizing the microcracks)
- Before drawing becomes general a crack forms at a center of a craze and propagates to give final fracture

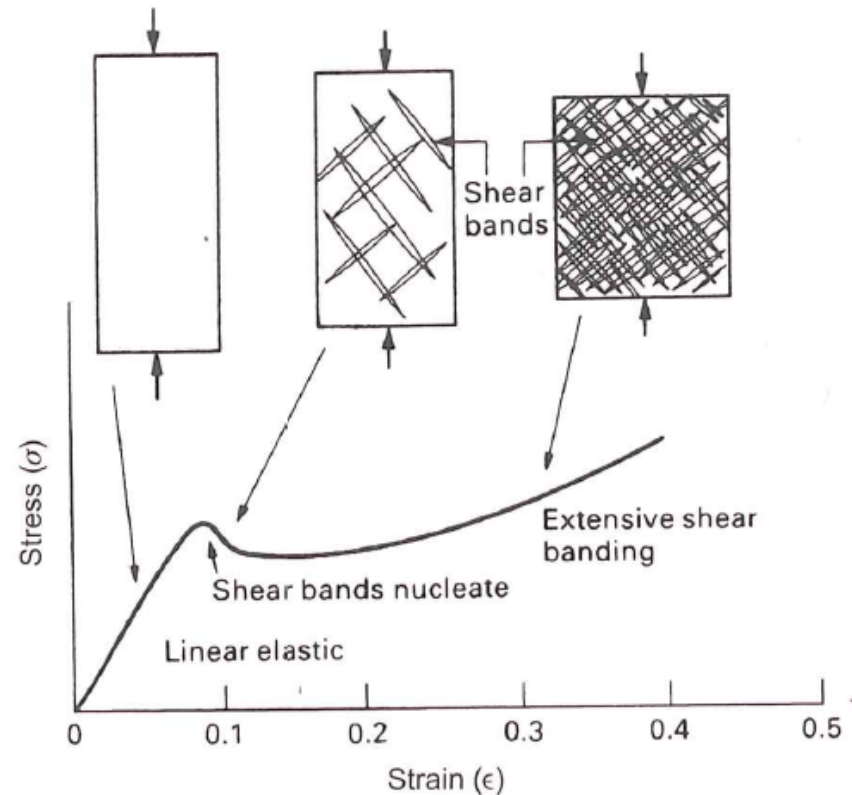


Example of polystyrene at room temperature (typical behavior of a linear polymer)

Strength & Failure: Compression

Shear banding

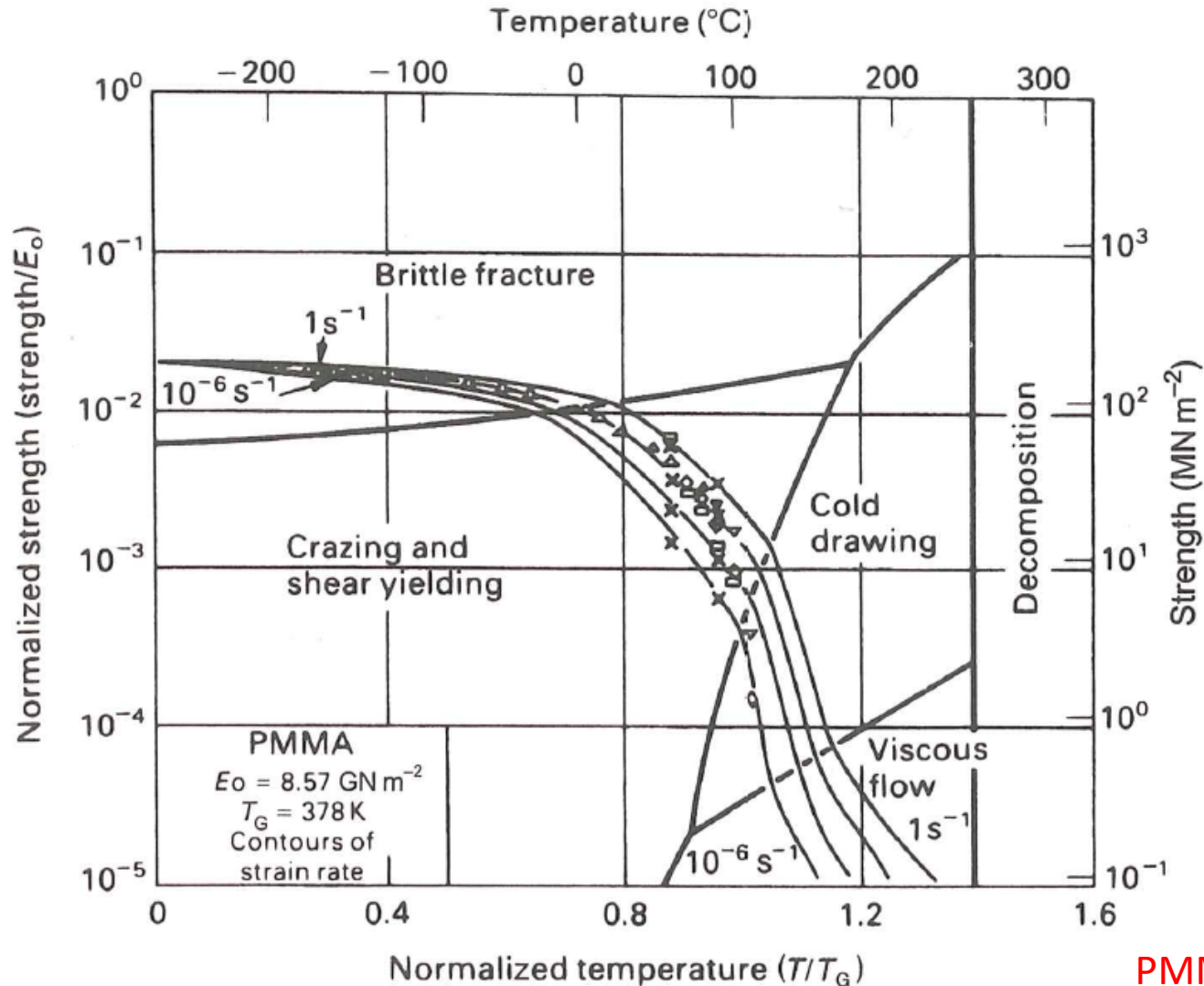
- $T \sim [0.75 T_G - T_G]$
- Shear banding is a form of polymer plasticity which appears in compression
- Within each band a finite shear takes place
- As the number of bands increases the total overall strain accumulates





Strength & Failure

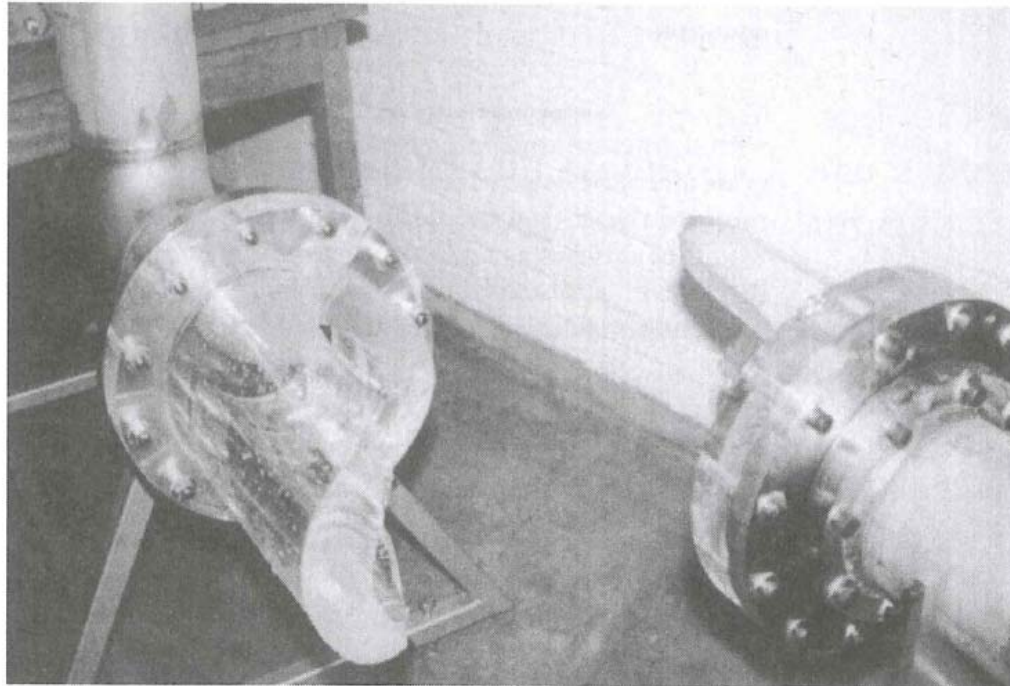
Strength diagrams for polymers



PMMA in tension



Example: Explosion of a Pressure Window



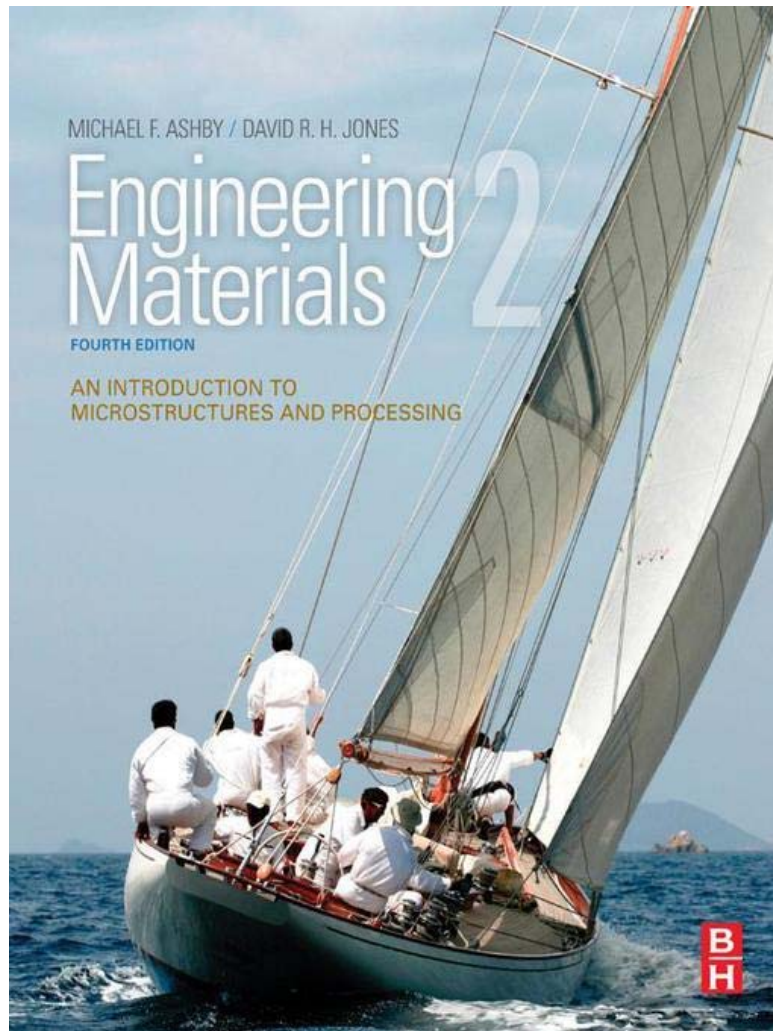
Flange connector in an internally pressurized piping system

The connector is made up of PMMA and failed catastrophically during the testing phase at a pressure much lower than expected.

Investigate the possible reason for failure...



Reference Book



Chapters:
23, 24



Forming of Polymers



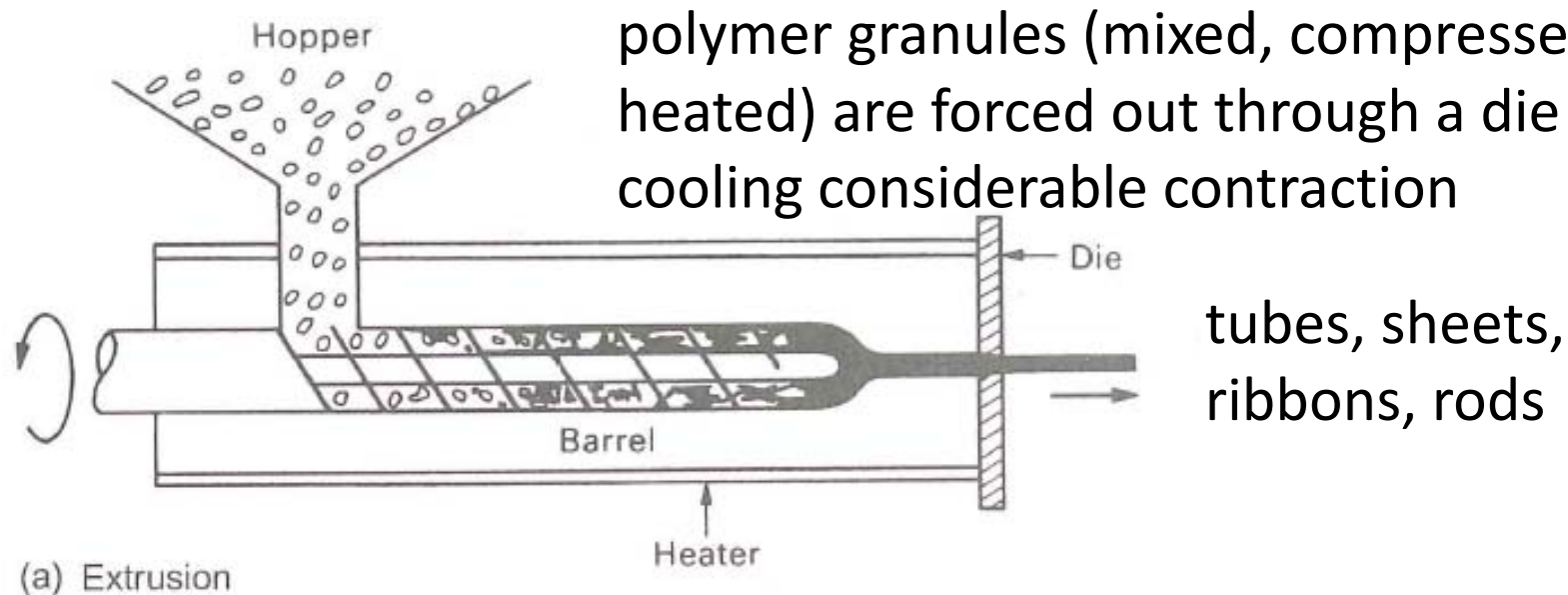
Forming Polymers

- **Thermoplastic:**
 - soften when heated → injection molding, vacuum forming, blow molding, compression molding
- **Thermosets:**
 - heated, formed and cured simultaneously by compression molding
- **Rubbers:**
 - formed like thermosets by pressing and heating a mix of elastomers and vulcanizing agent



Forming Polymers: Extrusion

- cheap continuous process to produce shapes of constant section (→ semi finished products)

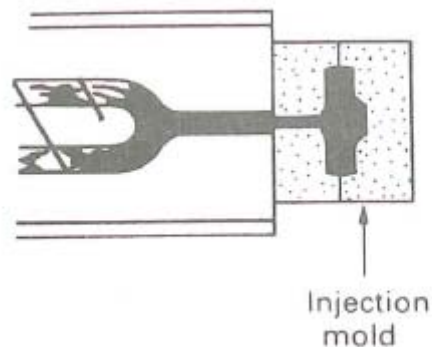


- shear flow in the die orients the polymer chains in the extrusion direction → increase strength and anisotropy
- 60 % of thermoplastics



Forming Polymers: Injection Molding

- slower and more expensive than extrusion



molded polymer is forced into a mold which is cooled below T_G
excess polymer is injected to compensate for contraction

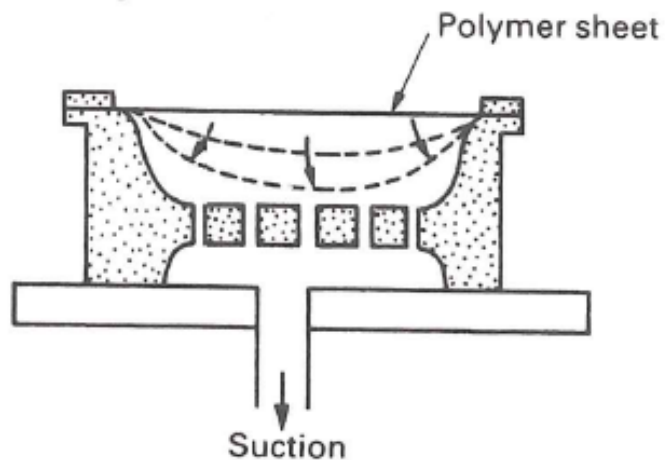
- again shear flow in the die orients the polymer chains in the extrusion direction → increase strength and anisotropy
- high precision as the polymers cool under applied pressure
- Molding parameters: T [150 – 350 °C], P [30 – 120 MPa]



Forming Polymers: Vacuum & Blow

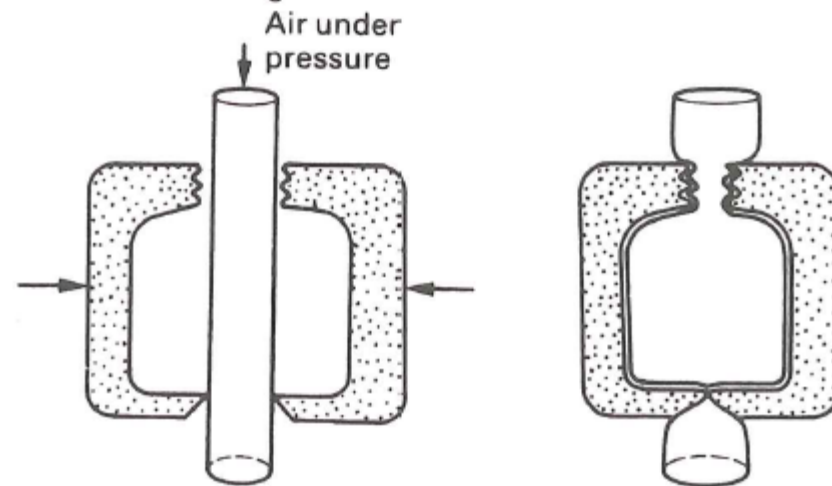
- In vacuum and blow forming, sheets produced by extrusion are shaped by vacuum or pressure forming

Vacuum forming



Heat softened is pressed into a mold

(b) Blow molding

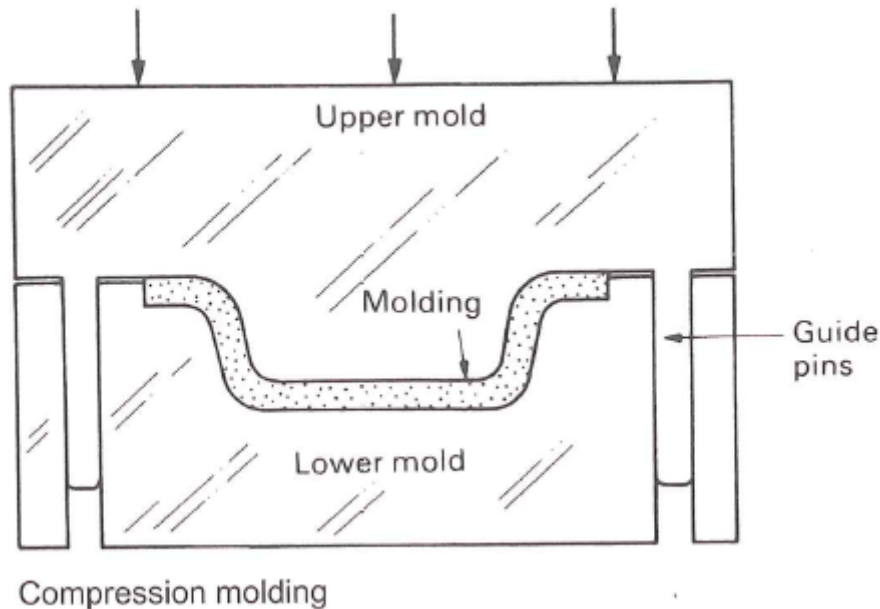


Heated tube is clamped in a split mold and expanded (plastic bottles)



Forming Polymers: **Compression Molding**

- Used both for thermoplastics and thermosets

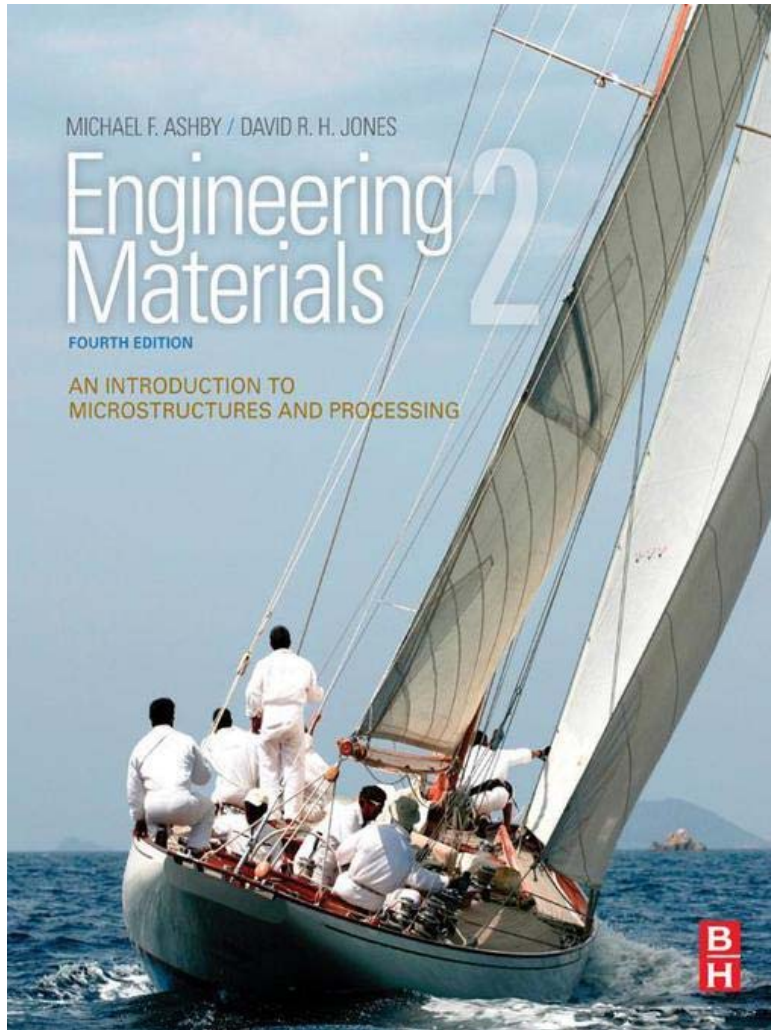


the polymer or resin is heated and compressed between dies
used to make car bumpers

- since a thermoset can be removed while still hot → forming time ranges from 10 seconds (small parts) to 10 minutes
- pressure is lower than for injection molding



Reference Book



Chapter: 25