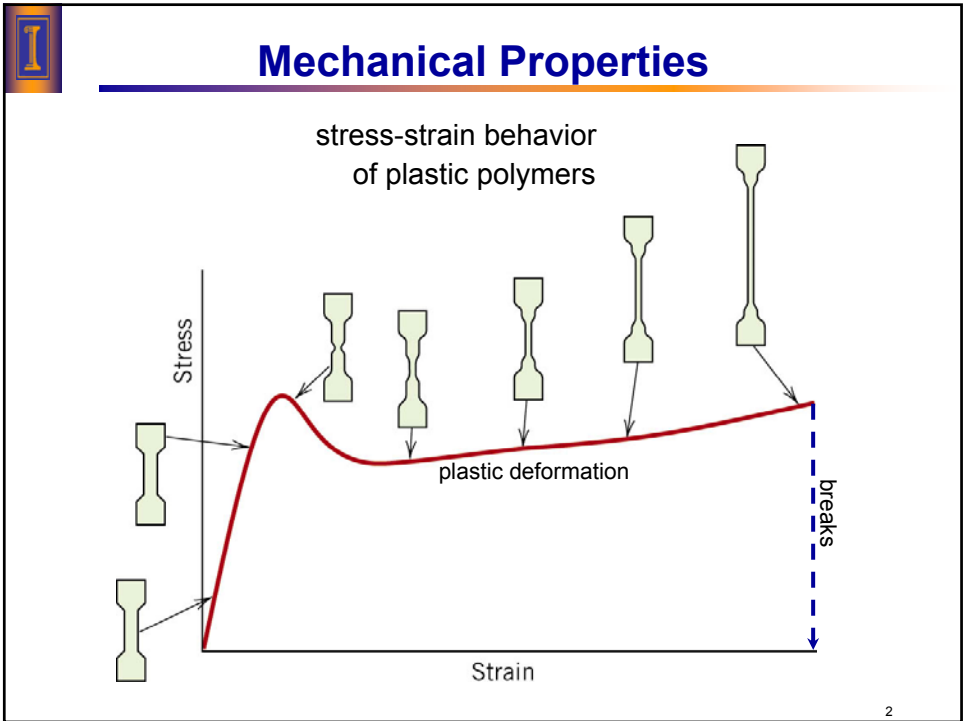


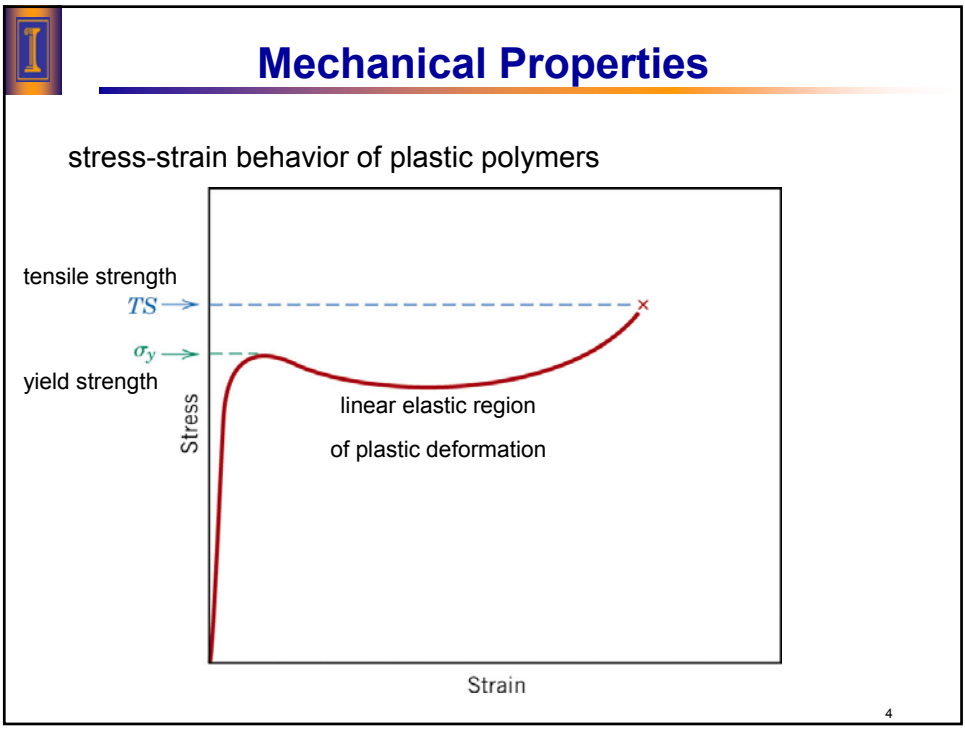
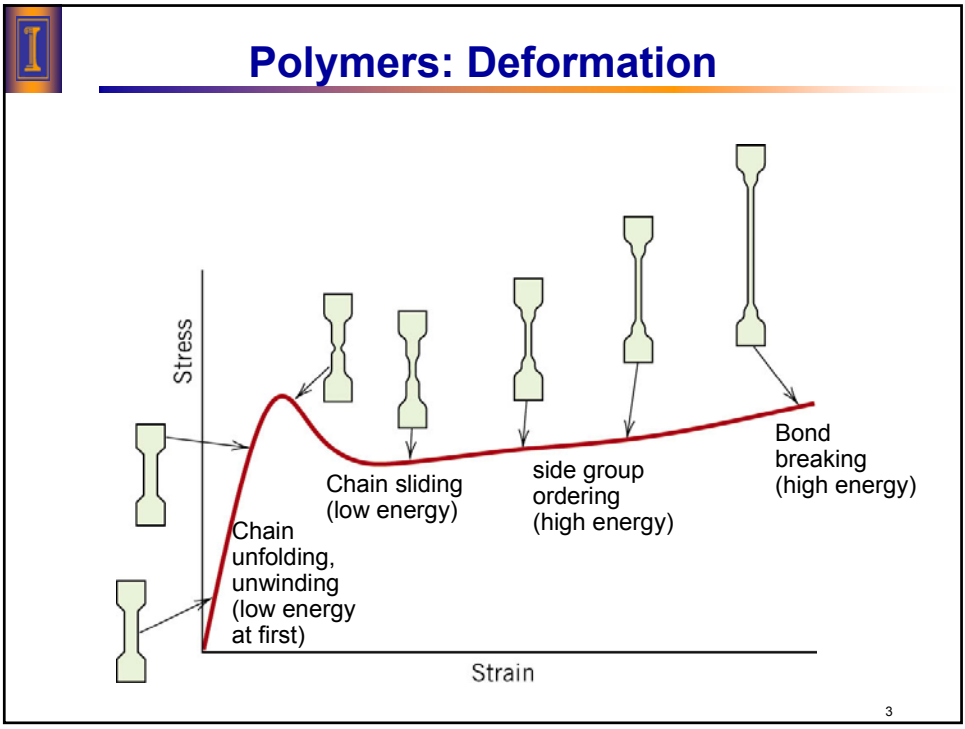
**Characteristics, Applications & Processing of Polymers**

**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?

1

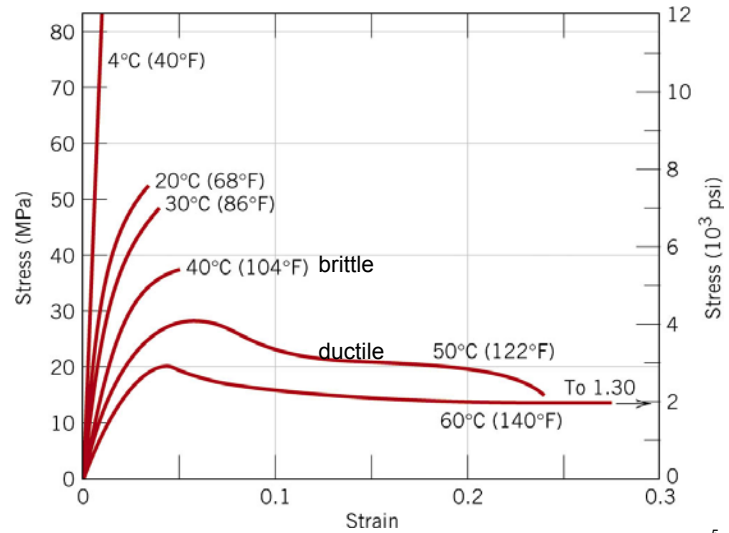






## Mechanical Properties

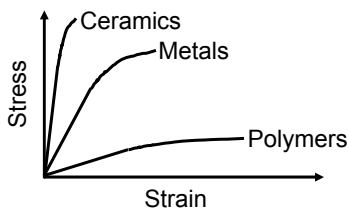
stress-strain behavior of polymethylmethacrylate



5

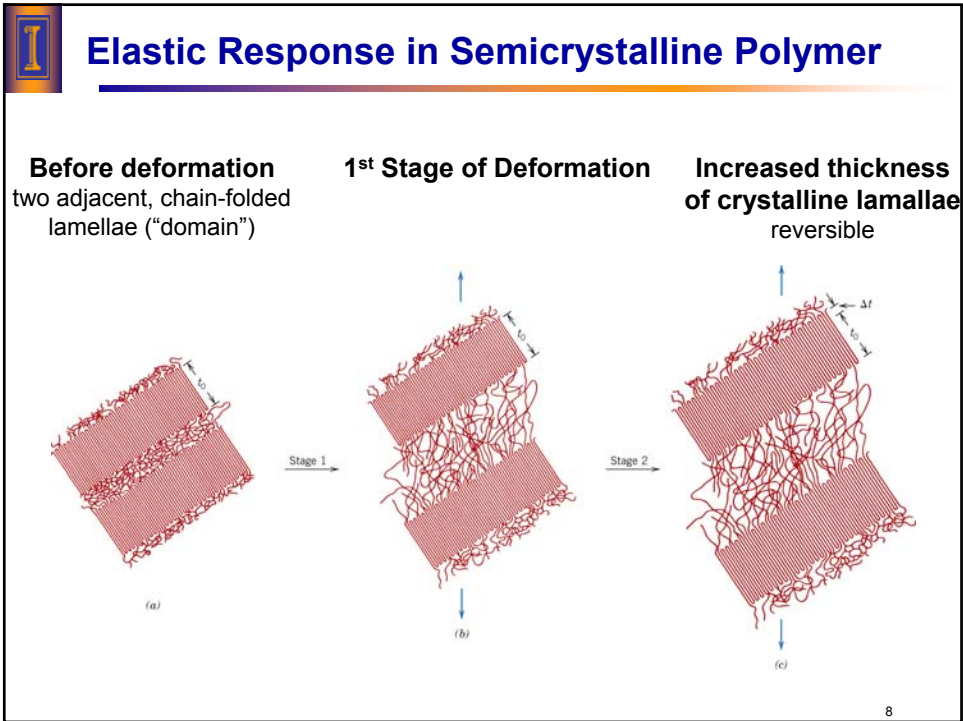
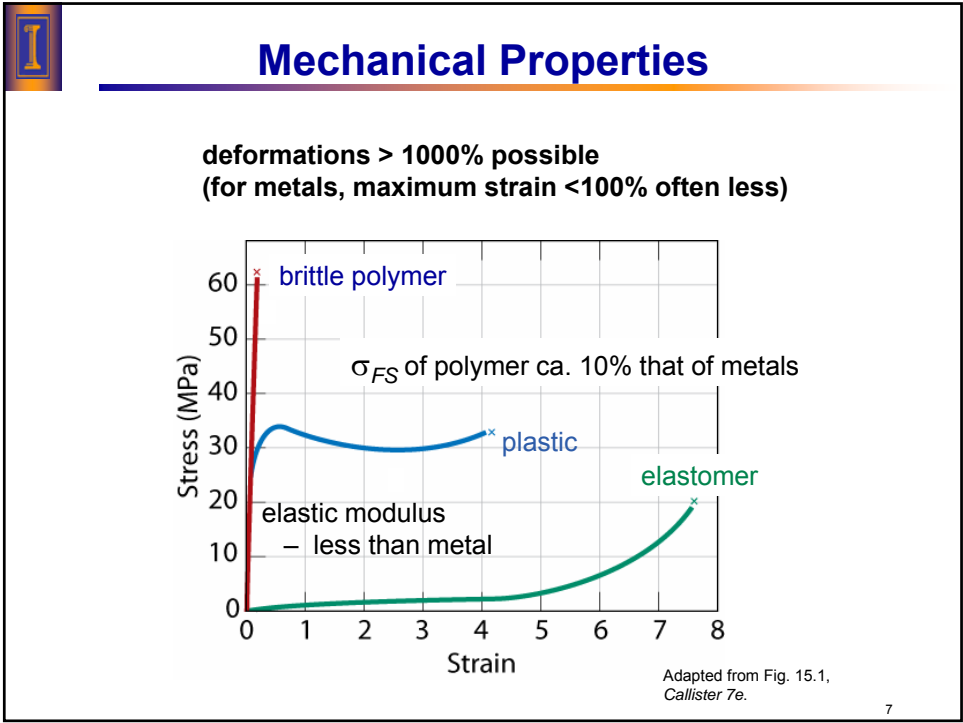


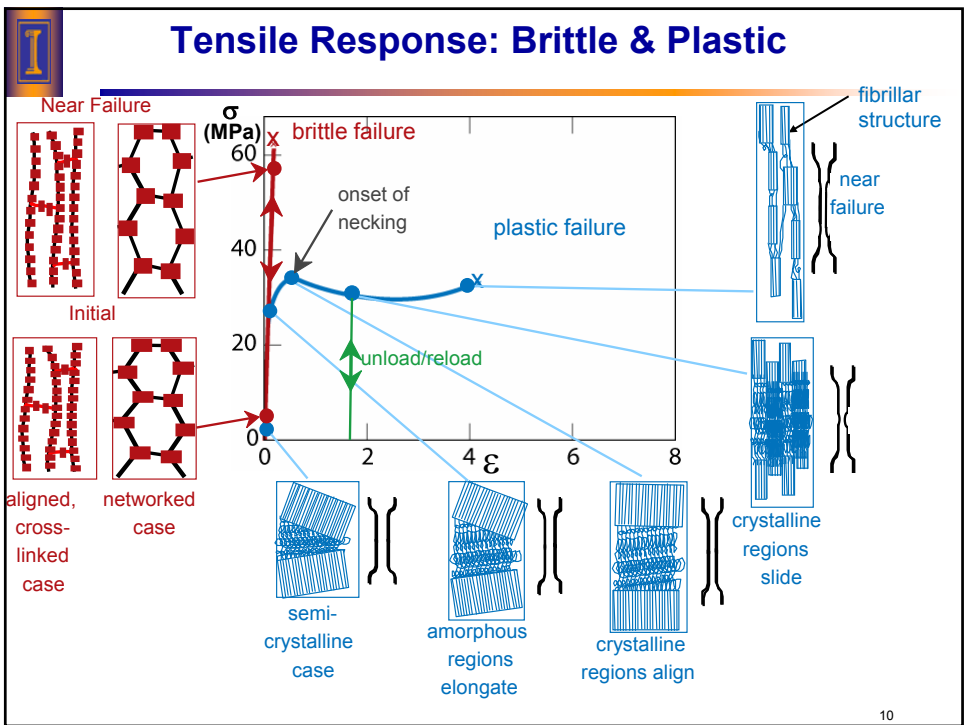
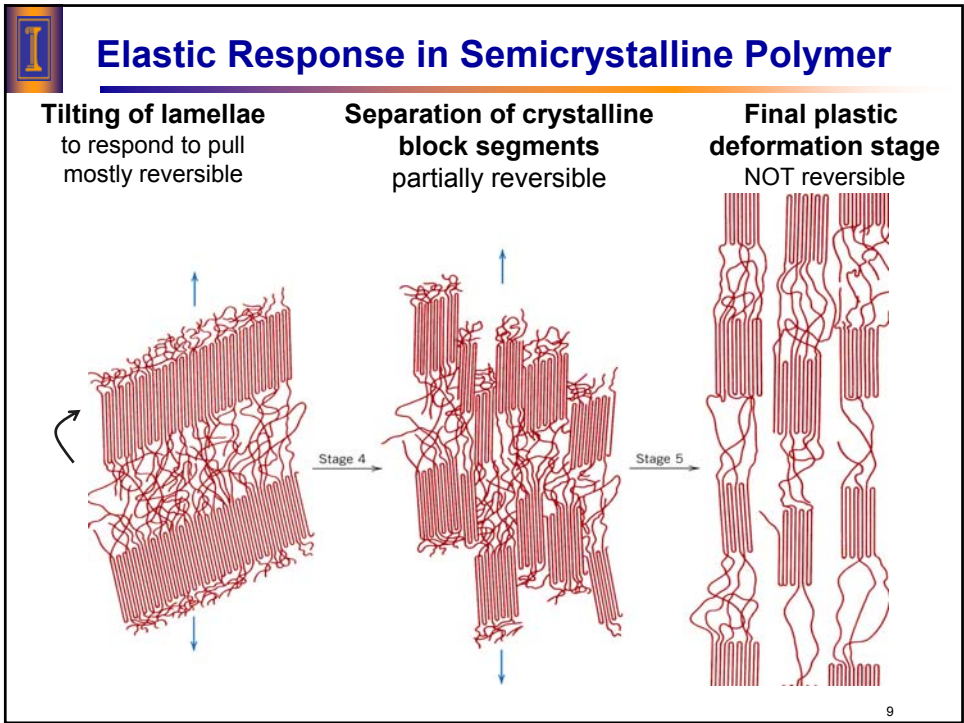
## Polymers: Deformation



- Lower elastic modulus, yield and ultimate properties
- Greater post-yield deformability
- Greater failure strain

6

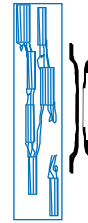






## Predeformation by Drawing

- **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.)

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## Polymers: Thermal Properties

- In the liquid/melt state enough thermal energy for random motion (Brownian motion) of chains
- Motions decrease as the melt is cooled
- Motion ceases at “glass transition temperature”
- Polymer hard and glassy below  $T_g$ , rubbery above  $T_g$

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## Polymers: Thermal Properties

### Below $T_g$ :

Polymer chains “frozen” into place, only bond stretching possible.

Polymer is “glassy”: stiff, strong and brittle

### Above $T_g$ :

Polymer chains free to move around and change shape

→ Elastomers: chain motion restricted by cross-linking

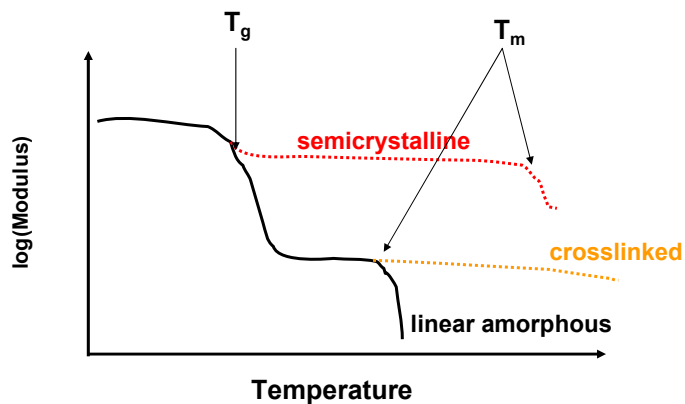
→ Semi-crystalline polymers: amorphous sections pinned by crystalline regions

→ Amorphous polymers: slight restriction on chain motion provided by entanglements, but resistance to deformation drops rapidly with temperature, until material flows → Amorphous polymers generally used below  $T_g$

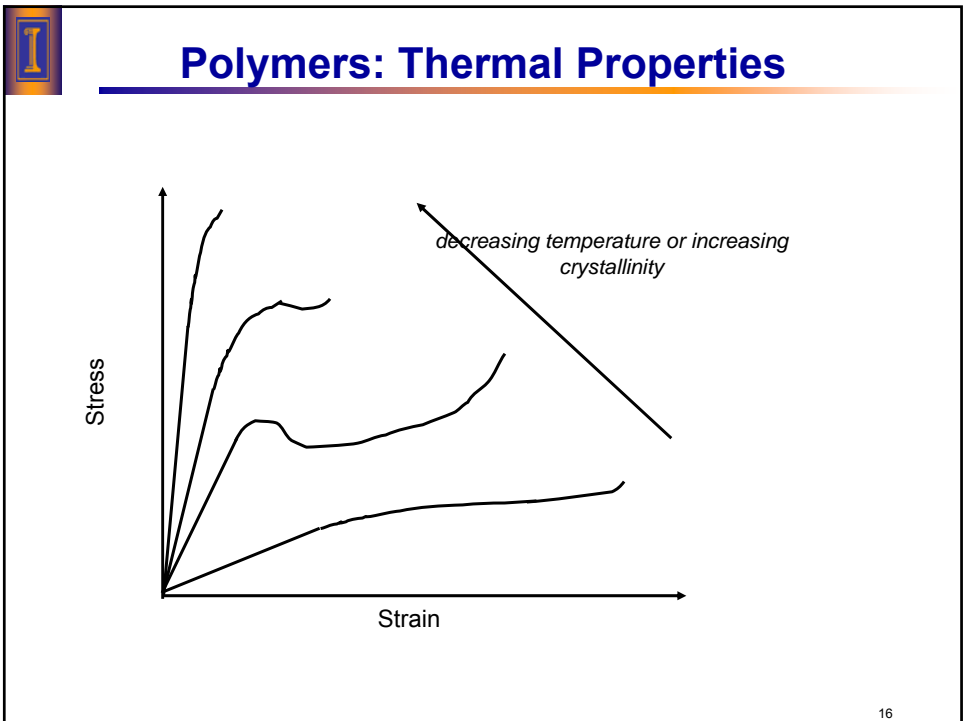
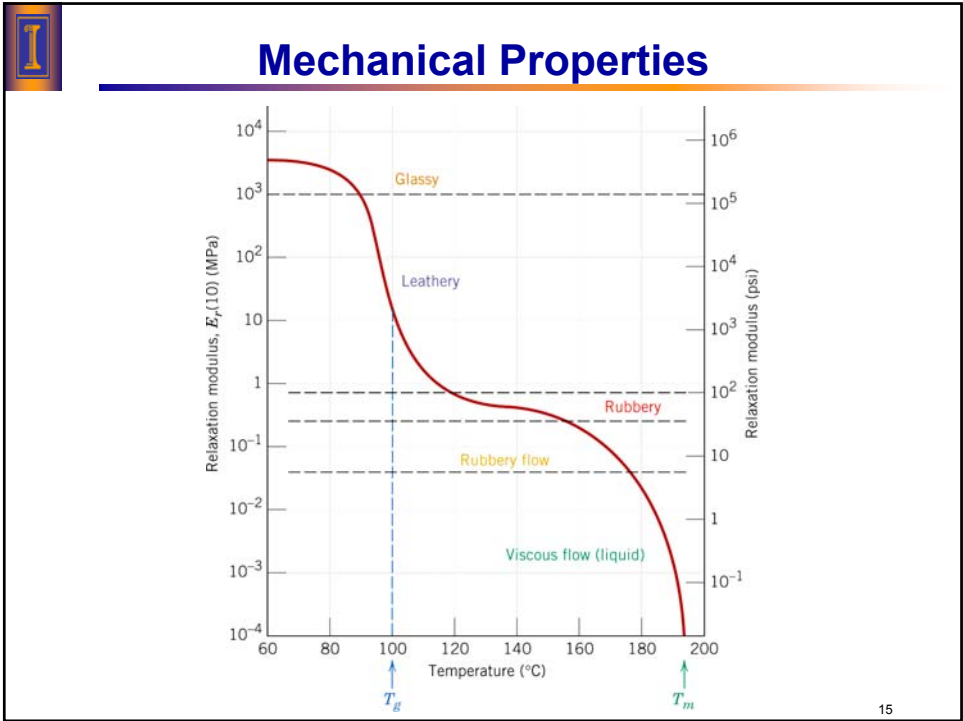
13



## Polymers: Thermal Properties



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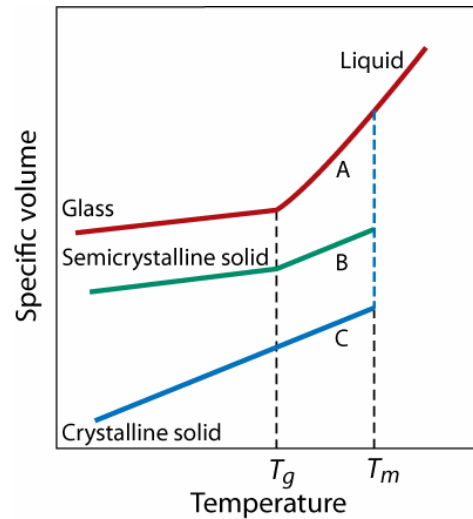




## Melting vs. Glass Transition Temp.

What factors affect  $T_m$  and  $T_g$ ?

- Both  $T_m$  and  $T_g$  increase with increasing chain stiffness
- Chain stiffness increased by
  - Bulky sidegroups
  - Polar groups or sidegroups
  - Double bonds or aromatic chain groups
- Regularity – effects  $T_m$  only

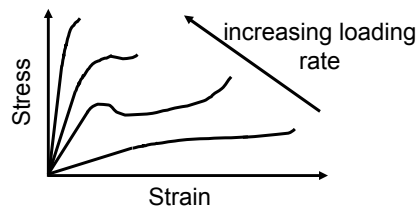


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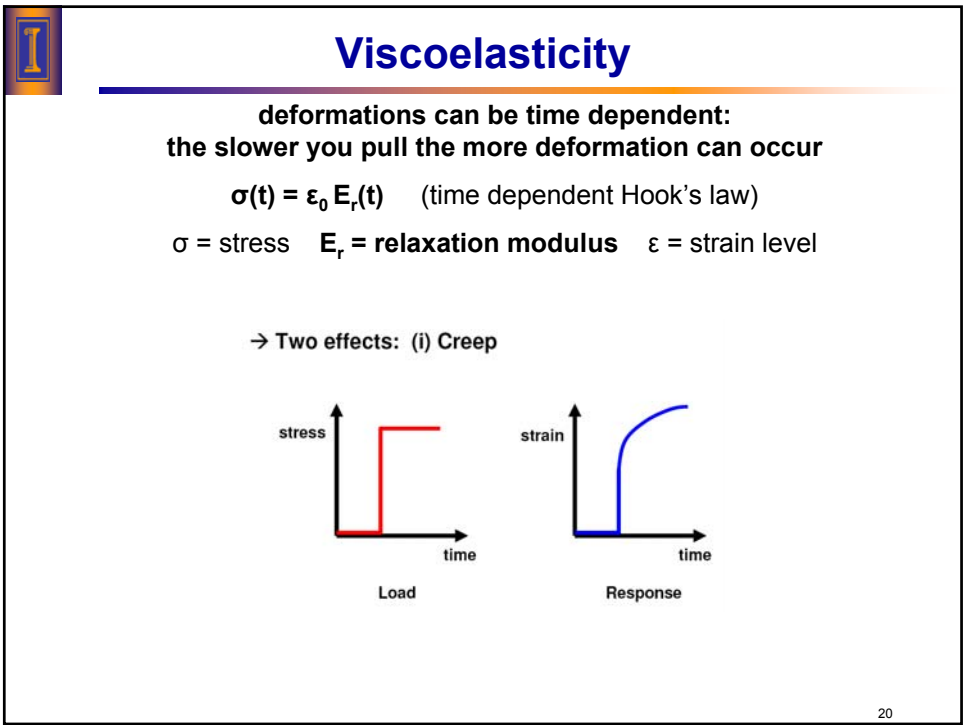
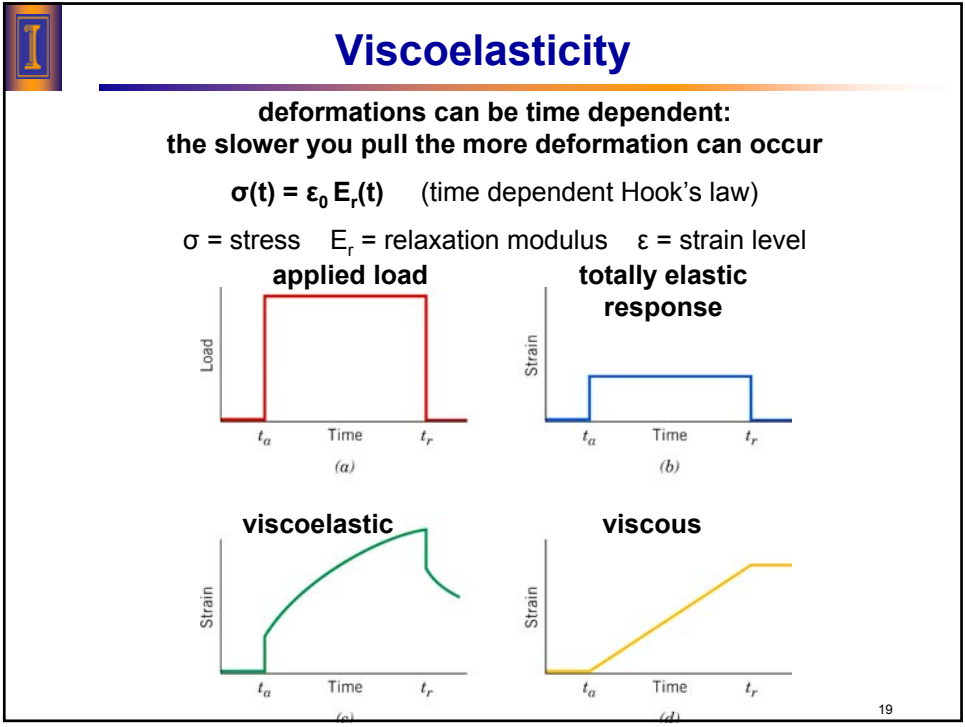


## Polymers: Viscoelasticity

- **Viscoelasticity: Time-dependent stress-strain relationship**
- **Dependency of stress-strain behavior on time and loading rate**
- **Due to mobility of chains wrt each other**
- **Crosslinking may affect viscoelastic response**



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## Viscoelasticity

**deformations can be time dependent:  
the slower you pull the more deformation can occur**

$\sigma(t) = \epsilon_0 E_r(t)$  (time dependent Hook's law)

$\sigma$  = stress    $E_r$  = relaxation modulus    $\epsilon$  = strain level

→ Two effects: (ii) Stress relaxation

strain

time

Load

stress

time

Response

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## Viscoelasticity

**deformations can be time dependent:  
the slower you pull the more deformation can occur**

$\sigma(t) = \epsilon_0 E_r(t)$  (time dependent Hook's law)

$\sigma$  = stress    $E_r$  = relaxation modulus    $\epsilon$  = strain level

Viscoelastic materials can be considered as composite materials:

Viscous component (amorphous areas) + elastic component (crystalline areas)

→ model using a Maxwell element:

spring
dashpot

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## Time Dependent Deformation

- Stress relaxation test:**
  - strain to  $\epsilon_0$  and hold.
  - observe decrease in stress with time.

tensile test

Data: Large drop in  $E_r$  for  $T > T_g$  (amorphous polystyrene)

- Relaxation modulus:**

$$E_r(t) = \frac{\sigma(t)}{\epsilon_0}$$
- Sample  $T_g$  (°C) values:**

PE (low density)	- 110	
PE (high density)	- 90	
PVC	+ 87	Selected values from Table 15.2, Callister 7e.
PS	+100	
PC	+150	

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## Polymer Fracture

**Crazing**  $\cong$  Griffith cracks in metals

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

aligned chains

fibrillar bridges

microvoids

crack

0.5  $\mu$ m

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## Polymer Additives

Improve mechanical properties, processability, durability, etc.

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

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## 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**
  - Br/Cl/F & Borates

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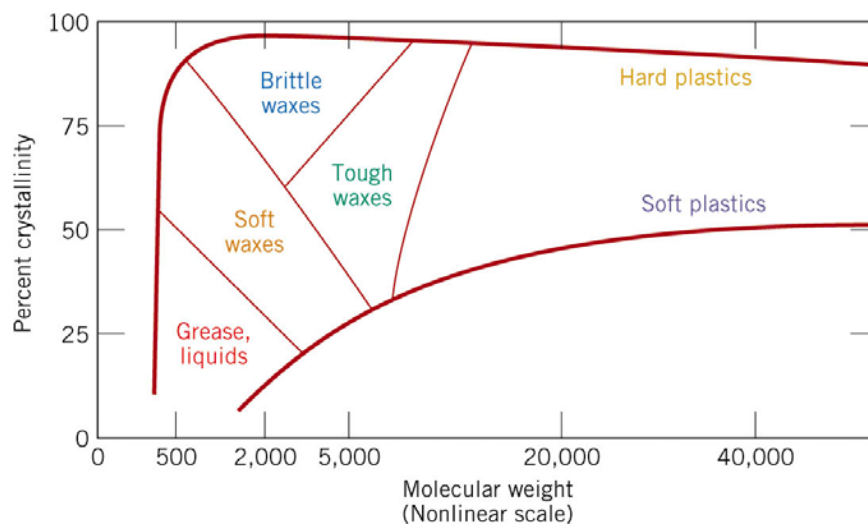
## Processing of Plastics

- **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

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## Crystallinity of Thermoplastics



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## Thermoplastics

- **Thermoplastics:**
  - little crosslinking
  - ductile
  - soften w/ heating

polyethylene  
polypropylene  
polycarbonate  
polystyrene

$T_g \sim 0.5 \text{ to } 0.8 T_m$

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## Thermosets

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

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## 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. )

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## Processing Plastics - Molding

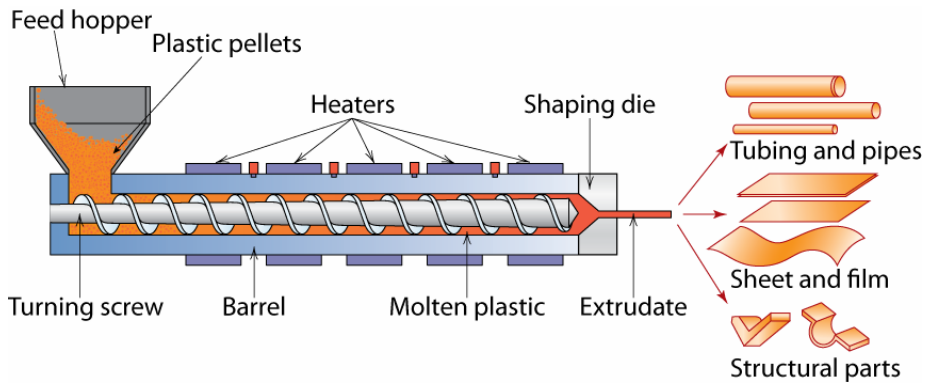
- **Injection molding**

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. )

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## Processing Plastics – Extrusion



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

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## Polymer Types: Elastomers

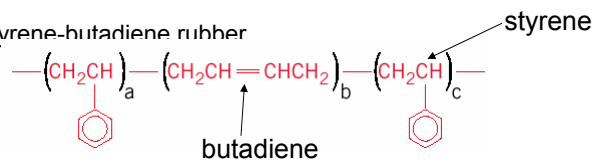
Elastomers – rubber

- Crosslinked materials

Natural rubber

Synthetic rubber and thermoplastic elastomers

SBR- styrene-butadiene rubber



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## Polymer Types: Elastomers

(a) (b)

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## Tensile Response: Elastomer Case

initial: amorphous chains are kinked, cross-linked. Deformation is reversible! final: chains are straight, still cross-linked

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

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## 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
    - rayon – dissolved in solvent then pumped through die head to make fibers
  - the fibers are drawn
  - leads to highly aligned chains- fibrillar structure

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## Polymer Types

- **Coatings** – thin film on surface – i.e. paint, varnish

To protect item

Improve appearance

Electrical insulation

- **Adhesives** – produce bond between two adherands

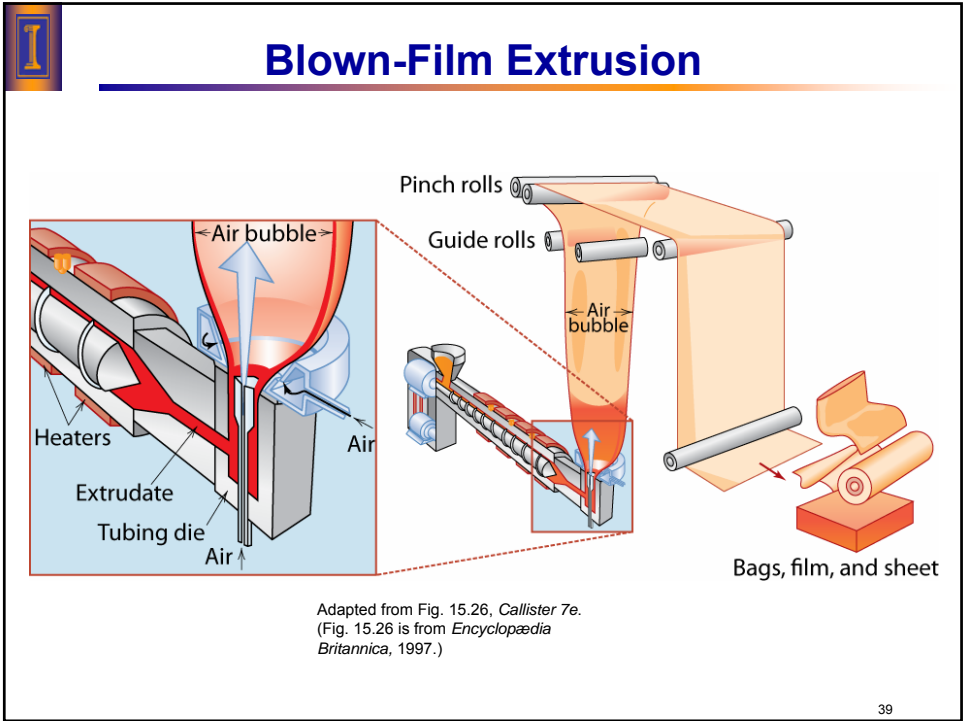
Usually bonded by:

Secondary bonds

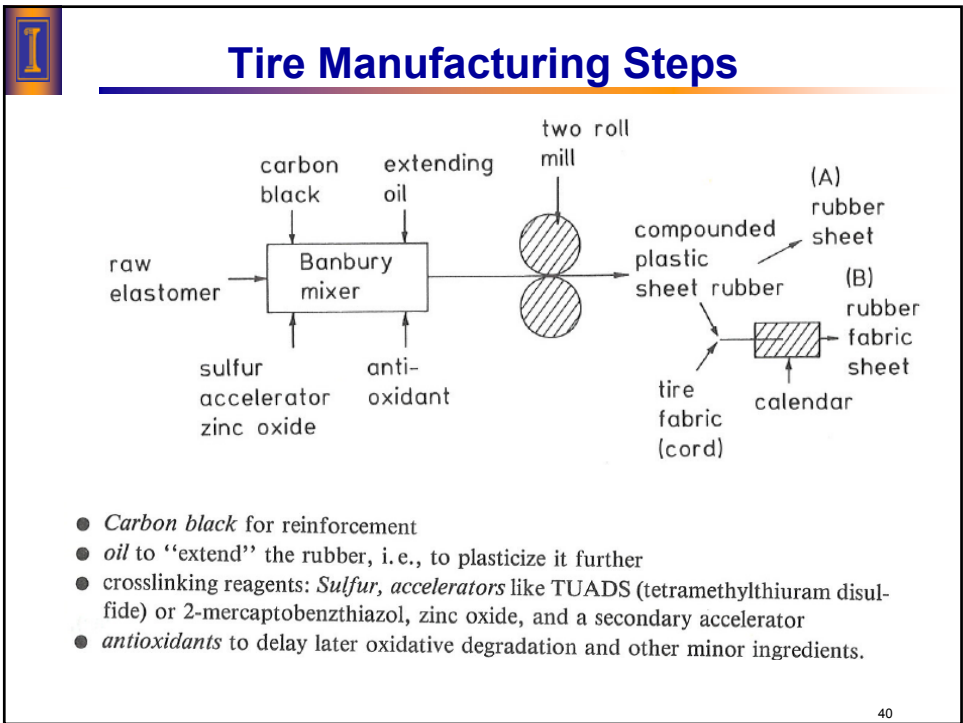
Mechanical bonding

- **Films** – blown film extrusion
- **Foams** – gas bubbles in plastic

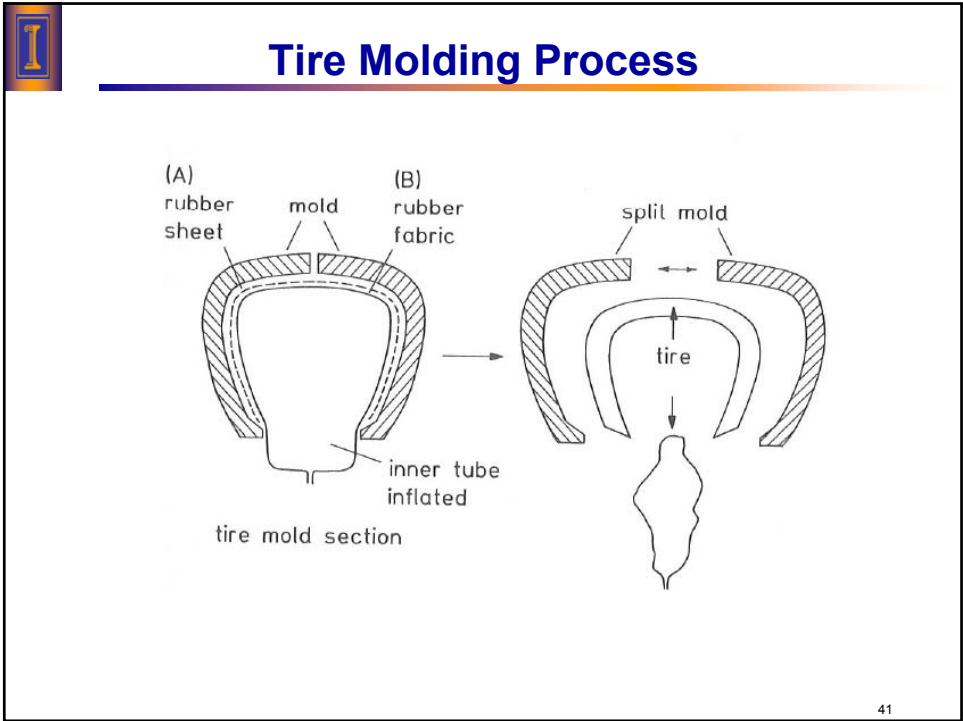
38



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## Advanced Polymers

- Ultrahigh molecular weight polyethylene (UHMWPE)
  - Molecular weight  $\sim 4 \times 10^6$  g/mol
  - Excellent properties for variety of appl.
    - bullet-proof vests
    - golf ball covers
    - hip joints

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## **Polymers: Biomedical Applications**

- **Polyethylene (PE)**
  - five density grades: ultrahigh, high, low, linear low and very low density
  - UHMWPE and HDPE more crystalline
  - UHMWPE has better mechanical properties, stability and lower cost
  - UHMWPE can be sterilized
- **UHMWPE: acetabular caps in hip implants and patellar surface of knee joints**
- **HDPE used as pharmaceutical bottles, fabrics**
- **Others used as bags, pouches, tubes etc.**

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## **Polymers: Biomedical Applications**

- **Polymethylmethacrylate (PMMA, lucite, acrylic, plexiglas)**
  - transparent
  - tough
  - biocompatible
- **Used in dental restorations, membrane for dialysis, ocular lenses, contact lenses, bone cements**

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## **Polymers: Biomedical Applications**

- **Polyamides (PA, nylon)**
  - high degree of crystallinity
  - interchain hydrogen bonds provide superior mechanical strength  
(Kevlar fibers stronger than metals)
  - plasticized by water, not good in physiological environment
- **Used as sutures**

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## **Polymers: Biomedical Applications**

- **Polyvinylchloride (PVC)**
  - amorphous, hard and brittle due to Cl side chains
  - additives prevent thermal degradation
- **Used as blood and solution bags, packaging, IV sets, dialysis devices, catheter, bottles, cannulae**

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## **Polymers: Biomedical Applications**

- **Polypropylene (PP)**
  - properties similar to HDPE
  - good fatigue resistance
- **Used as syringes, oxygenator membranes, sutures, fabrics, vascular grafts**
  
- **Polyesters (PE)**
  - hydrophobic (beverage container PET)
  - molded into complex shapes
- **Used as vascular grafts, sutures, heart valves, catheter housings**

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## **Polymers: Biomedical Applications**

- **Polytetrafluoroethylene (PTFE, teflon)**
  - low coefficient of friction (low interfacial forces between its surface and another material)
  - very low surface energy
  - high crystallinity
  - low modulus and strength
  - difficult to process
- **catheters, artificial vascular grafts**

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## **Polymers: Biomedical Applications**

- **Rubbers**
  - latex, silicone
  - good biocompatibility
- **Used as maxillofacial prosthetics (Happy Halloween)**

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## **Polymers: Biomedical Applications**

- **Polyurethanes**
  - block copolymer structure
  - good mechanical properties
  - good biocompatibility
- **tubing, vascular grafts, pacemaker lead insulation, heart assist balloon pumps**

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## Summary

- General drawbacks to polymers:  
 $E$ ,  $\sigma_y$ , TS,  $T_{ap}$  are generally small.  
Deformation is often  $T$  and time dependent.  
Result: polymers benefit from composite reinforcement.
- **Thermoplastics** (PE, PS, PP, PC):  
Smaller  $E$ ,  $\sigma_y$ ,  $T_{ap}$   
small TS, but not brittle  
Easier to form and recycle
- **Elastomers** (rubber):  
Large reversible strains!
- **Thermosets** (epoxies, polyesters):  
Larger  $E$ ,  $\sigma_y$ ,  $T_{ap}$   
larger TS (but brittle)

$E$  relaxation modulus  
 $\sigma_y$  yield strength  
TS tensile strength  
 $T_{ap}$  Temp limit of an application