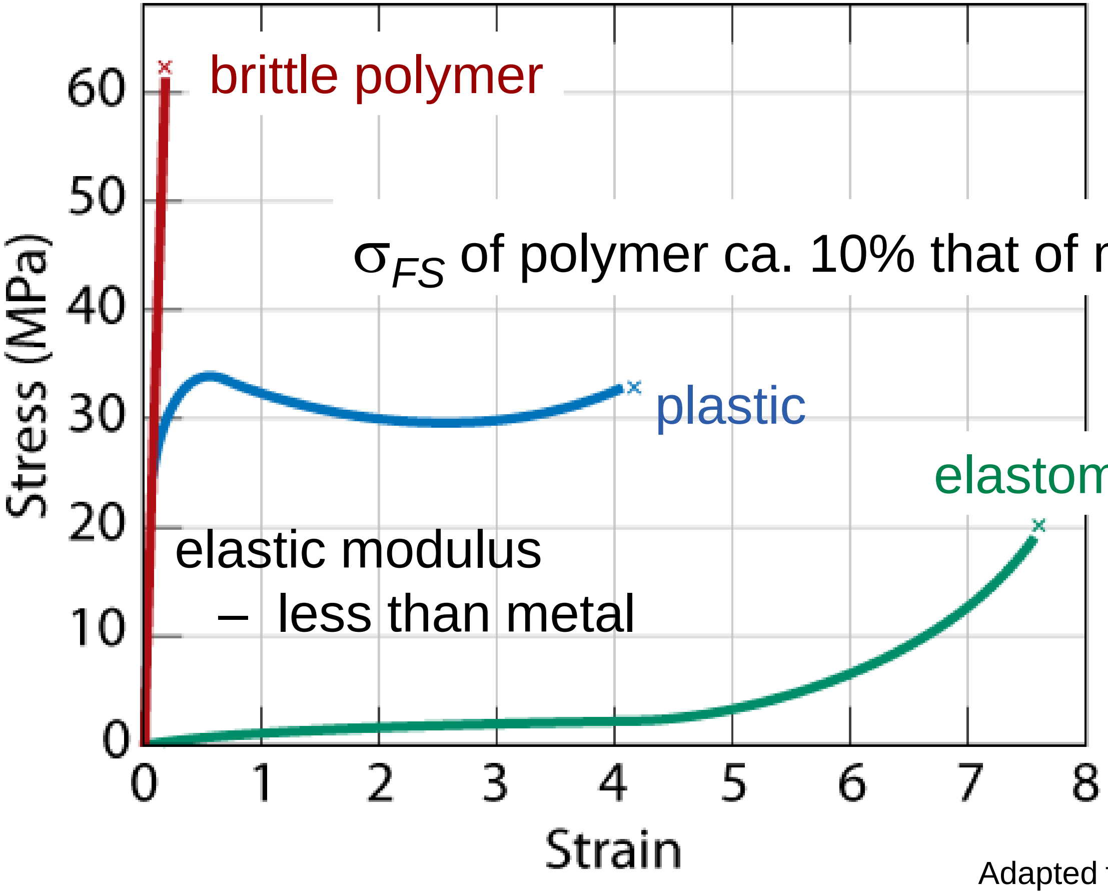
Chapter 15:
Characteristics, Applications & Processing of Polymers

ISSUES TO ADDRESS...

- What are the tensile properties of polymers and how are they affected by basic microstructural features?
- Hardening, anisotropy, and annealing in polymers.
- How does the elevated temperature mechanical response of polymers compare to ceramics and metals?
- What are the primary polymer processing methods?

Mechanical Properties

- i.e. stress-strain behavior of polymers



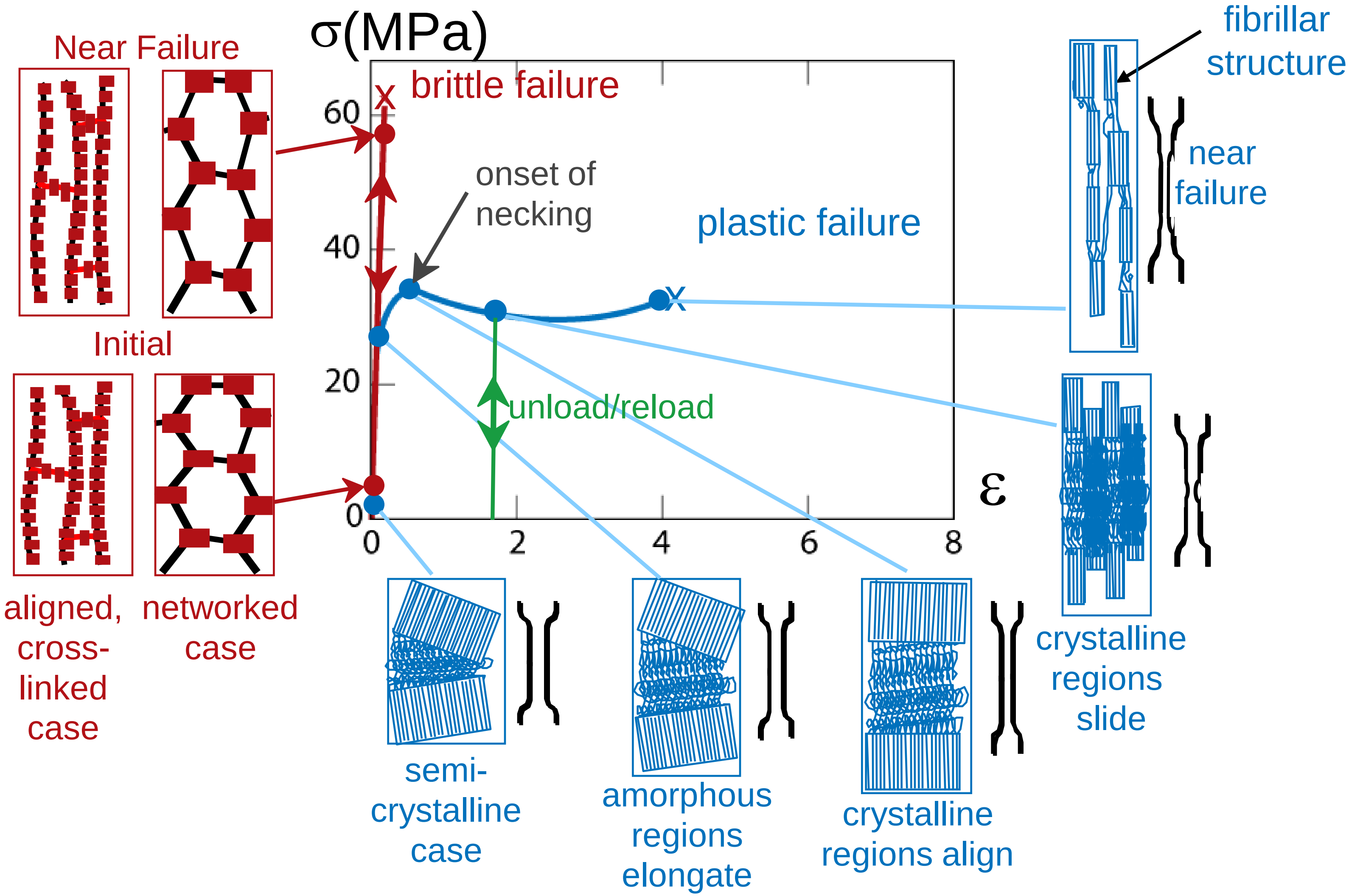
σ_{FS} of polymer ca. 10% that of metals

elastic modulus
– less than metal

Adapted from Fig. 15.1, *Callister 7e*.

Strains – deformations > 1000% possible
(for metals, maximum strain ca. 10% or less)

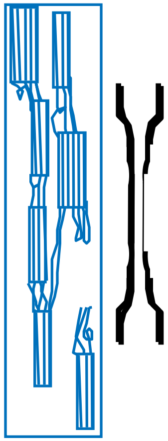
Tensile Response: Brittle & Plastic



Stress-strain curves adapted from Fig. 15.1, *Callister 7e.* Inset figures along plastic response curve adapted from Figs. 15.12 & 15.13, *Callister 7e*. (Figs. 15.12 & 15.13 are from J.M. Schultz, *Polymer Materials Science*, Prentice-Hall, Inc., 1974, pp. 500-501.)

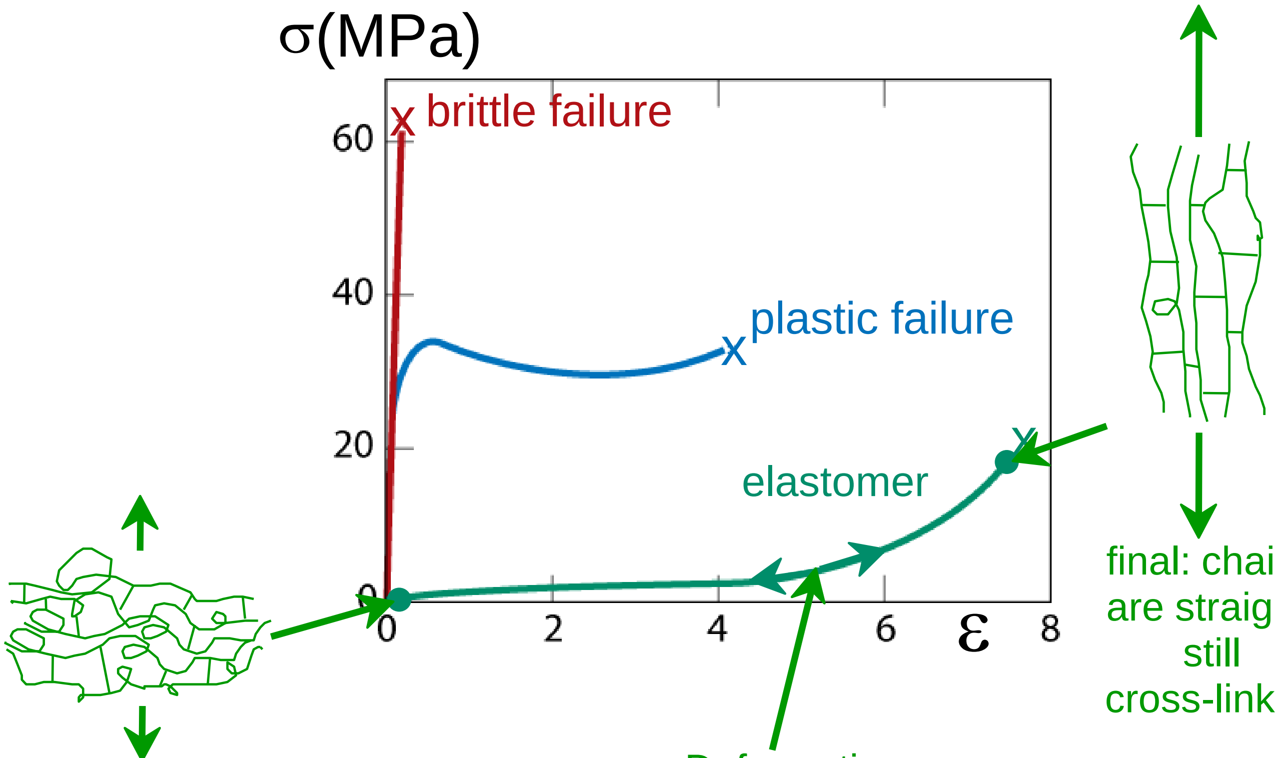
Predeformation by Drawing

- Drawing…(ex: monofilament fishline)
  - -- stretches the polymer prior to use
  - -- aligns chains in the stretching direction
- Results of drawing:
  - -- increases the elastic modulus (*E*) in the stretching direction
  - -- increases the tensile strength (*TS*) in the stretching direction
  - -- decreases ductility (%*EL*)
- Annealing after drawing...
  - -- decreases alignment
  - -- reverses effects of drawing.
- Compare to cold working in metals!



Adapted from Fig. 15.13, *Callister 7e*. (Fig. 15.13 is from J.M. Schultz, *Polymer Materials Science*, Prentice-Hall, Inc., 1974, pp. 500-501.)

Tensile Response: Elastomer Case



initial: amorphous chains are
kinked, cross-linked.

Deformation
is reversible!

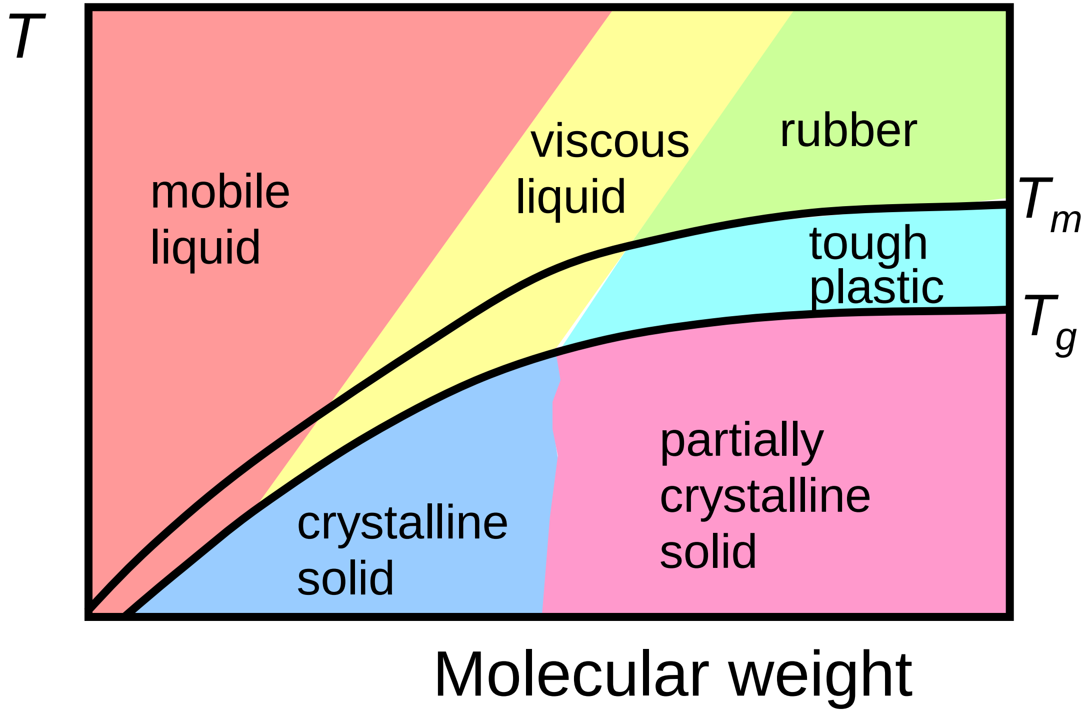
final: chains
are straight,
still
cross-linked

Stress-strain curves adapted from Fig. 15.1, *Callister 7e.* Inset figures along elastomer curve (green) adapted from Fig. 15.15, *Callister 7e*. (Fig. 15.15 is from Z.D. Jastrzebski, *The Nature and Properties of Engineering Materials*, 3rd ed., John Wiley and Sons, 1987.)

- Compare to responses of other polymers:
  - -- brittle response (aligned, crosslinked & networked polymer)
  - -- plastic response (semi-crystalline polymers)

Thermoplastics vs. Thermosets

- Thermoplastics:
  -- little crosslinking
  -- ductile
  -- soften w/heating
  -- polyethylene
  polypropylene
  polycarbonate
  polystyrene

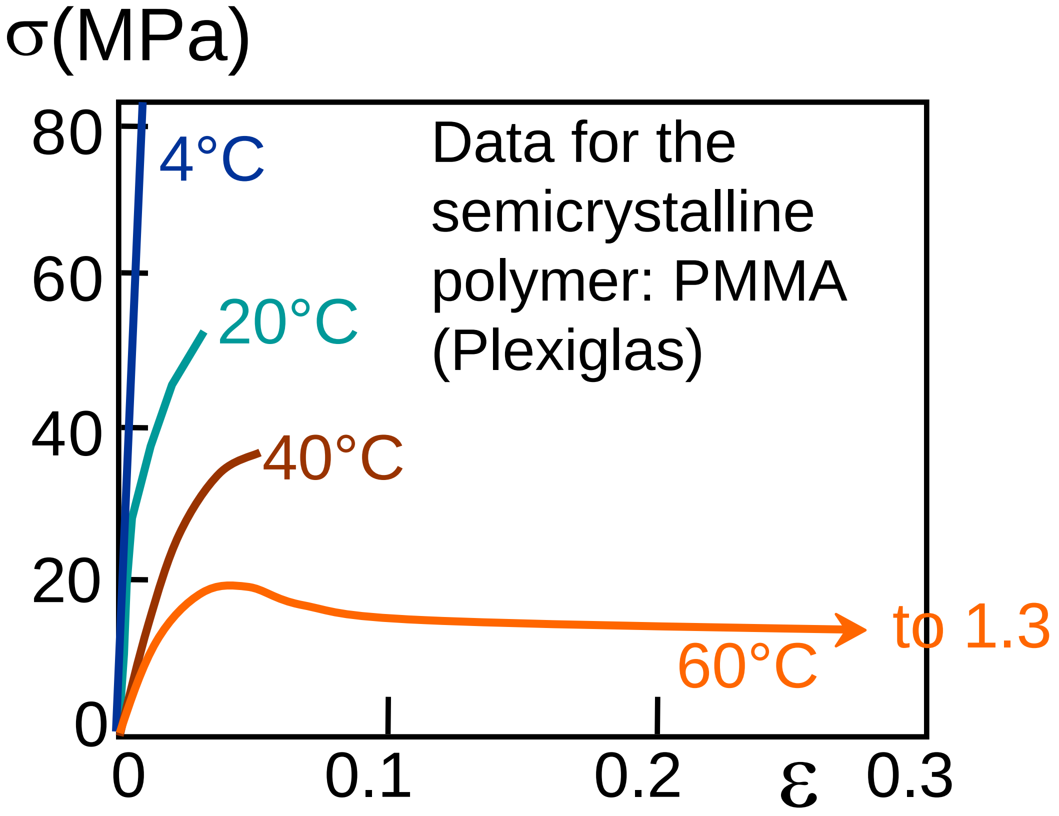


Adapted from Fig. 15.19, *Callister 7e*. (Fig. 15.19 is from F.W. Billmeyer, Jr., *Textbook of Polymer Science*, 3rd ed., John Wiley and Sons, Inc., 1984.)

- Thermosets:
  -- large crosslinking
  (10 to 50% of mers)
  -- hard and brittle
  -- do NOT soften w/heating
  -- vulcanized rubber, epoxies,
  polyester resin, phenolic resin

T and Strain Rate: Thermoplastics

- Decreasing *T*...
  - -- increases *E*
  - -- increases *TS*
  - -- decreases %*EL*
- Increasing strain rate...
  - -- same effects as decreasing *T*.



Data for the semicrystalline polymer: PMMA (Plexiglas)

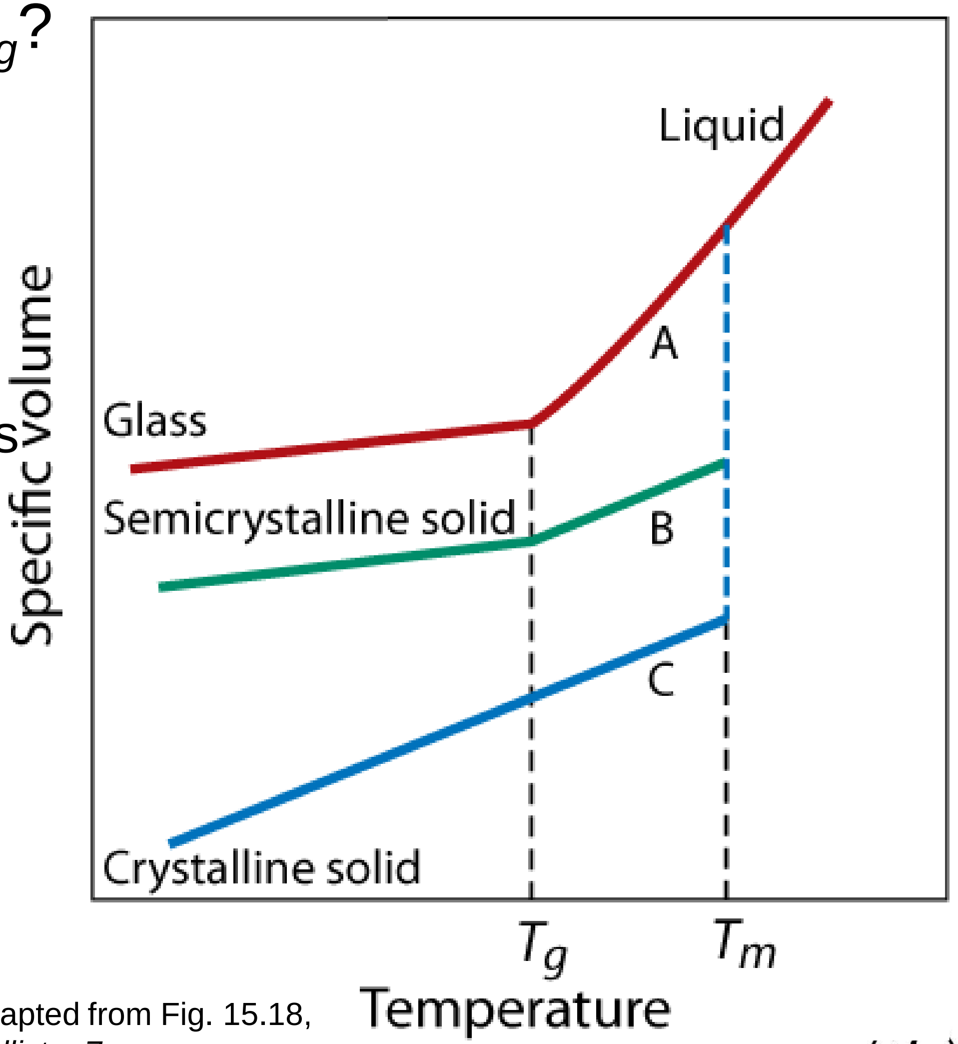
Adapted from Fig. 15.3, *Callister 7e*. (Fig. 15.3 is from T.S. Carswell and J.K. Nason, 'Effect of Environmental Conditions on the Mechanical Properties of Organic Plastics", *Symposium on Plastics*, American Society for Testing and Materials, Philadelphia, PA, 1944.)

Melting vs. Glass Transition Temp.

What factors affect T_m and T_g?

- Both T_m *and* T_g increase with increasing chain stiffness
- Chain stiffness increased by
  1. Bulky sidegroups
  2. Polar groups or sidegroups
  3. Double bonds or aromatic chain groups

- Regularity – effects T_m only



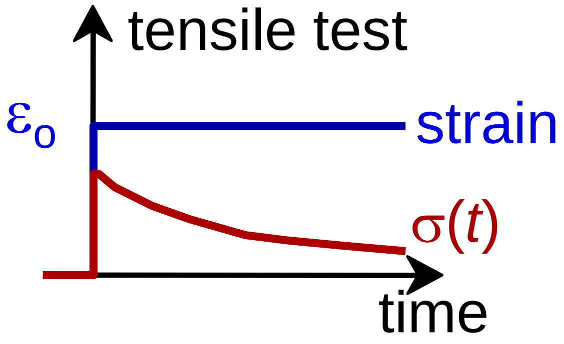
Adapted from Fig. 15.18, *Callister 7e*.

Time Dependent Deformation

- Stress relaxation test:

  -- strain to ε_o and hold.

  -- observe decrease in stress with time.

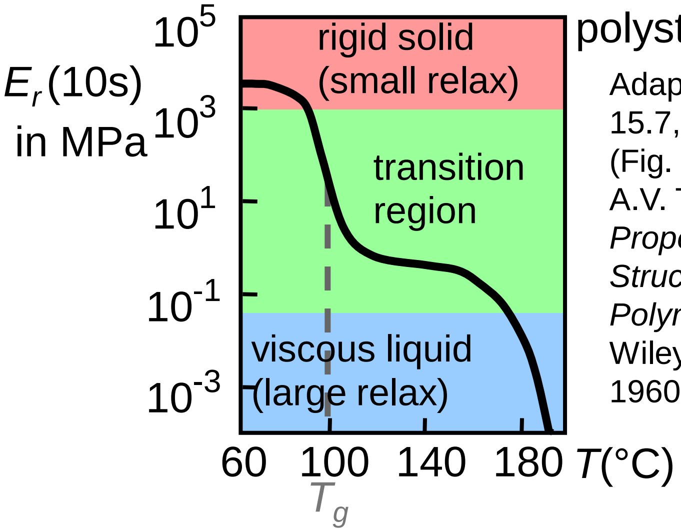


- Relaxation modulus:

$$E_r(t) = \frac{\sigma(t)}{\varepsilon_o}$$

- Data: Large drop in E_r for $T > T_g$.

(amorphous polystyrene)



Adapted from Fig. 15.7, *Callister 7e*. (Fig. 15.7 is from A.V. Tobolsky, *Properties and Structures of Polymers*, John Wiley and Sons, Inc., 1960.)

- Sample T_g(°C) values:

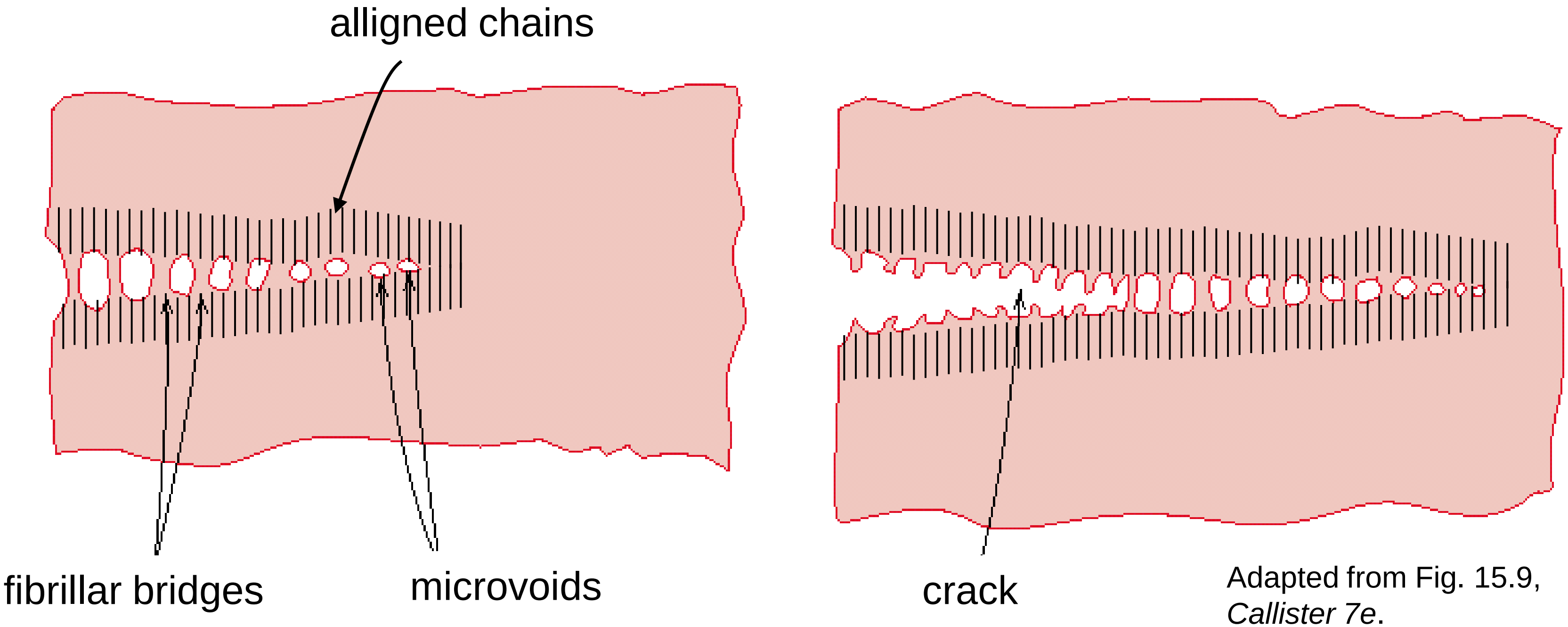
PE (low density)	- 110
PE (high density)	- 90
PVC	+ 87
PS	+100
PC	+150

Selected values from Table 15.2, *Callister 7e*.

Polymer Fracture

Crazing ≅ Griffith cracks in metals

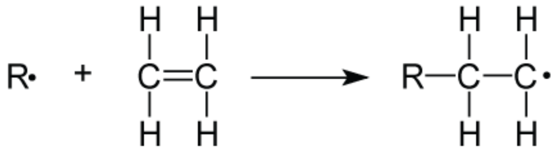
- spherulites plastically deform to fibrillar structure
- microvoids and fibrillar bridges form



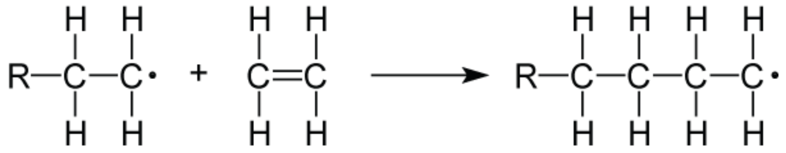
Adapted from Fig. 15.9, *Callister 7e*.

Addition (Chain) Polymerization

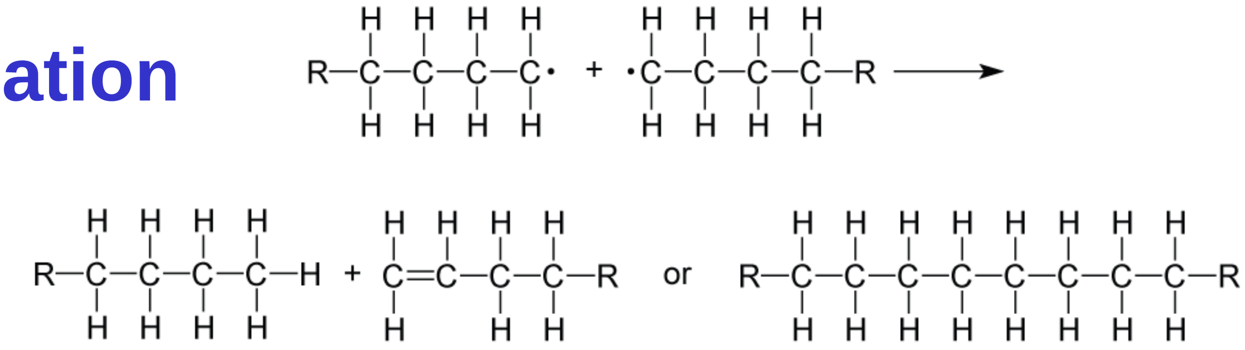
- **Initiation**



- **Propagation**



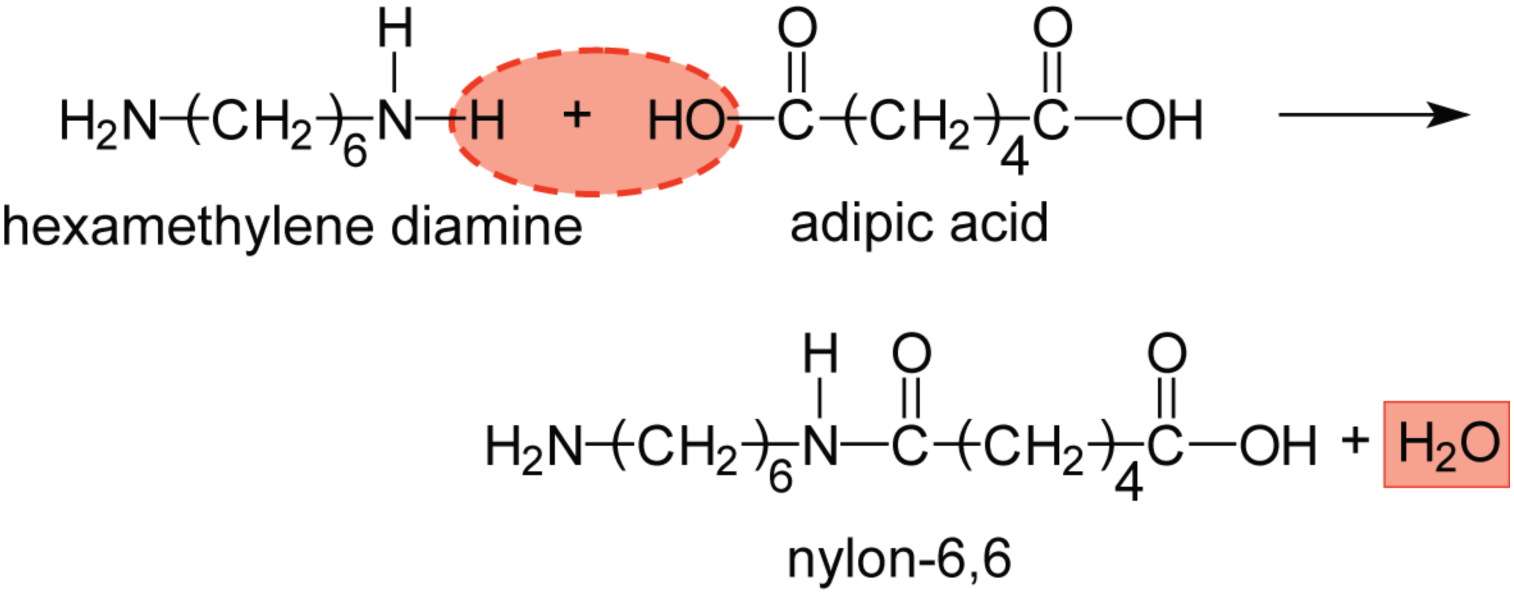
- **Termination**



Disproportionation

Combination

Condensation (Step) Polymerization



$$H_2N\text{—}(CH_2)_6\text{—}\overset{\displaystyle H}{\overset{|}{N}}\text{—}H + HO\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}(CH_2)_4\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}OH \longrightarrow$$

hexamethylene diamine

adipic acid

$$H_2N\text{—}(CH_2)_6\text{—}\overset{\displaystyle H}{\overset{|}{N}}\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}(CH_2)_4\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}OH + \boxed{H_2O}$$

nylon-6,6

Polymer Additives

Improve mechanical properties, processability, durability, etc.

- Fillers
  - Added to improve tensile strength & abrasion resistance, toughness & decrease cost
  - ex: carbon black, silica gel, wood flour, glass, limestone, talc, etc.
- Plasticizers
  - Added to reduce the glass transition temperature T_g
  - commonly added to PVC - otherwise it is brittle

Polymer Additives

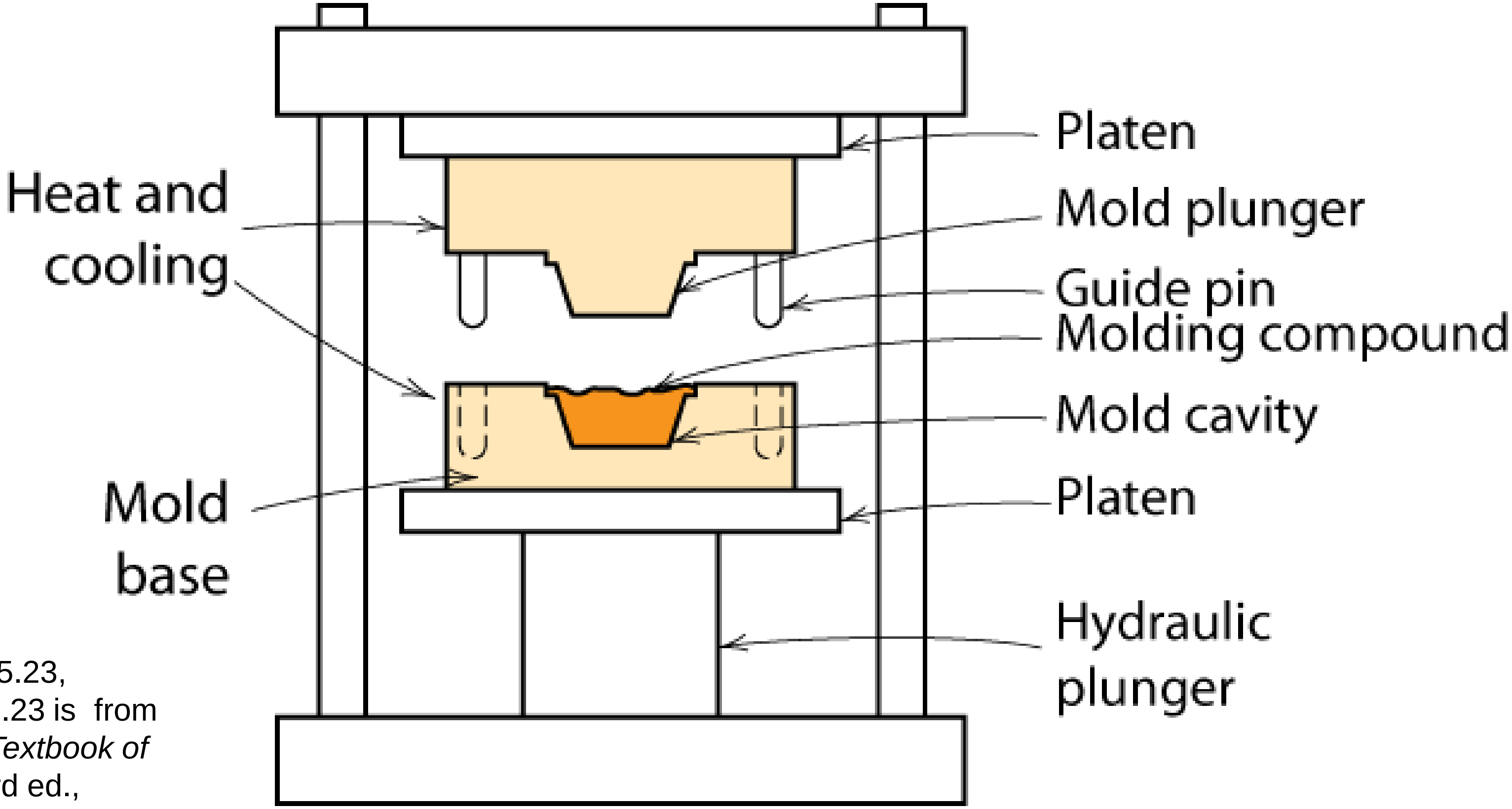
- Stabilizers
  - Antioxidants
  - UV protectants
- Lubricants
  - Added to allow easier processing
  - “slides” through dies easier – ex: Na stearate
- Colorants
  - Dyes or pigments
- Flame Retardants
  - Cl/F & B

Processing of Plastics

- Thermoplastic –
  - – can be reversibly cooled & reheated, i.e. recycled
  - – heat till soft, shape as desired, then cool
  - – ex: polyethylene, polypropylene, polystyrene, etc.
- Thermoset
  - – when heated forms a network
  - – degrades (not melts) when heated
  - – mold the prepolymer then allow further reaction
  - – ex: urethane, epoxy

Processing Plastics - Molding

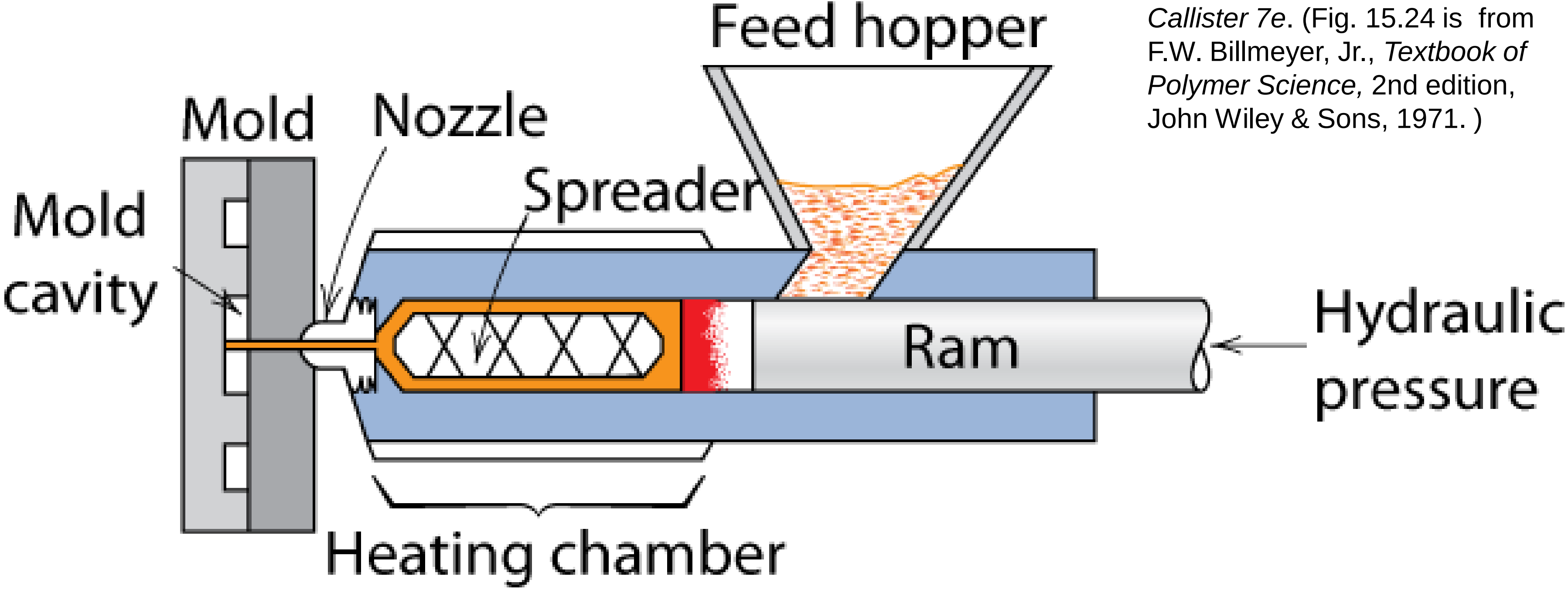
- Compression and transfer molding
  - thermoplastic or thermoset



Adapted from Fig. 15.23, *Callister 7e*. (Fig. 15.23 is from F.W. Billmeyer, Jr., *Textbook of Polymer Science,* 3rd ed., John Wiley & Sons, 1984.)

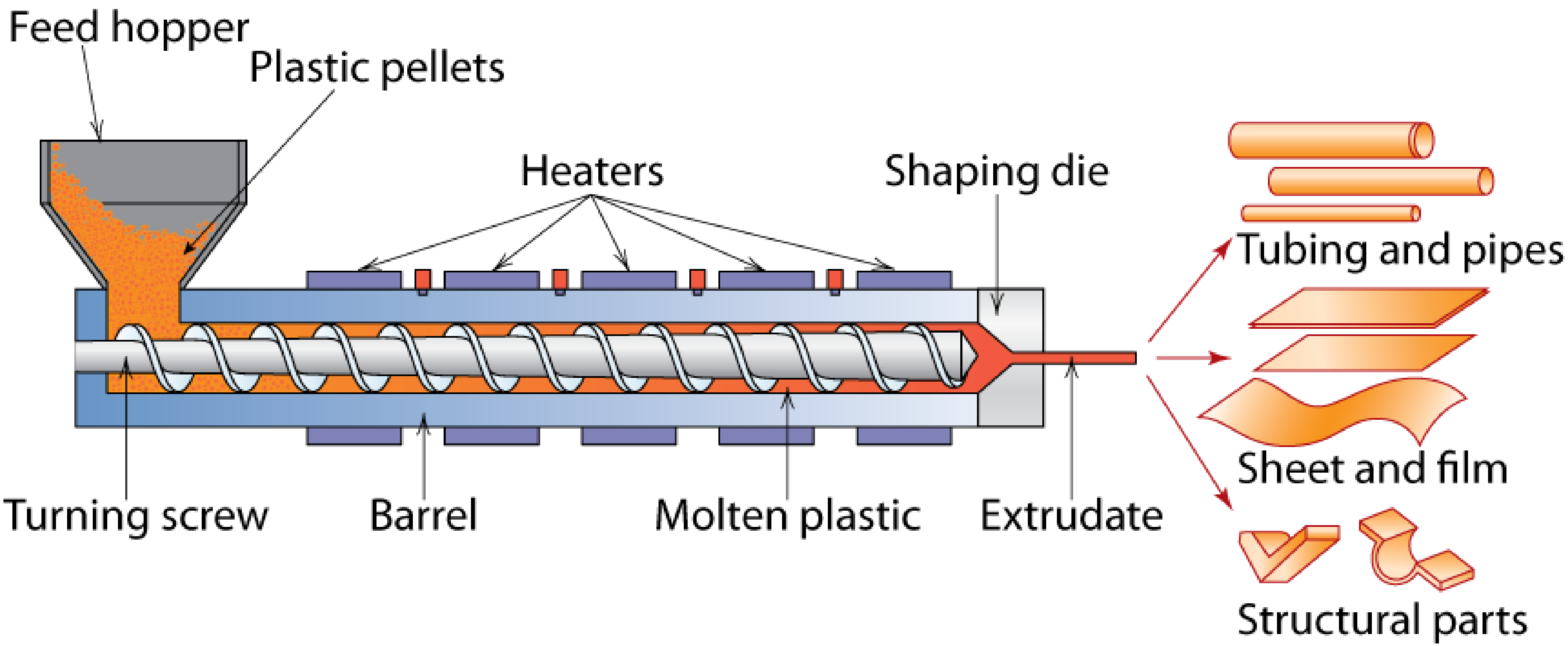
Processing Plastics - Molding

- Injection molding
  - – thermoplastic & some thermosets



Adapted from Fig. 15.24, *Callister 7e*. (Fig. 15.24 is from F.W. Billmeyer, Jr., *Textbook of Polymer Science,* 2nd edition, John Wiley & Sons, 1971.)

Processing Plastics – Extrusion

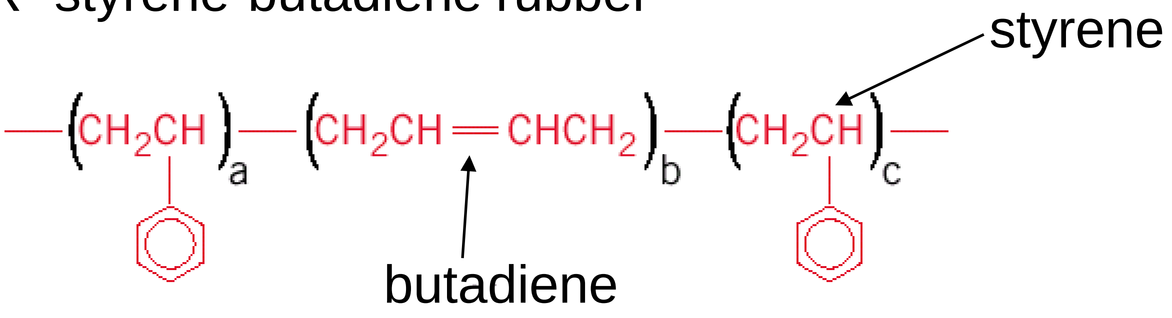


Adapted from Fig. 15.25,
Callister 7e. (Fig. 15.25 is from
Encyclopædia Britannica, 1997.)

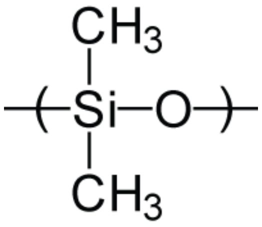
Polymer Types: Elastomers

Elastomers – rubber

- Crosslinked materials
  - Natural rubber
  - Synthetic rubber and thermoplastic elastomers
    - SBR- styrene-butadiene rubber



  - Silicone rubber



$$-\!\left(\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}\right)\!-$$

Polymer Types: Fibers

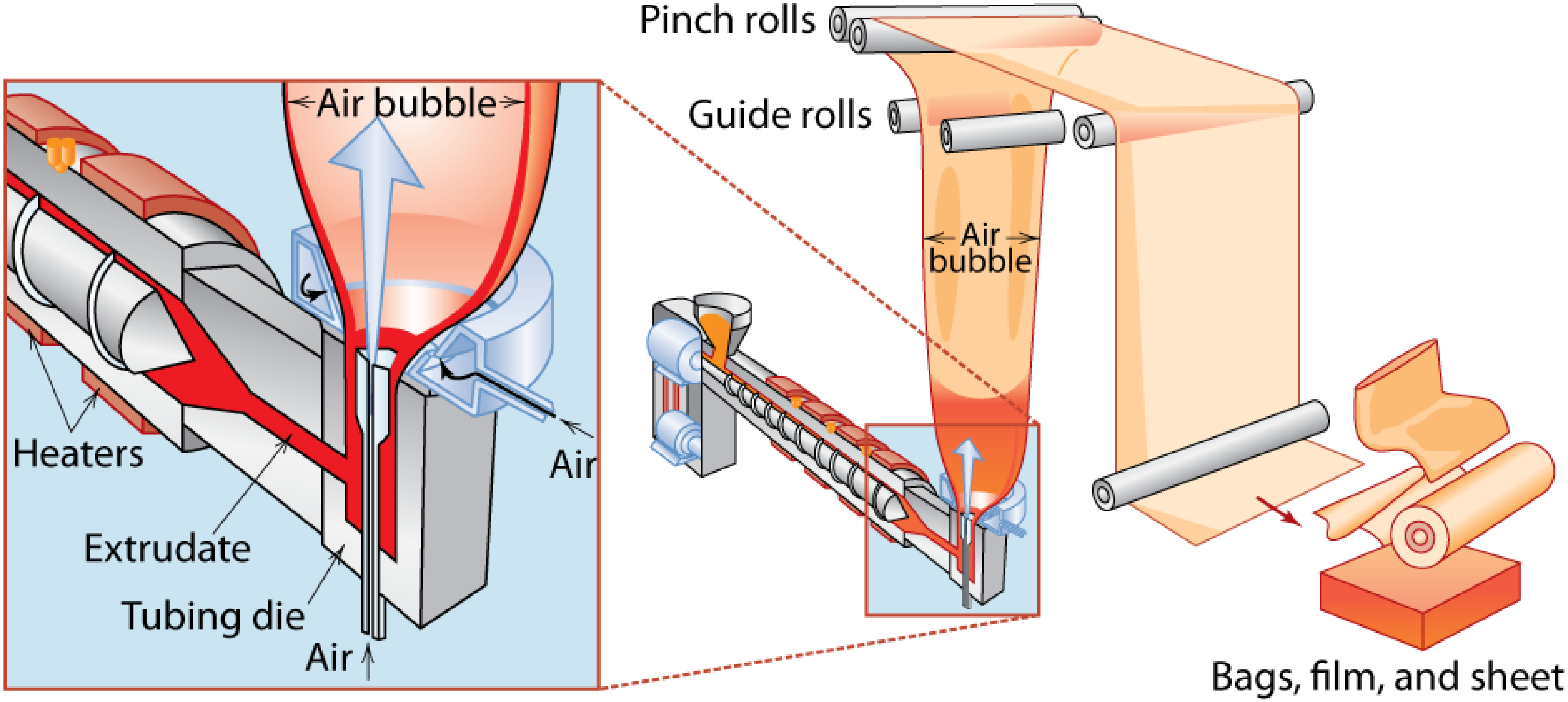
Fibers - length/diameter >100

- Textiles are main use
  - Must have high tensile strength
  - Usually highly crystalline & highly polar
- Formed by spinning
  - ex: extrude polymer through a spinnerette
    - Pt plate with 1000's of holes for nylon
    - ex: rayon – dissolved in solvent then pumped through die head to make fibers
  - the fibers are drawn
  - leads to highly aligned chains- fibrillar structure

Polymer Types

- Coatings – thin film on surface – i.e. paint, varnish
  - To protect item
  - Improve appearance
  - Electrical insulation
- Adhesives – produce bond between two adherands
  - Usually bonded by:
    1. Secondary bonds
    2. Mechanical bonding
- Films – blown film extrusion
- Foams – gas bubbles in plastic

Blown-Film Extrusion



Adapted from Fig. 15.26, *Callister 7e*.
(Fig. 15.26 is from *Encyclopædia Britannica,* 1997.)

Advanced Polymers

- Ultrahigh molecular weight polyethylene (UHMWPE)
  - Molecular weight ca. 4×10^6 g/mol
  - Excellent properties for variety of applications
    - bullet-proof vest, golf ball covers, hip joints, etc.

Adapted from chapter-opening photograph, Chapter 22, *Callister 7e.*

Summary

- General drawbacks to polymers:
  - -- E, σ_y, K_c, $T_{\text{application}}$ are generally small.
  - -- Deformation is often T and time dependent.
  - -- Result: polymers benefit from composite reinforcement.
- Thermoplastics (PE, PS, PP, PC):
  - -- Smaller E, σ_y, $T_{\text{application}}$
  - -- Larger K_c
  - -- Easier to form and recycle
- Elastomers (rubber):
  - -- Large reversible strains!
- Thermosets (epoxies, polyesters):
  - -- Larger E, σ_y, $T_{\text{application}}$
  - -- Smaller K_c

Table 15.3 *Callister 7e*:

Good overview
of applications
and trade names
of polymers.

ANNOUNCEMENTS

Reading:

Core Problems:

Self-help Problems: