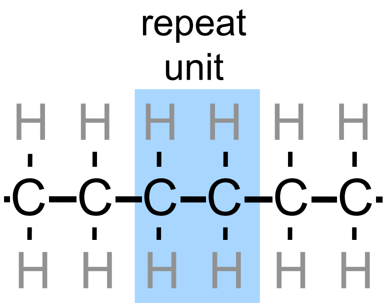
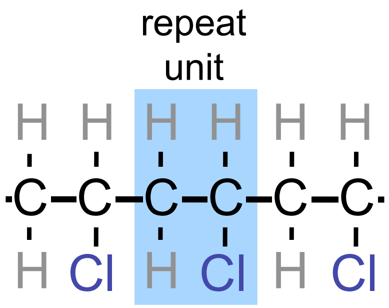
Polymers

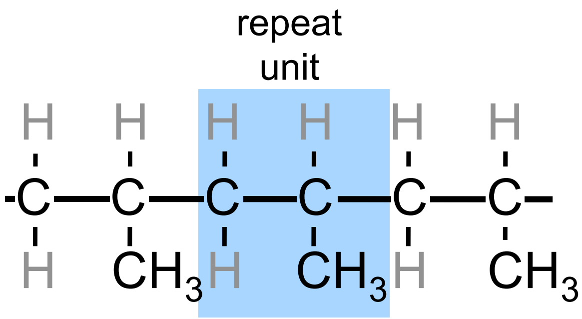
Poly	mer
many	repeat unit



Polyethylene (PE)



Polyvinyl chloride (PVC)



Polypropylene (PP)

Adapted from Fig. 14.2, *Callister 7e.*

Bulk or commodity polymers

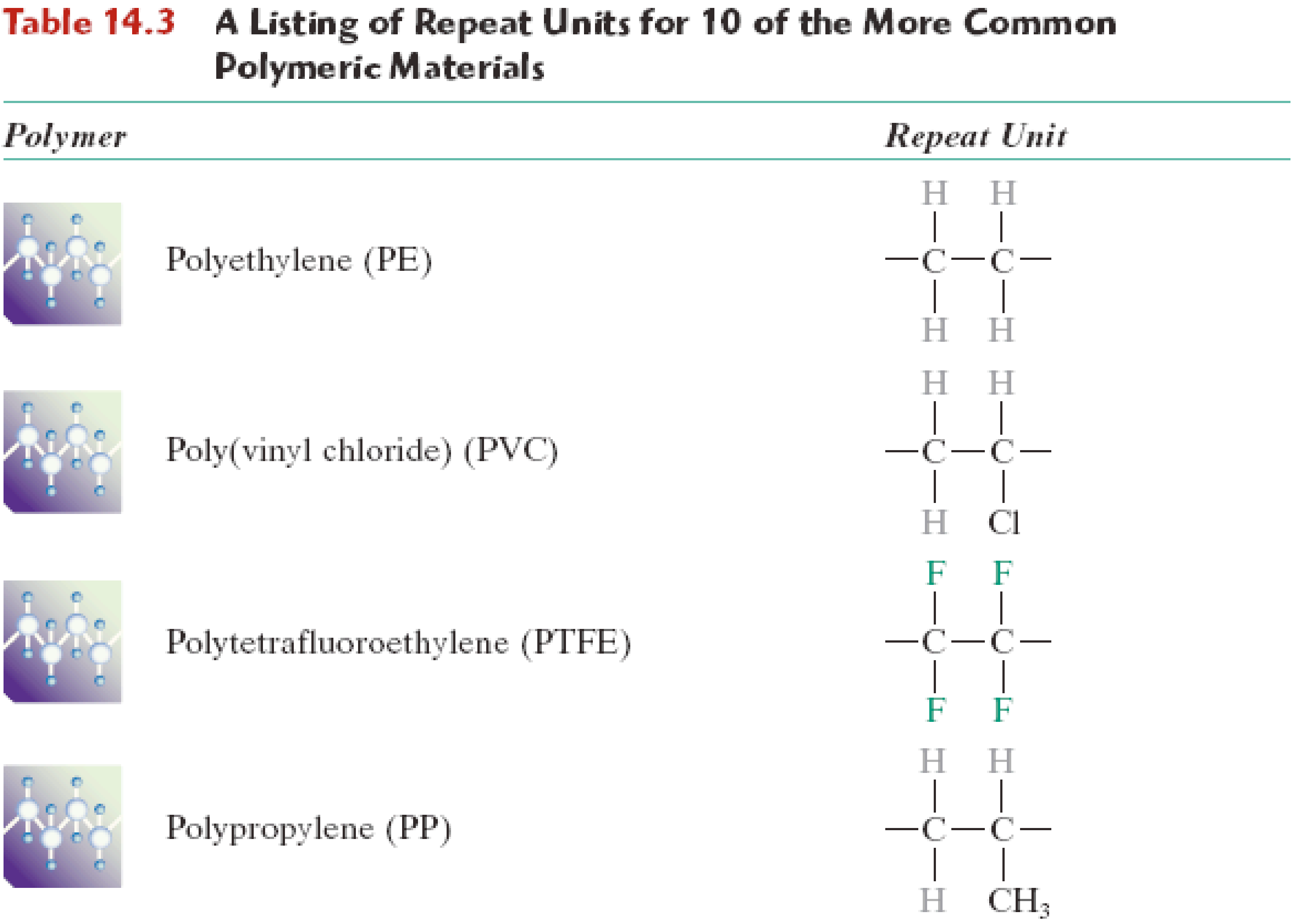
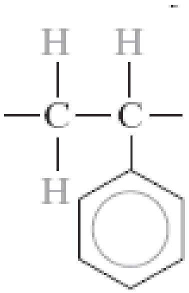


Table 14.3 **A Listing of Repeat Units for 10 of the More Common Polymeric Materials**

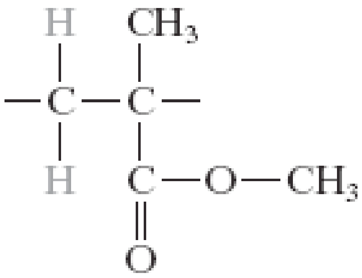
Polymer	*Repeat Unit*
Polyethylene (PE)	$-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-$
Poly(vinyl chloride) (PVC)	$-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{Cl}{C}}-$
Polytetrafluoroethylene (PTFE)	$-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}-$
Polypropylene (PP)	$-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{CH_3}{C}}-$

Bulk or commodity polymers

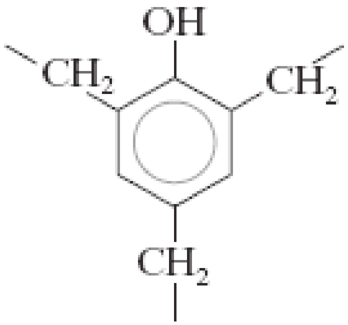
Polystyrene (PS)



Poly(methyl methacrylate) (PMMA)



Phenol-formaldehyde (Bakelite)



Bulk or commodity polymers

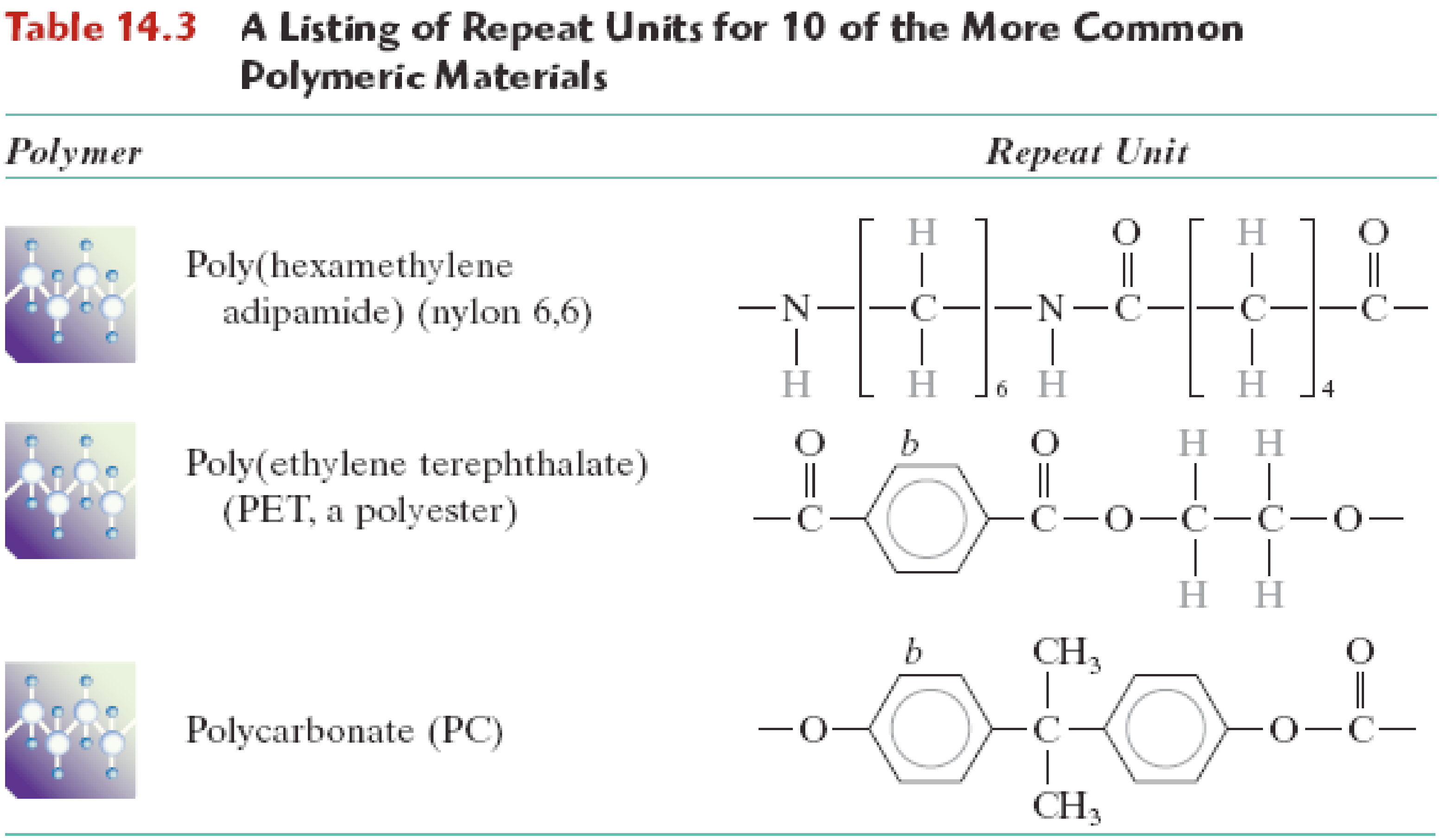
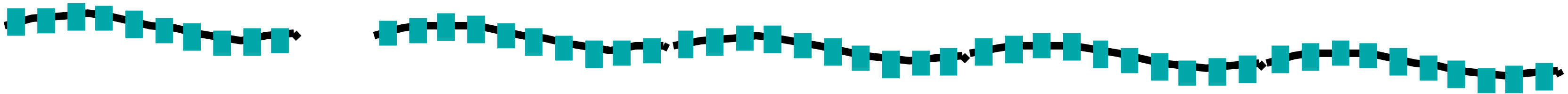


Table 14.3 **A Listing of Repeat Units for 10 of the More Common Polymeric Materials**

Polymer	*Repeat Unit*
Poly(hexamethylene adipamide) (nylon 6,6)	$-\underset{\mid \atop H}{N}-\left[-\overset{H \atop \mid}{\underset{\mid \atop H}{C}}-\right]_6-\underset{\mid \atop H}{N}-\overset{O \atop \parallel}{C}-\left[-\overset{H \atop \mid}{\underset{\mid \atop H}{C}}-\right]_4-\overset{O \atop \parallel}{C}-$
Poly(ethylene terephthalate) (PET, a polyester)	[b]
Polycarbonate (PC)	[b]

Molecular weight

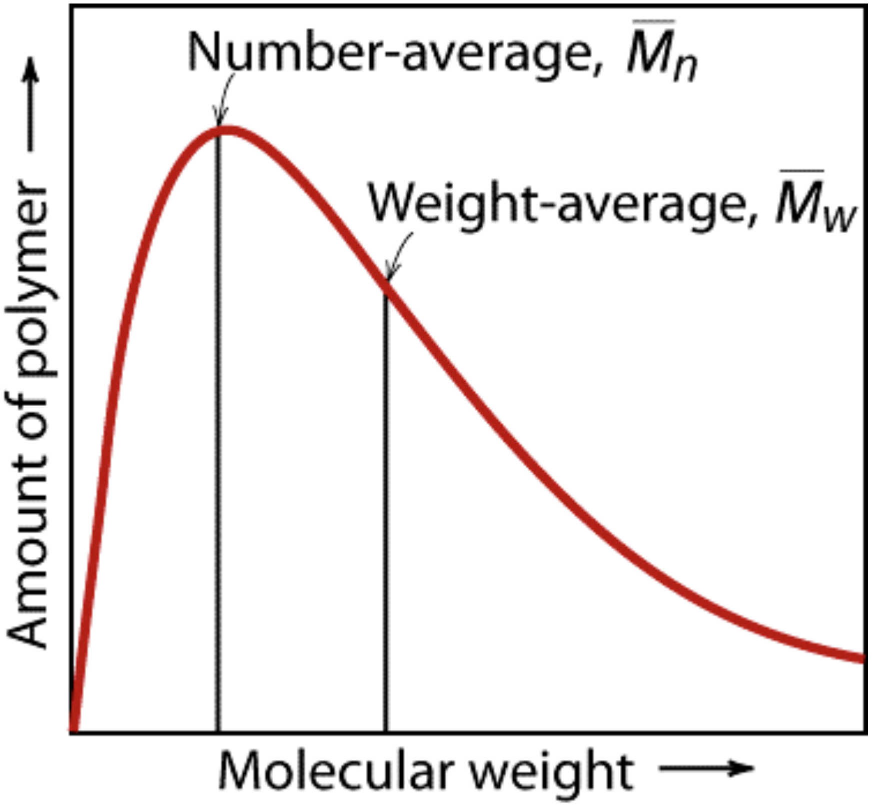
- Molecular weight, M_i: Mass of a mole of chains.



$$\overline{M}_n = \frac{\text{total wt of polymer}}{\text{total \# of molecules}}$$

$$\overline{M}_n = \Sigma x_i M_i$$
$$\overline{M}_w = \Sigma w_i M_i$$

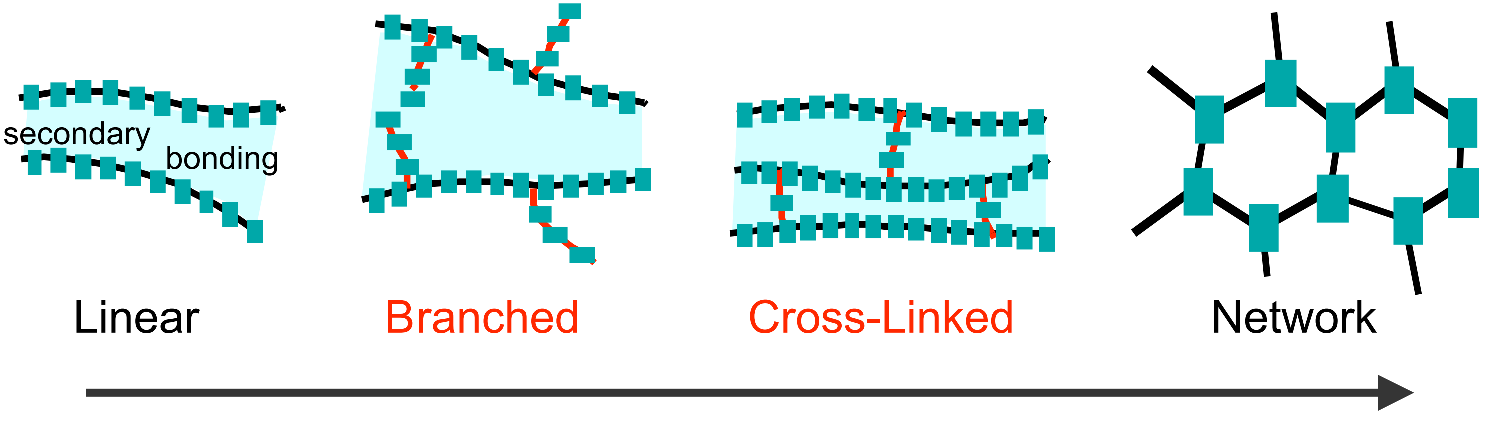
$\overline{M}_w$ is more sensitive to higher molecular weights



Adapted from Fig. 14.4, *Callister 7e.*

Molecular structures

- Covalent chain configurations and strength:

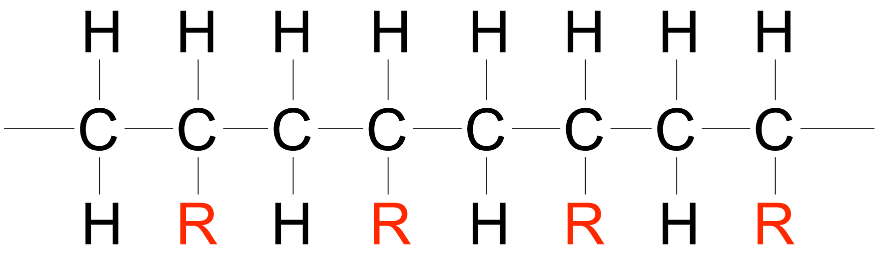


Adapted from Fig. 14.7, *Callister 7e.*

Tacticity

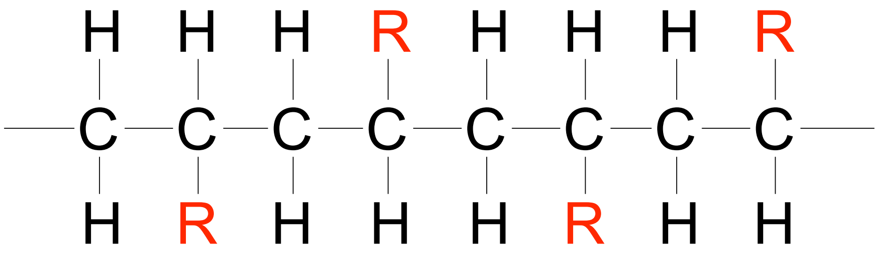
Tacticity – stereoregularity of chain

isotactic – all R groups on same side of chain



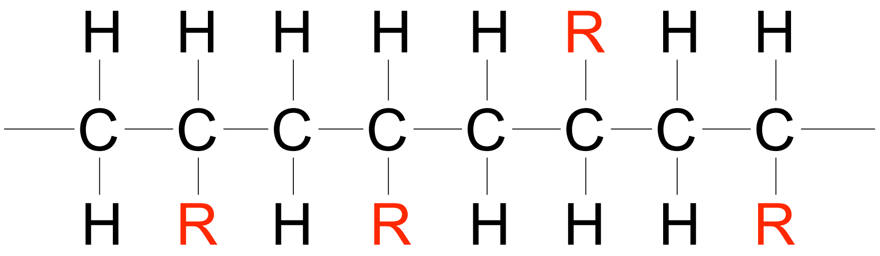
$$\begin{array}{ccccccccccccccccc}
 & H & & H & & H & & H & & H & & H & & H & & H & \\
 & | & & | & & | & & | & & | & & | & & | & & | & \\
- & C & - & C & - & C & - & C & - & C & - & C & - & C & - & C & - \\
 & | & & | & & | & & | & & | & & | & & | & & | & \\
 & H & & R & & H & & R & & H & & R & & H & & R &
\end{array}$$

syndiotactic – R groups alternate sides



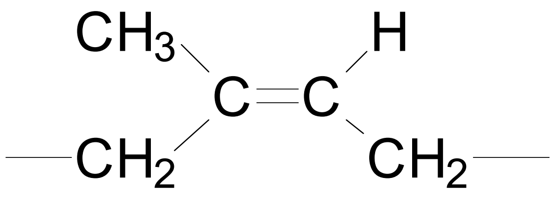
$$\begin{array}{ccccccccccccccccc}
 & H & & H & & H & & R & & H & & H & & H & & R & \\
 & | & & | & & | & & | & & | & & | & & | & & | & \\
- & C & - & C & - & C & - & C & - & C & - & C & - & C & - & C & - \\
 & | & & | & & | & & | & & | & & | & & | & & | & \\
 & H & & R & & H & & H & & H & & R & & H & & H &
\end{array}$$

atactic – R groups random



$$\begin{array}{ccccccccccccccccc}
 & H & & H & & H & & H & & H & & R & & H & & H & \\
 & | & & | & & | & & | & & | & & | & & | & & | & \\
- & C & - & C & - & C & - & C & - & C & - & C & - & C & - & C & - \\
 & | & & | & & | & & | & & | & & | & & | & & | & \\
 & H & & R & & H & & R & & H & & H & & H & & R &
\end{array}$$

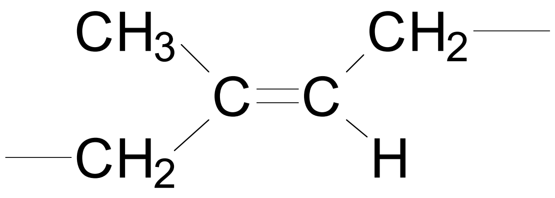
Cis and trans isomerism



cis

cis-isoprene
(natural rubber)

bulky groups on same side of chain



trans

trans-isoprene
(gutta percha)

bulky groups on opposite sides of chain

Copolymers

two or more monomers polymerized together

random – A and B randomly vary in chain

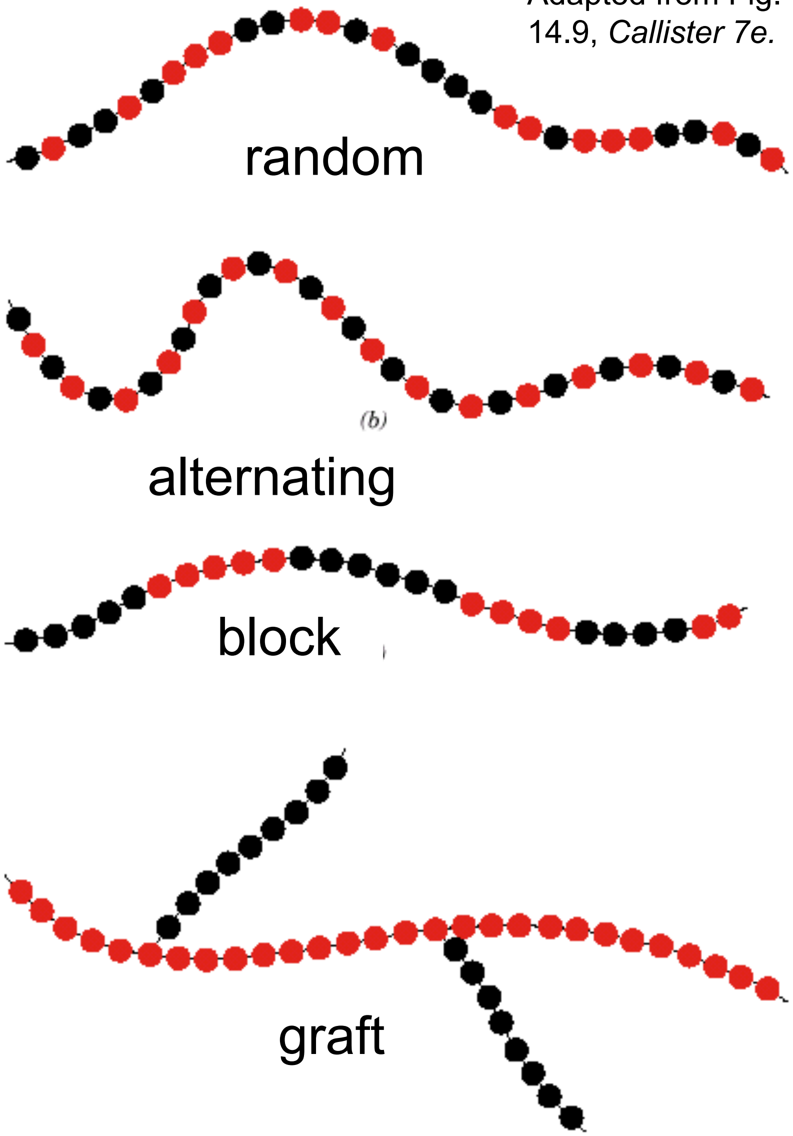
alternating – A and B alternate in polymer chain

block – large blocks of A alternate with large blocks of B

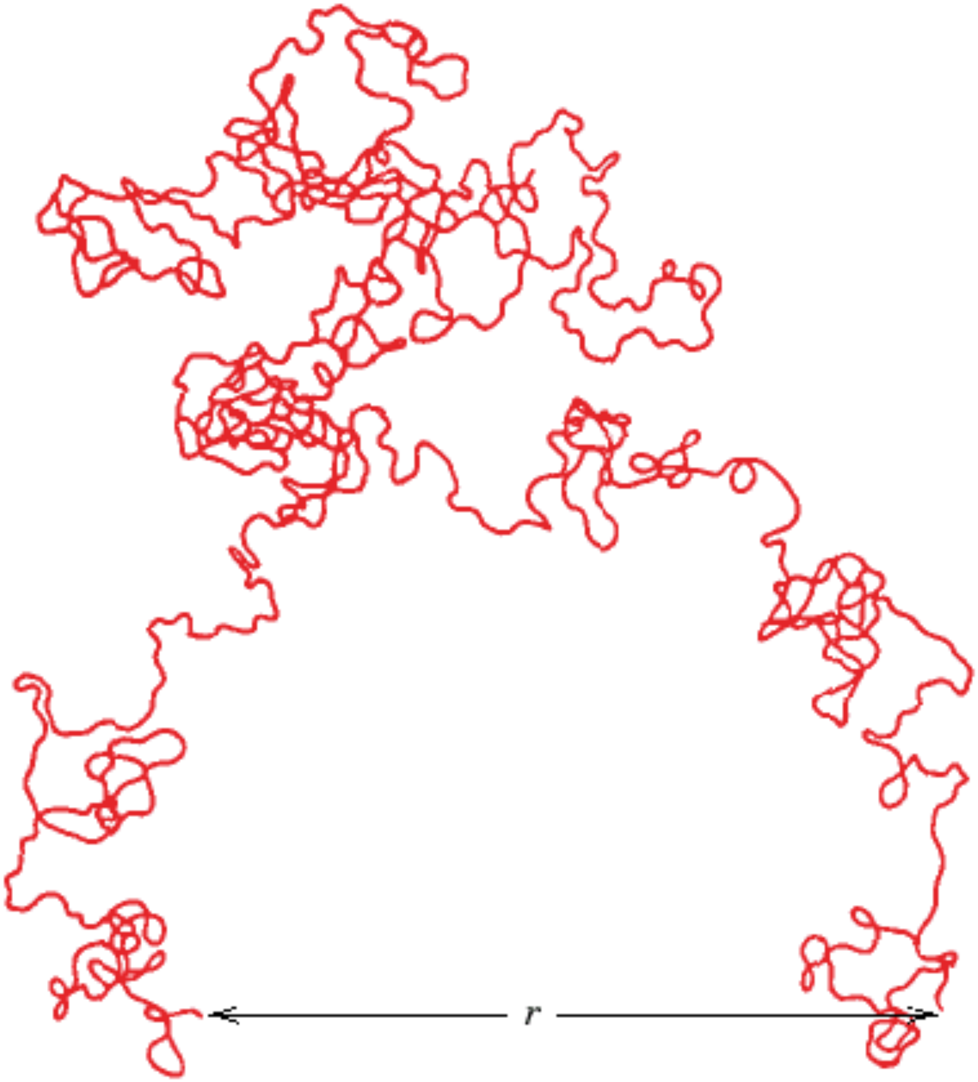
graft – chains of B grafted on to A backbone

A – 🔴 B – ⚫

Adapted from Fig. 14.9, *Callister 7e.*



End to end distance



Adapted from Fig. 14.6, *Callister 7e.*

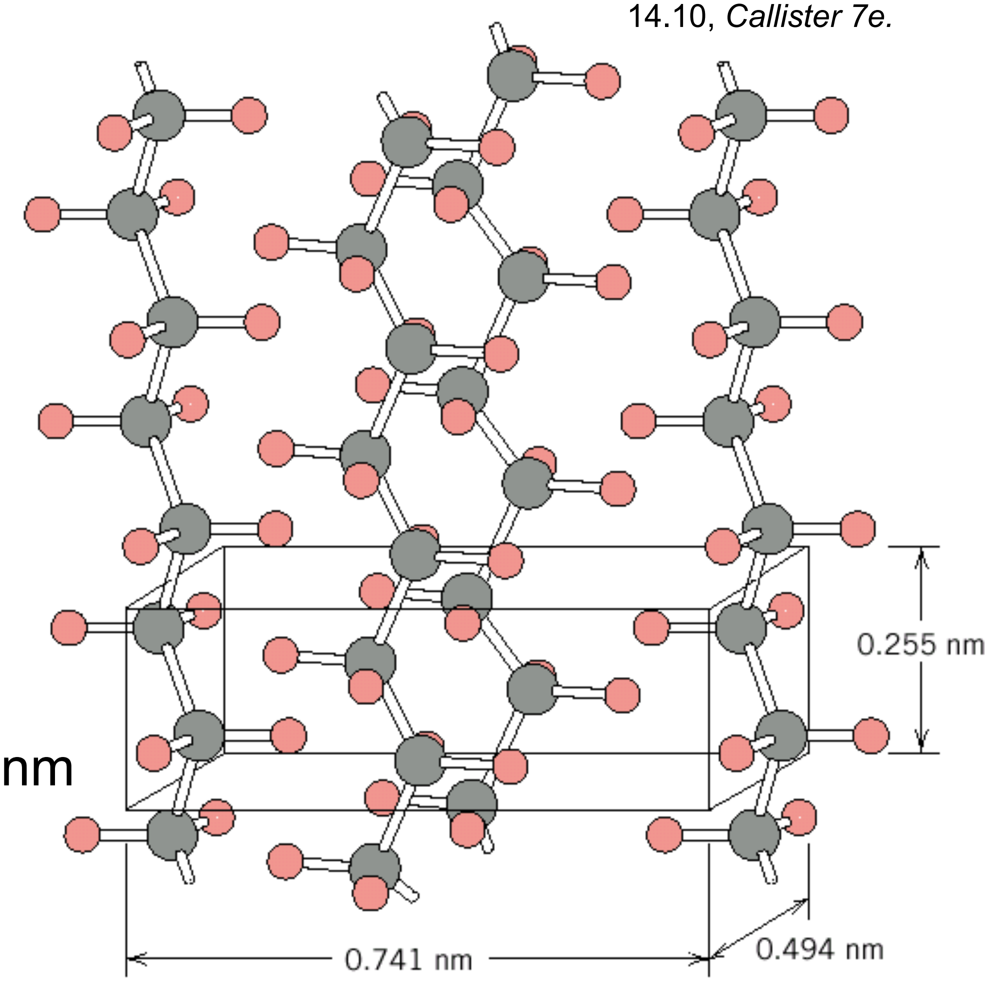
Polymer crystalline structure

Ex: polyethylene unit cell

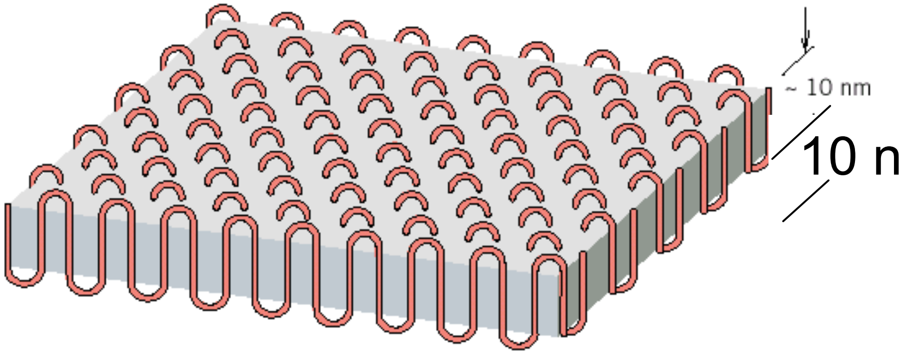
Crystals must contain the polymer chains in some way

Chain folded structure

Adapted from Fig. 14.10, *Callister 7e.*



Adapted from Fig. 14.12, *Callister 7e.*



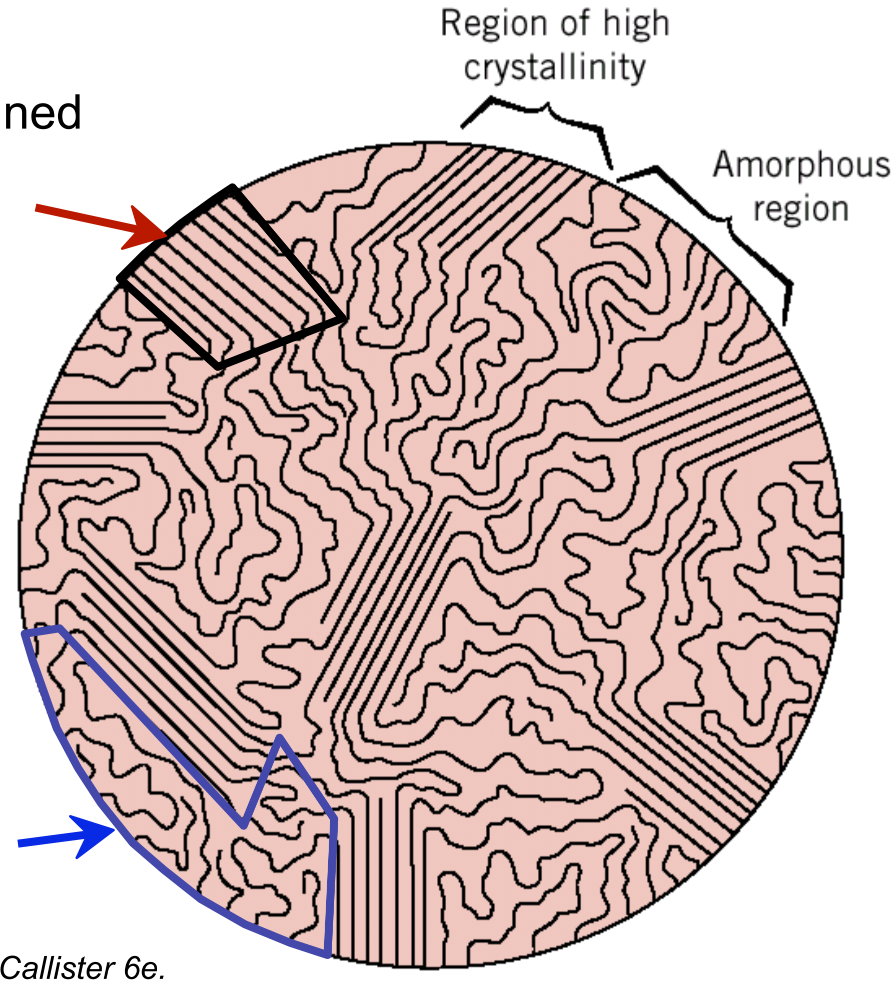
10 nm

Polymer crystalline structure

Polymers rarely 100% crystalline

Too difficult to get all those chains aligned

- % Crystallinity: % of material that is crystalline.
  - -- *TS* and *E* often increase with % crystallinity.
  - -- Annealing causes crystalline regions to grow. % crystallinity increases.



crystalline region

amorphous region

Adapted from Fig. 14.11, *Callister 6e.*
(Fig. 14.11 is from H.W. Hayden, W.G. Moffatt, and J. Wulff, *The Structure and Properties of Materials*, Vol. III, *Mechanical Behavior*, John Wiley and Sons, Inc., 1965.)

T_m and T_g

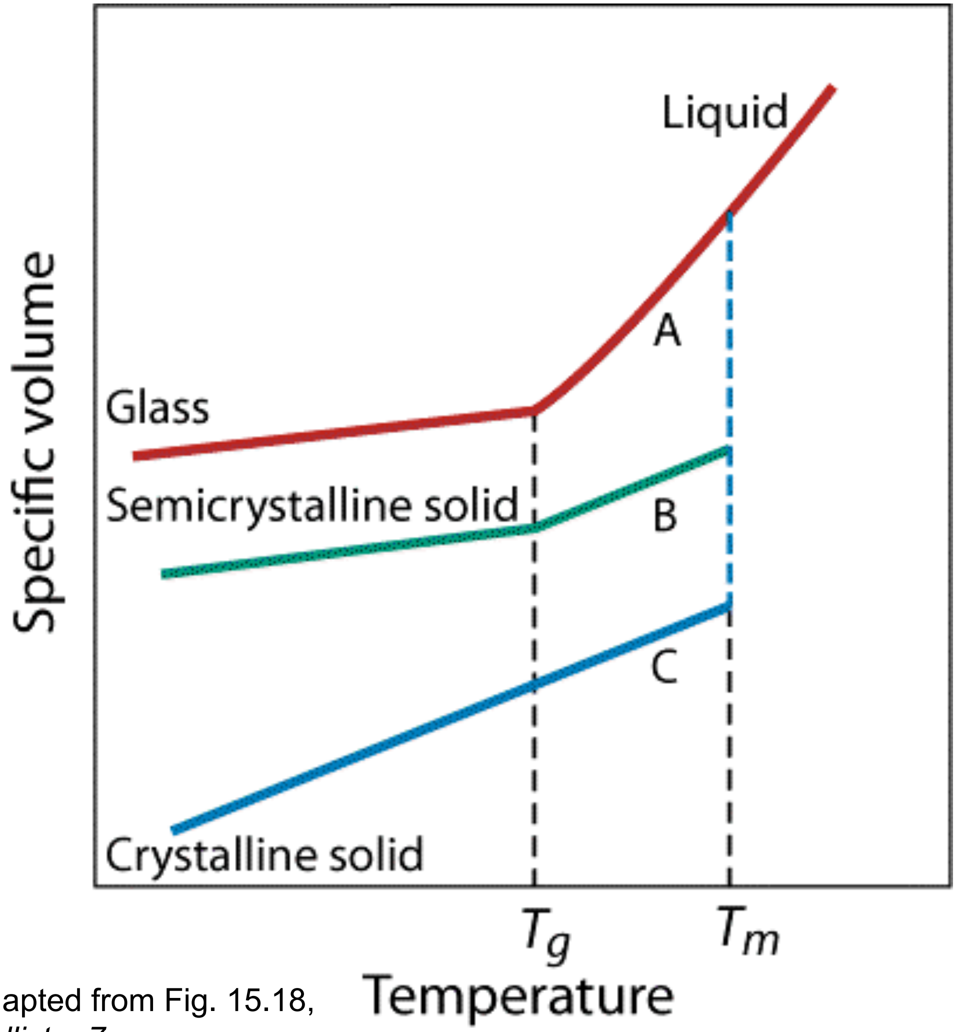
What factors affect T_m and T_g?

Both T_m *and* T_g increase with increasing chain stiffness

Chain stiffness increased by

- Bulky sidegroups
- Polar groups or sidegroups
- Double bonds or aromatic chain groups

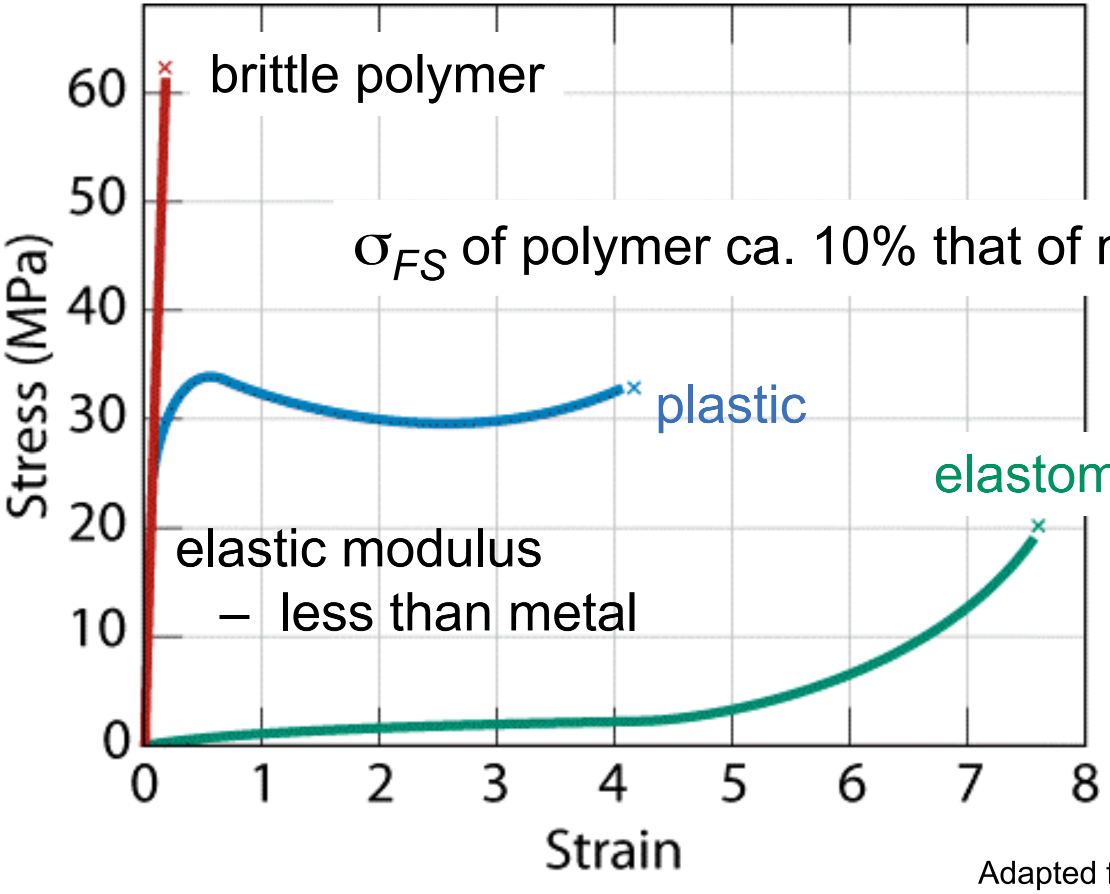
Regularity – effects T_m only



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

Mechanical properties

i.e. stress-strain behavior of polymers



brittle polymer

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

plastic

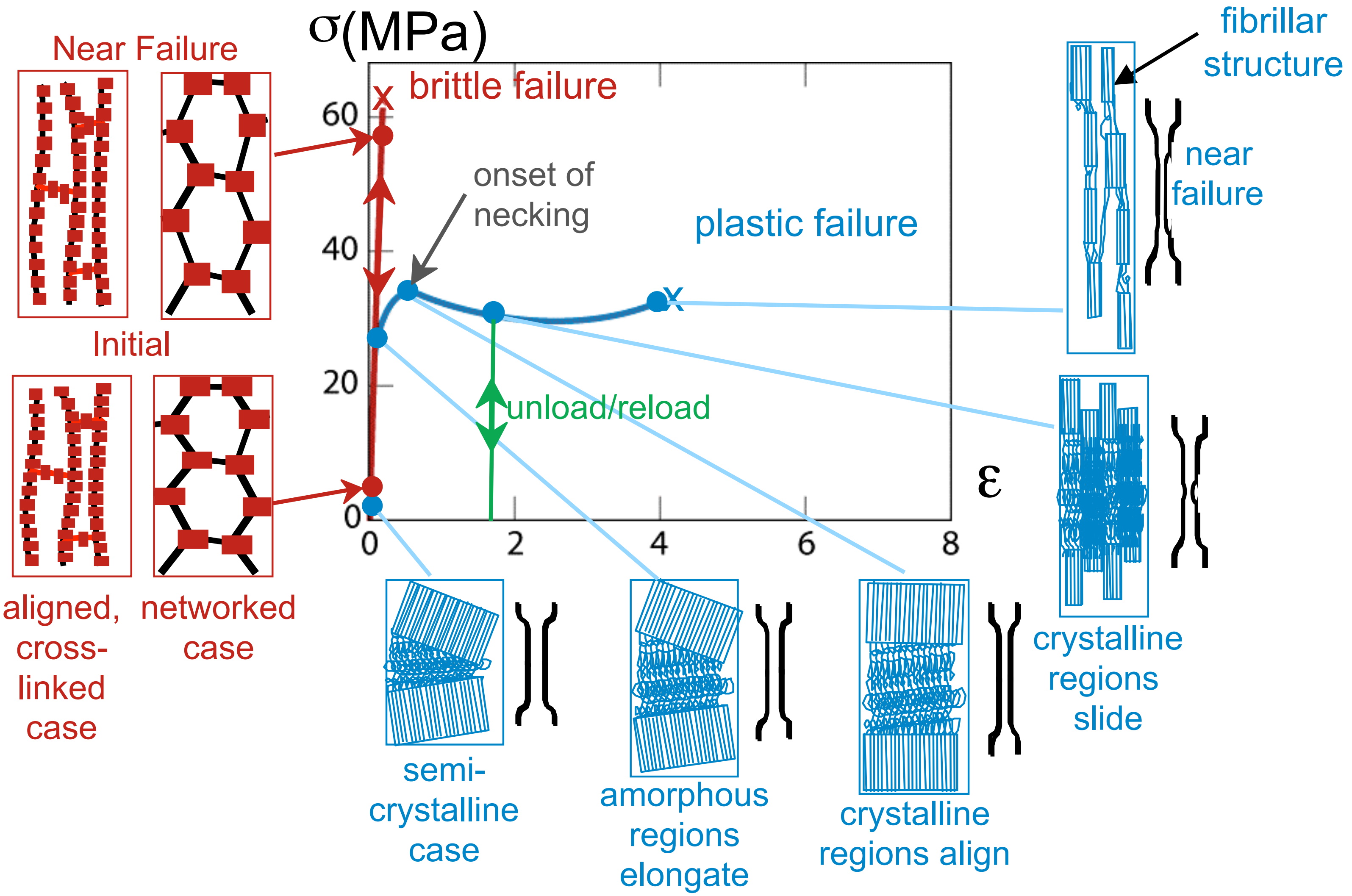
elastomer

elastic modulus
- less than metal

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

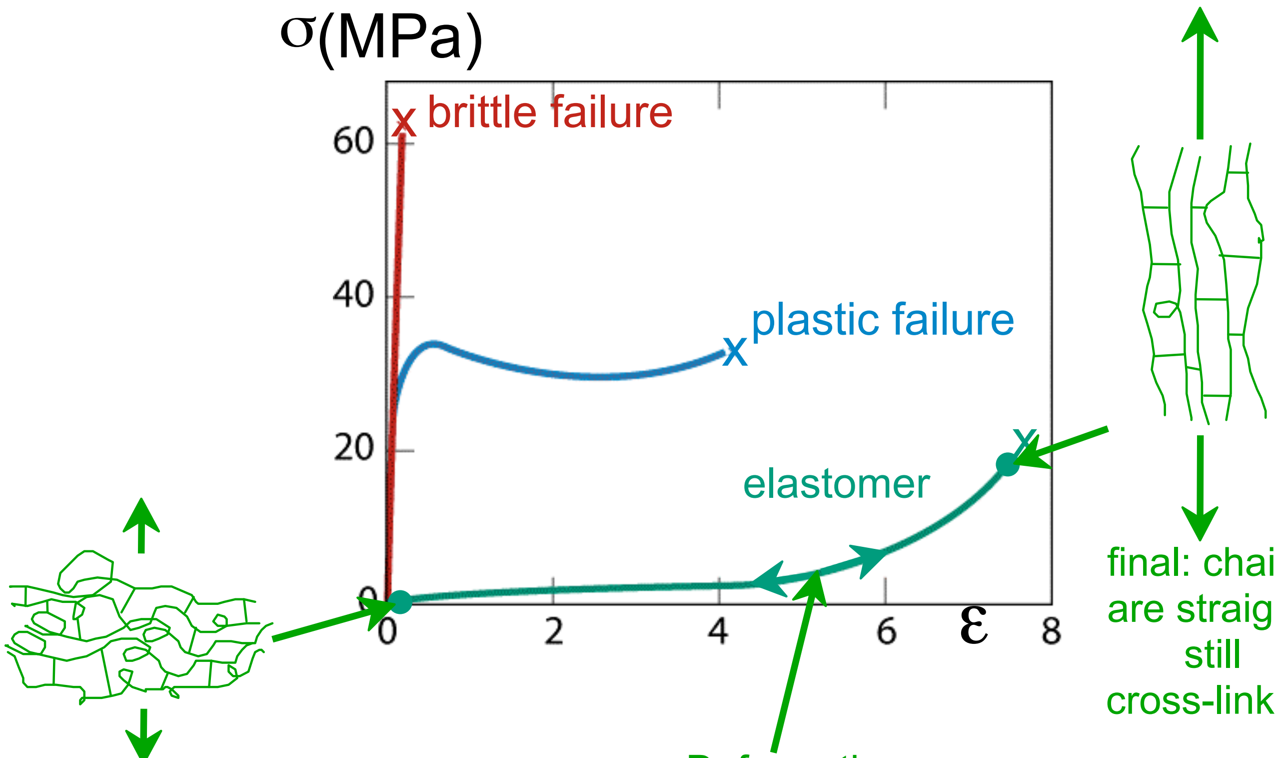
Strains – deformations > 1000% possible
(for metals, maximum strain ca. 10% or less)

Brittle and plastic behavior



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.)

Tensile response: elastomers



initial: amorphous chains are
kinked, cross-linked.

Deformation
is reversible!

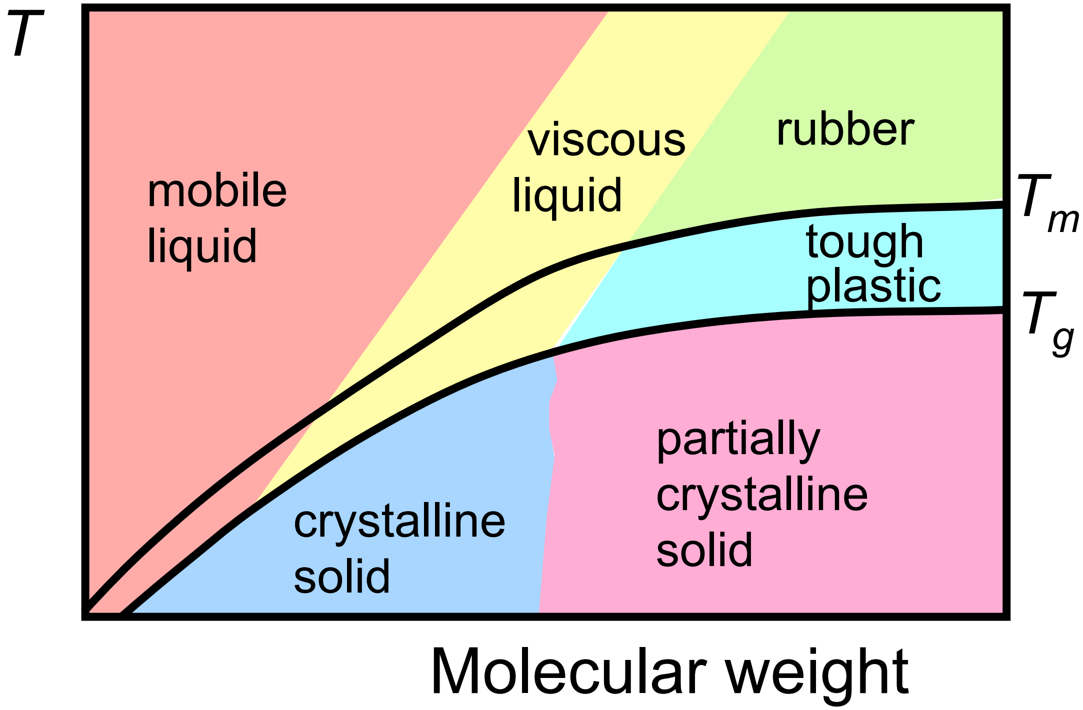
final: chains
are straight,
still
cross-linked

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)

Thermoplastic vs. thermosets

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

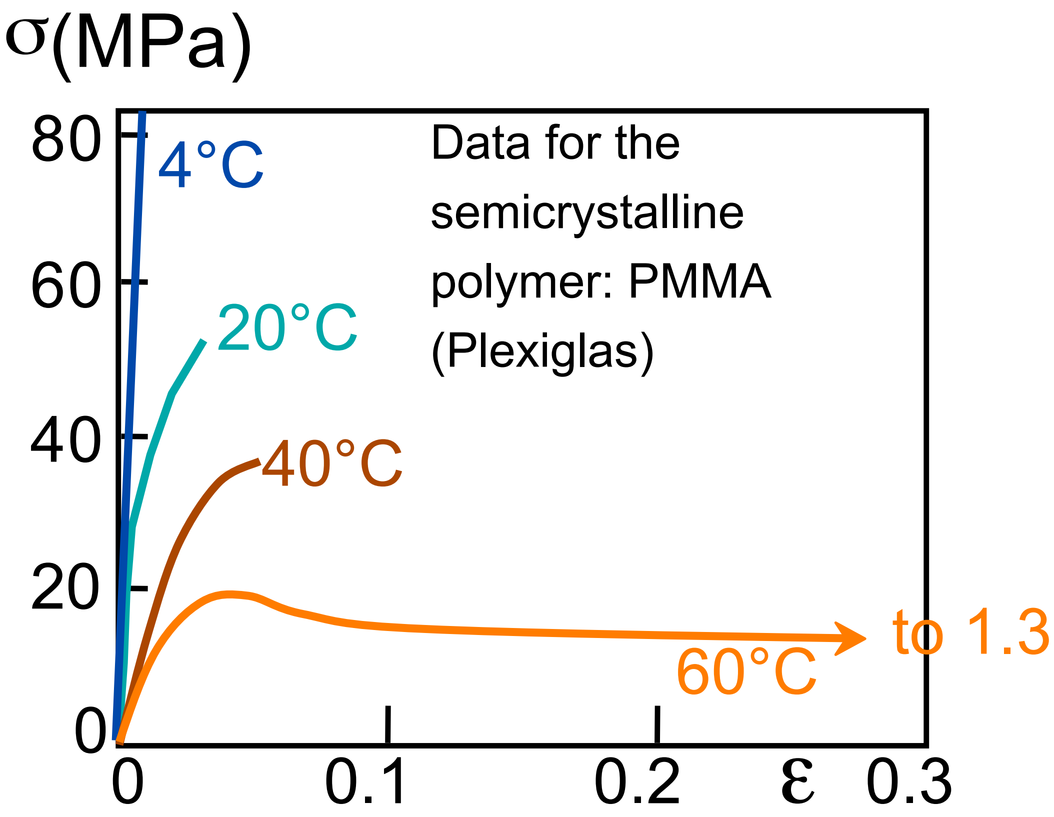


Adapted from Fig. 15.19, *Callister 7e*. (Fig. 15.19 is from F.W. Billmeyer, Jr., *Textbook of Polymer Science*, 3rd ed., John Wiley and Sons, Inc., 1984.)

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

Strain rates and T

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



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.)

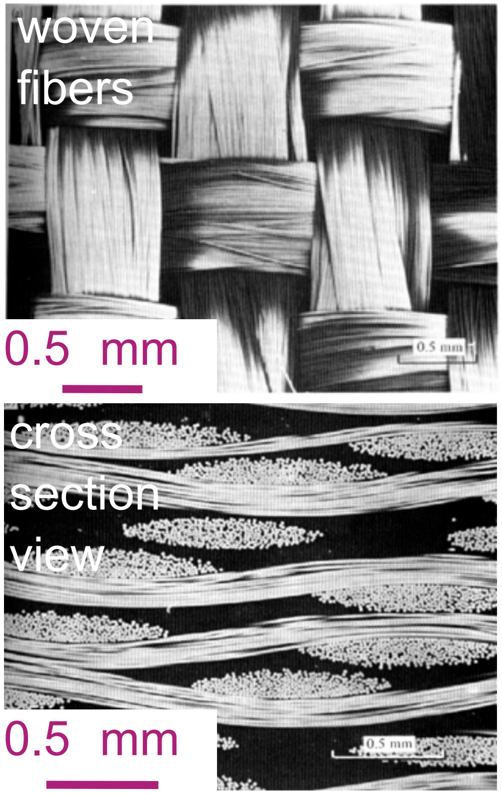
Composites

- Composites:
  -- Multiphase material w/significant proportions of each phase.

- Matrix:
  -- The continuous phase
  -- Purpose is to:
    - transfer stress to other phases
    - protect phases from environment
  -- Classification: MMC, CMC, PMC

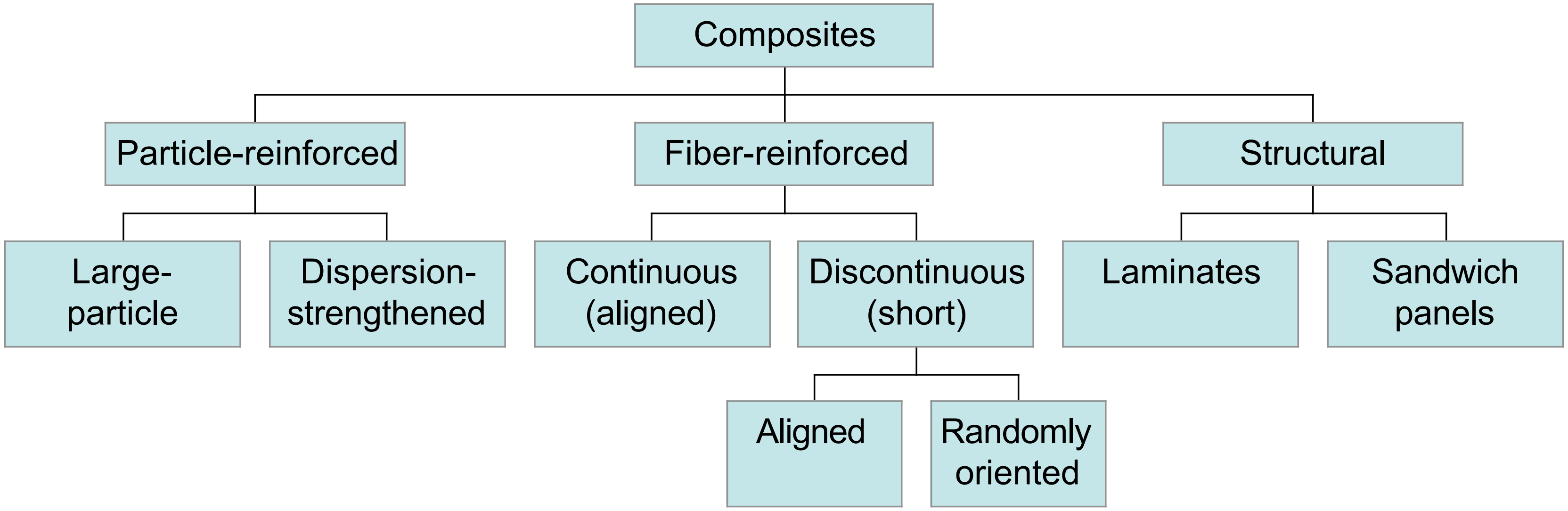
  metal ceramic polymer

- Dispersed phase:
  -- Purpose: enhance matrix properties.
    MMC: increase σ_y, *TS*, creep resist.
    CMC: increase *Kc*
    PMC: increase *E*, σ_y, *TS*, creep resist.
  -- Classification: Particle, fiber, structural



Reprinted with permission from D. Hull and T.W. Clyne, *An Introduction to Composite Materials*, 2nd ed., Cambridge University Press, New York, 1996, Fig. 3.6, p. 47.

Composite classifications



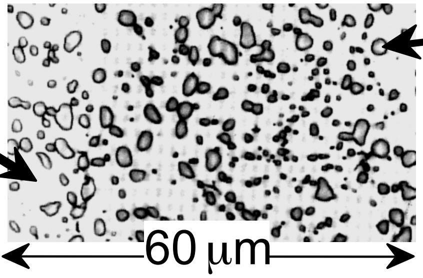
Adapted from Fig. 16.2, *Callister 7e*.

Composite classifications

Particle-reinforced Fiber-reinforced Structural

- Examples:
  - Spheroidite steel

matrix: ferrite (α) (ductile)

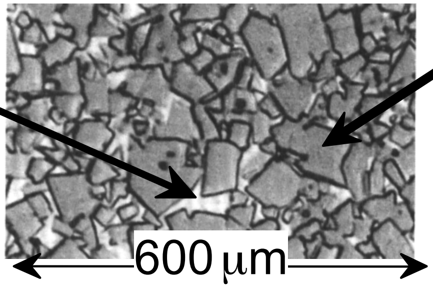


particles: cementite (Fe_3C) (brittle)

Adapted from Fig. 10.19, *Callister 7e*. (Fig. 10.19 is copyright United States Steel Corporation, 1971.)

- WC/Co cemented carbide

matrix: cobalt (ductile)
V_m:
10-15 vol%!

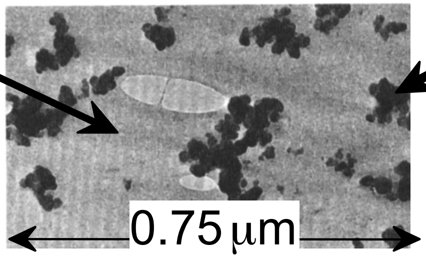


particles: WC (brittle, hard)

Adapted from Fig. 16.4, *Callister 7e*. (Fig. 16.4 is courtesy Carboloy Systems, Department, General Electric Company.)

- Automobile tires

matrix: rubber (compliant)



particles: C (stiffer)

Adapted from Fig. 16.5, *Callister 7e*. (Fig. 16.5 is courtesy Goodyear Tire and Rubber Company.)

Composite classifications

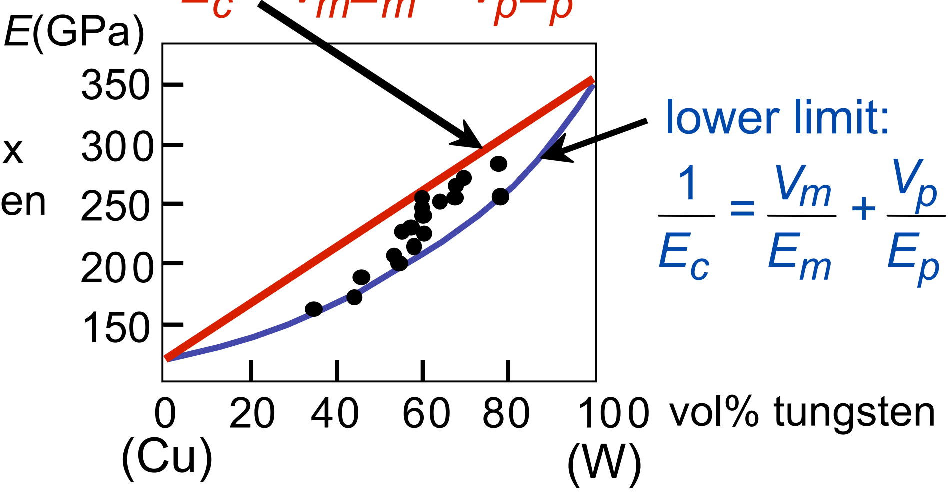
Particle-reinforced | Fiber-reinforced | Structural

- Elastic modulus, E_c, of composites:
  -- two approaches.

upper limit: “rule of mixtures”

$$E_c = V_m E_m + V_p E_p$$

Data:
Cu matrix
w/tungsten
particles



lower limit:

$$\frac{1}{E_c} = \frac{V_m}{E_m} + \frac{V_p}{E_p}$$

Adapted from Fig. 16.3, *Callister 7e*. (Fig. 16.3 is from R.H. Krock, *ASTM Proc*, Vol. 63, 1963.)

- Application to other properties:
  -- Electrical conductivity, σ_e: Replace E in equations with σ_e.
  -- Thermal conductivity, k: Replace E in equations with k.

Composite classifications

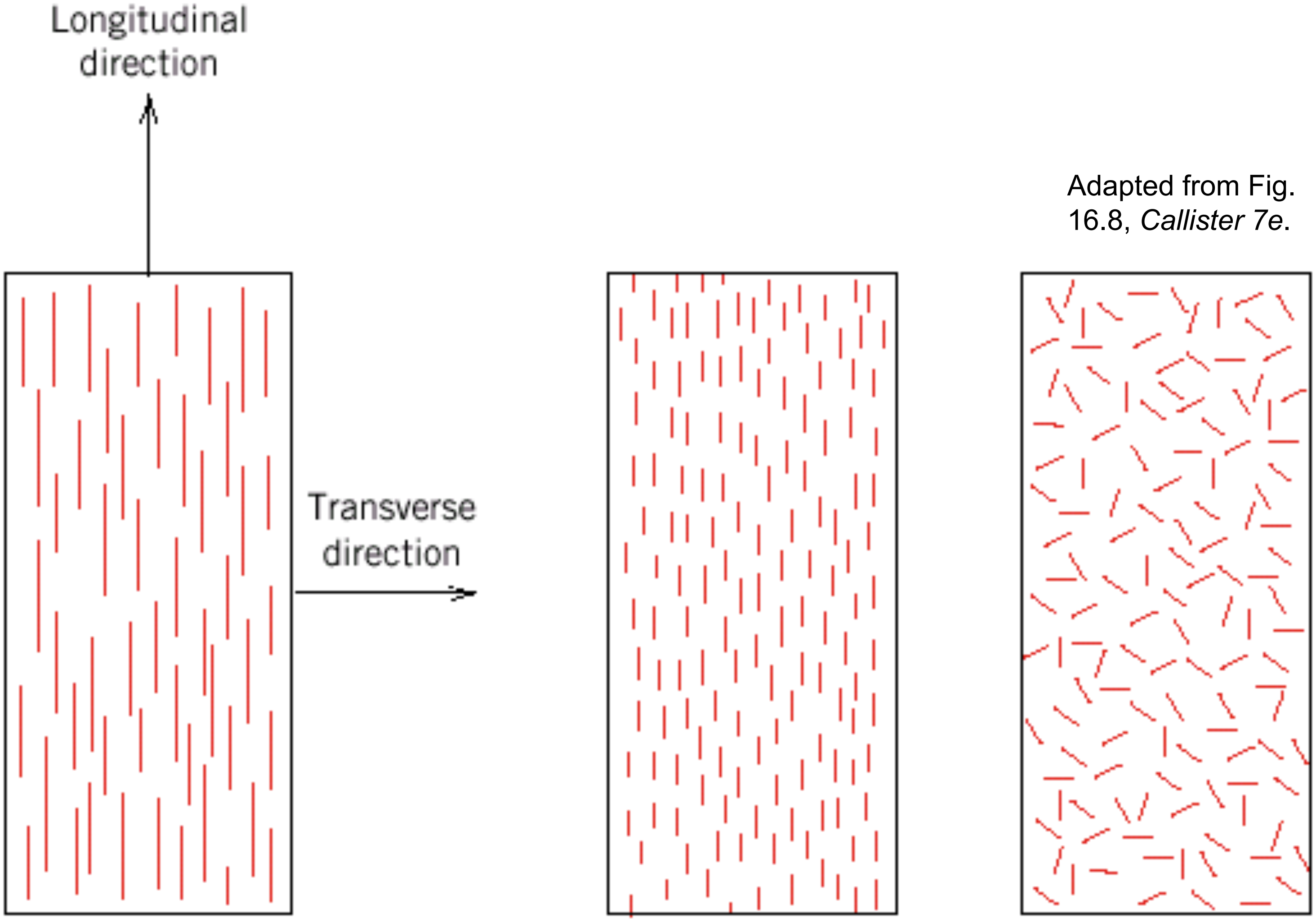
Particle-reinforced | **Fiber-reinforced** | Structural

Fiber Materials

- Whiskers - Thin single crystals - large length to diameter ratio
  graphite, SiN, SiC
  high crystal perfection – extremely strong, strongest known
  very expensive

- Fibers
  - polycrystalline or amorphous
  - generally polymers or ceramics
  - Ex: Al_2O_3 , Aramid, E-glass, Boron, UHMWPE
- Wires
  - Metal – steel, Mo, W

Fiber alignment



Adapted from Fig. 16.8, *Callister 7e*.

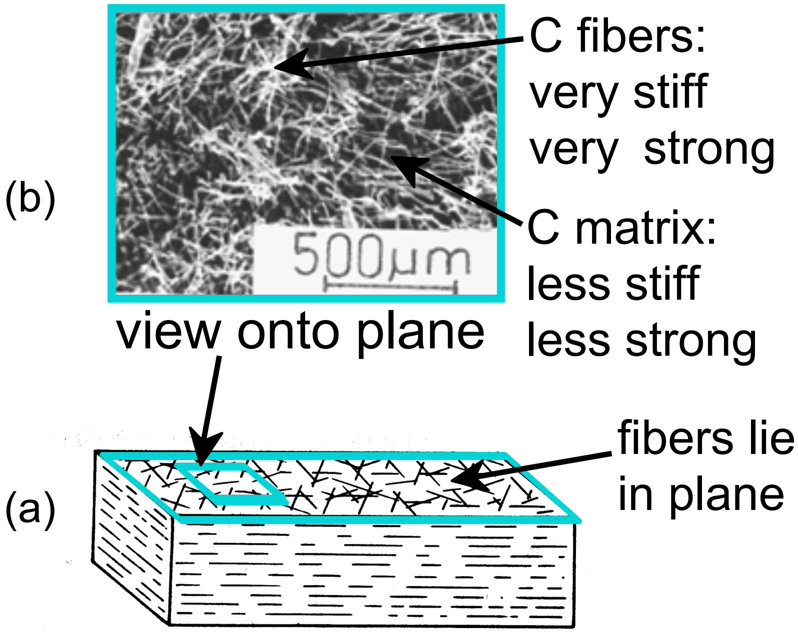
aligned
continuous

aligned
random
discontinuous

Fiber alignment

Particle-reinforced | Fiber-reinforced | Structural

- Discontinuous, random 2D fibers
- Example: Carbon-Carbon
  - -- process: fiber/pitch, then burn out at up to 2500ºC.
  - -- uses: disk brakes, gas turbine exhaust flaps, nose cones.



C fibers: very stiff very strong

C matrix: less stiff less strong

view onto plane

fibers lie in plane

- Other variations:
  - -- Discontinuous, random 3D
  - -- Discontinuous, 1D

Adapted from F.L. Matthews and R.L. Rawlings, *Composite Materials; Engineering and Science*, Reprint ed., CRC Press, Boca Raton, FL, 2000. (a) Fig. 4.24(a), p. 151; (b) Fig. 4.24(b) p. 151. (Courtesy I.J. Davies) Reproduced with permission of CRC Press, Boca Raton, FL.

Fiber alignment

Particle-reinforced

Fiber-reinforced

Structural

- Critical fiber length for effective stiffening & strengthening:

fiber strength in tension

fiber diameter

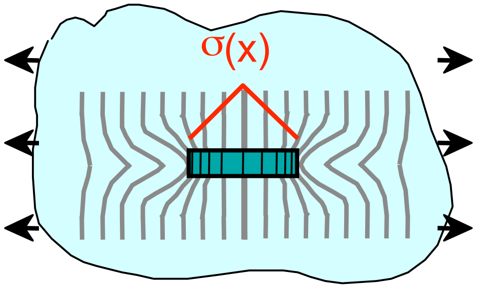
$$\text{fiber length} > 15\frac{\sigma_f d}{\tau_c}$$

shear strength of
fiber-matrix interface

- Ex: For fiberglass, fiber length > 15 mm needed

Shorter, thicker fiber:

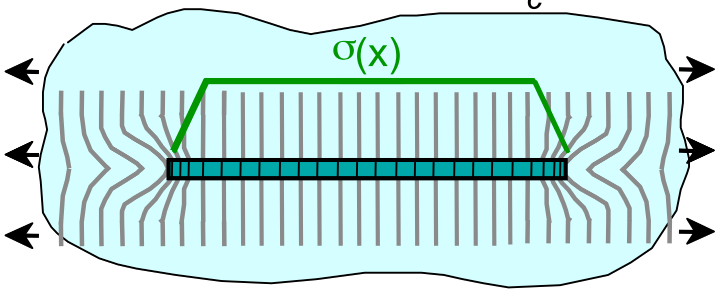
$$\text{fiber length} < 15\frac{\sigma_f d}{\tau_c}$$



Poorer fiber efficiency

Longer, thinner fiber:

$$\text{fiber length} > 15\frac{\sigma_f d}{\tau_c}$$



Better fiber efficiency

Adapted from Fig. 16.7, *Callister 7e*.

Fiber reinforcement

Particle-reinforced　**Fiber-reinforced**　Structural

- Estimate of E_c and *TS* for discontinuous fibers:

-- valid when $\text{fiber length} > 15\dfrac{\sigma_f d}{\tau_c}$

-- Elastic modulus in fiber direction:

$$E_c = E_m V_m + K E_f V_f$$

efficiency factor:

-- aligned 1D: $K = 1$ (aligned $||$)
-- aligned 1D: $K = 0$ (aligned $\perp$)
-- random 2D: $K = 3/8$ (2D isotropy)
-- random 3D: $K = 1/5$ (3D isotropy)

Values from Table 16.3, *Callister 7e*. (Source for Table 16.3 is H. Krenchel, *Fibre Reinforcement*, Copenhagen: Akademisk Forlag, 1964.)

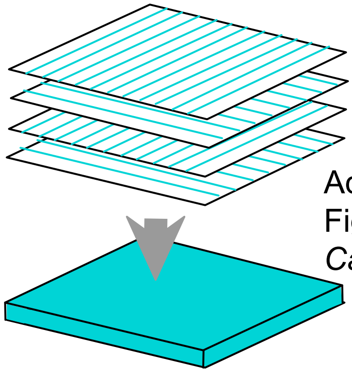
-- *TS* in fiber direction:

$$(TS)_c = (TS)_m V_m + (TS)_f V_f \qquad \text{(aligned 1D)}$$

Structural composites

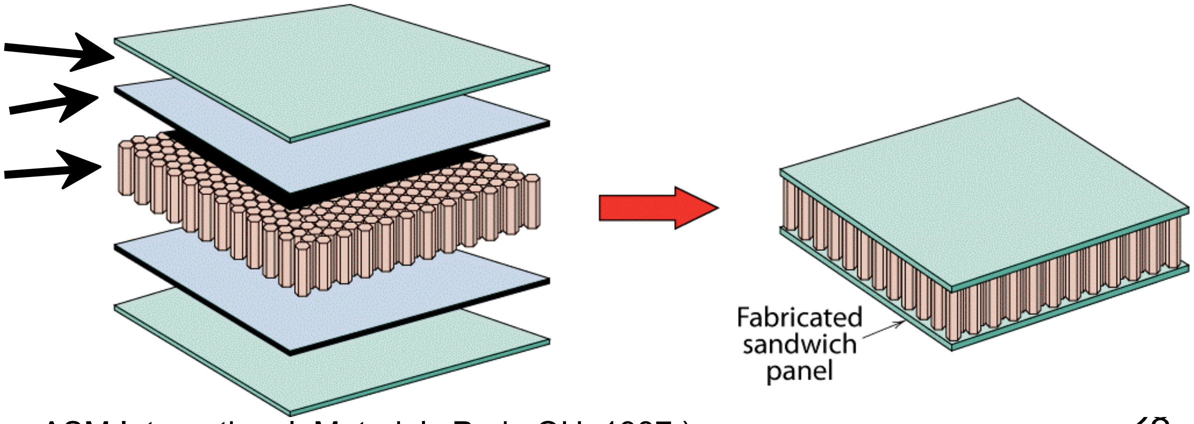
Particle-reinforced Fiber-reinforced **Structural**

- Stacked and bonded fiber-reinforced sheets
  - -- stacking sequence: e.g., 0º/90º
  - -- benefit: balanced, in-plane stiffness



Adapted from Fig. 16.16, *Callister 7e*.

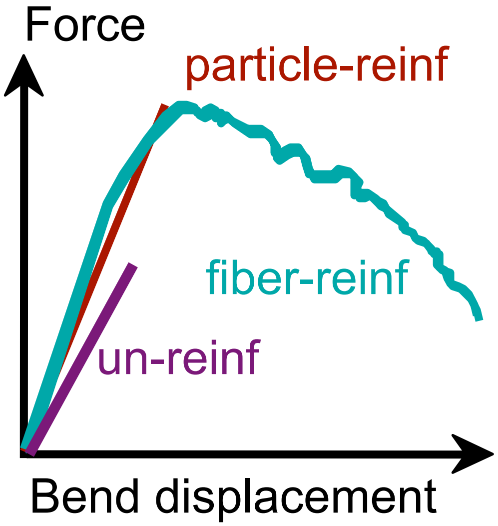
- Sandwich panels
  - -- low density, honeycomb core
  - -- benefit: small weight, large bending stiffness



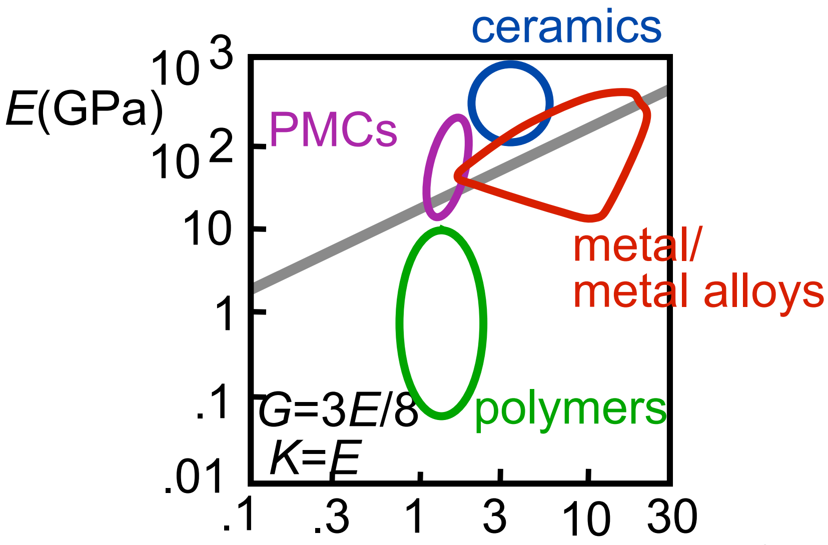
Adapted from Fig. 16.18, *Callister 7e*. (Fig. 16.18 is from *Engineered Materials Handbook*, Vol. 1, *Composites*, ASM International, Materials Park, OH, 1987.)

Composite benefits

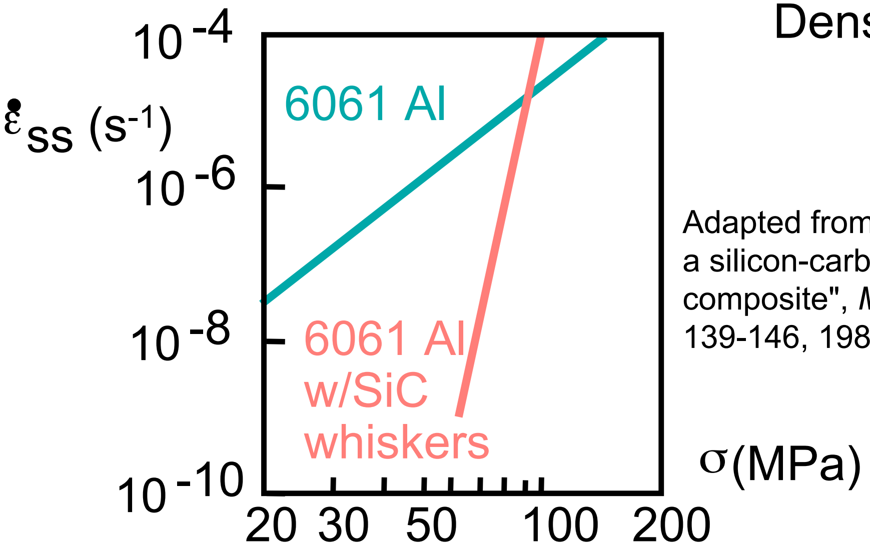
- CMCs: Increased toughness



- PMCs: Increased E/ρ



- MMCs:
  Increased creep resistance



Adapted from T.G. Nieh, "Creep rupture of a silicon-carbide reinforced aluminum composite", *Metall. Trans. A* Vol. 15(1), pp. 139-146, 1984. Used with permission.