Chap. 15: Characteristics & Applications 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?

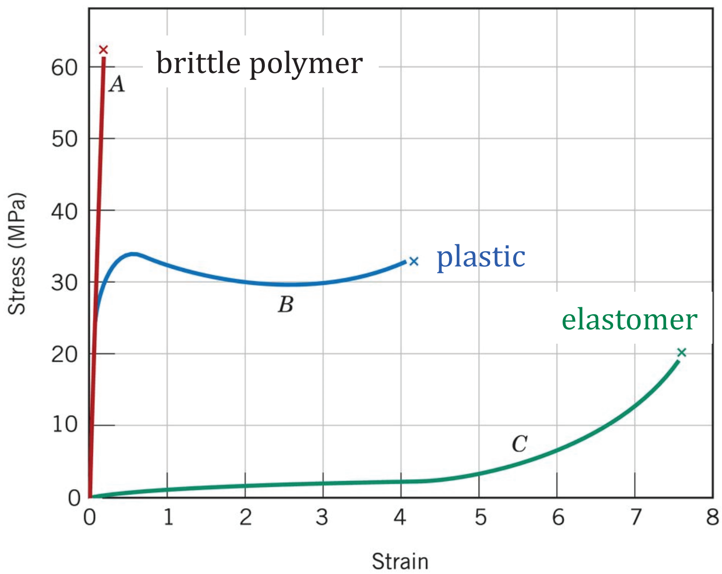
(a)

(b)

Billiard balls made of phenol-formaldehyde (Bakelite).

15.2 Stress-Strain Behavior of Polymers

- **The mechanical characteristics of polymers are highly sensitive to the rate of deformation (strain rate), the temperature, and the chemical nature of the environment (the presence of water, oxygen, organic solvents, etc.).**



- Elastic moduli of polymers: less than for metals
- Fracture strengths of polymers: about 10% of those for metals
- Deformation strains for polymers > 1000% (for most metals, deformation strains < 10%)

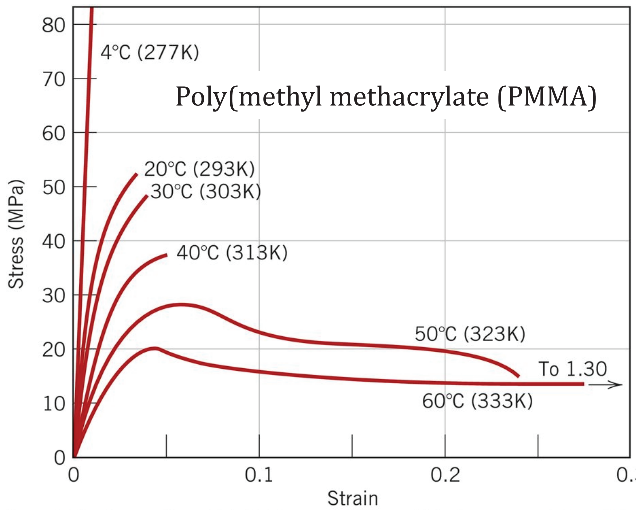
Adapted from Fig. 15.1, *Callister & Rethwisch 9e.*

Influence of T and Strain Rate on Thermoplastics

- **The mechanical characteristics of polymers are much more sensitive to temperature changes near room temperature.**

- **Increasing temperature produces**
  - (1) a decrease in elastic modulus
  - (2) a reduction in tensile strength
  - (3) an enhancement of ductility

- **Decreasing the strain rate has the same influence on the stress-strain characteristics as increasing the temperature.**



From T. S. Carswell and H. K. Nason, "Effect of Environmental Conditions on the Mechanical Properties of Organic Plastics," Symposium on Plastics, American Society for Testing and Materials, Philadelphia, 1944. Copyright, ASTM, 1916 Race Street, Philadelphia, PA 19103. Reprinted with permission.

Fig. 15.3, *Callister & Rethwisch 9e.*

15.3 Macroscopic Deformation

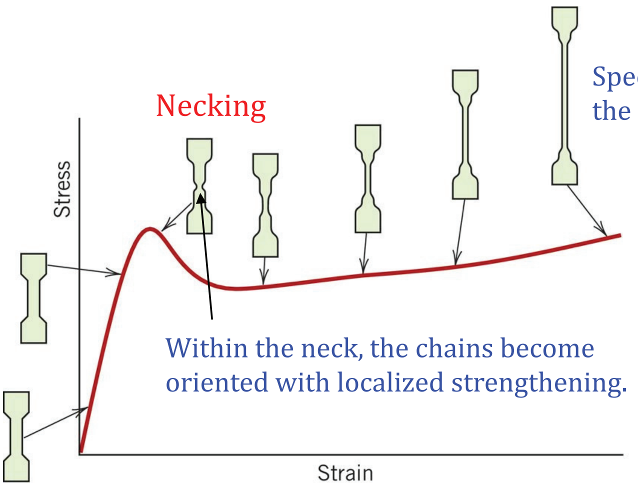


Fig. 15.4. Schematic tensile stress-strain curve for a semicrystalline polymer, *Callister & Rethwisch 9e.*

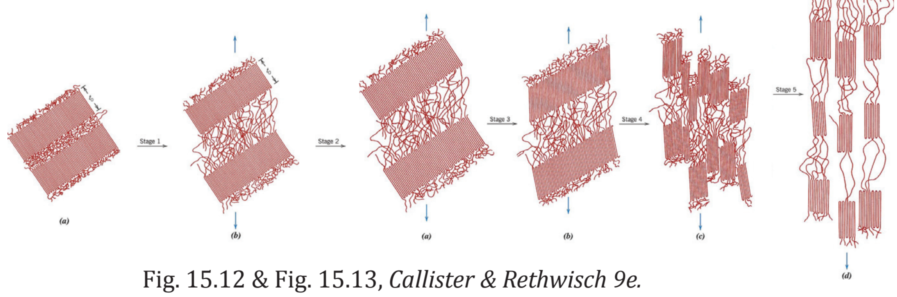


Fig. 15.12 & Fig. 15.13, *Callister & Rethwisch 9e.*

15.4 Viscoelastic Deformation

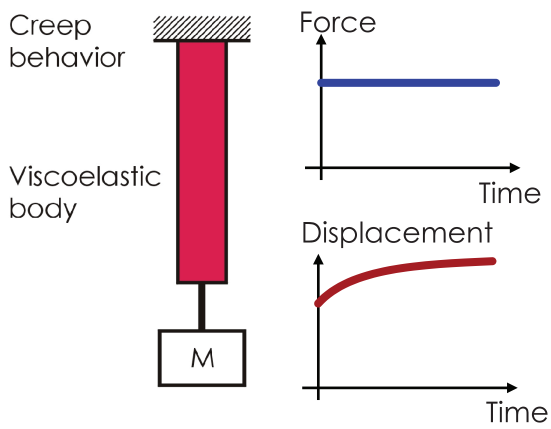
- **Two main types of ideal materials**
  - Elastic solid
    - Has a definite shape and deforms under external forces
    - Stores all energy that is obtained from external forces
    - Stored energy restores the original shape once the force is removed
  - Viscous liquid
    - No definite shape
    - Flows irreversibly under the action of external forces

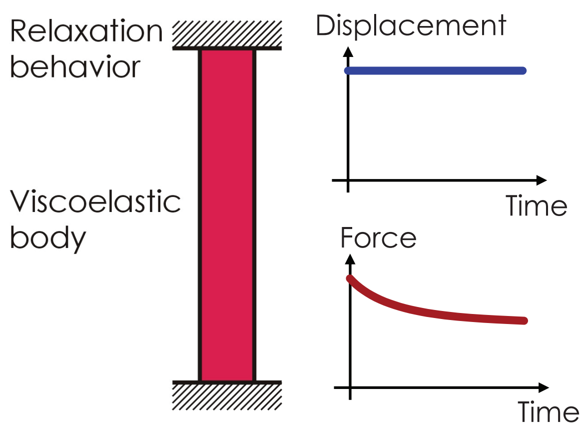
- **Viscoelasticity**
  - A polymer can exhibit all intermediate range of properties between an elastic solid and a viscous liquid.
  - Properties depends on temperature and experimental time scale.
  - Material response which combines both liquid and solid like features is termed Viscoelasticity.
  - Material possess a memory (fading) of past events.
  - Two types of viscoelastic behavior: creep vs. stress relaxation

15.4 Viscoelastic Deformation

- **Creep behavior**
  - Tendency of a solid material to move slowly or deform under the influence of mechanical stresses.
  - Occurs as a result of long-term exposure to high levels of stress that are still below the yield strength of the material.

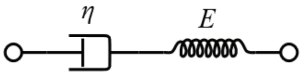
- **Stress relaxation behavior**
  - Stress relaxation is the observed decrease in stress in response to the same amount of strain generated in the structure





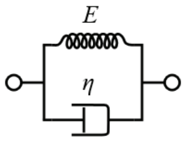
Mechanical Model of Viscoelastic Materials

- **Viscoelastic behavior can be described by mechanical models constructed using elastic springs and viscous dashpots**
- **Elastic springs follow Hooke's law: σ = Eε**
- **Viscous dashpots follow Newton's law of viscosity: σ = η(∂ε/∂t)**
- **Modelling of viscoelastic materials**
  - Maxwell model:



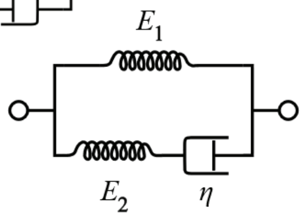
$$\frac{d\epsilon(t)}{dt} = \frac{1}{E}\frac{d\sigma(t)}{dt} + \frac{\sigma(t)}{\eta}$$

  - Kelvin–Voigt model:

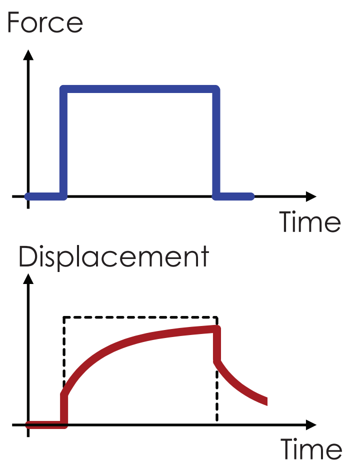


$$\sigma(t) = E\epsilon(t) + \eta\frac{d\epsilon(t)}{dt}$$

  - Standard linear solid model:



$$(E_1 + E_1)\frac{d\epsilon(t)}{dt} + \frac{E_1E_2}{\eta}\epsilon(t) = \frac{d\sigma(t)}{dt} + \frac{E_2}{\eta}\sigma(t)$$

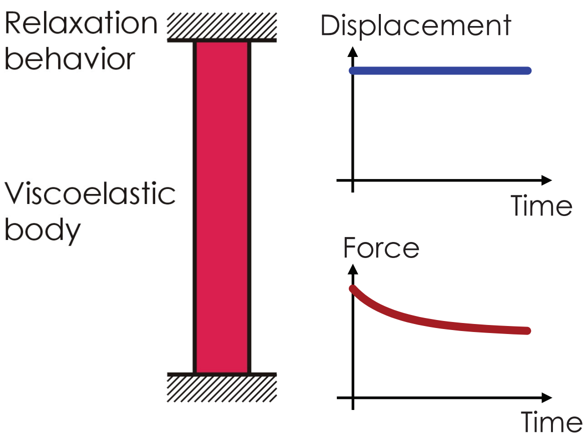


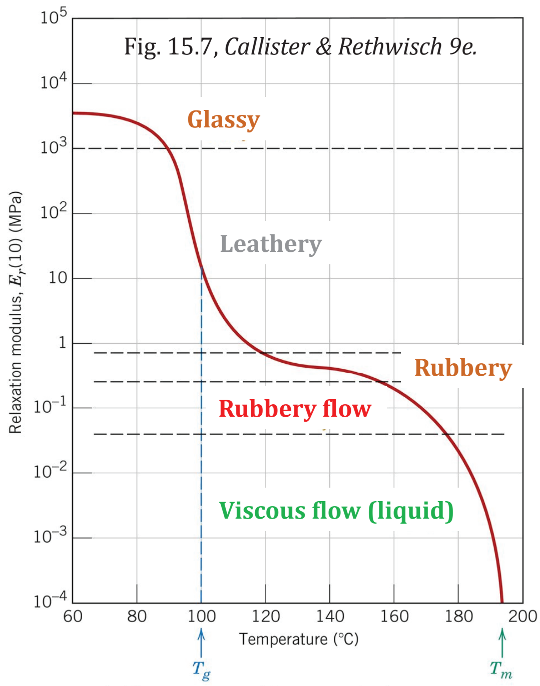
Viscoelastic Relaxation Modulus

- **Relaxation modulus**

$$\sigma(t) = E_r(t)\varepsilon_0$$

$$\therefore E_r(t) = \frac{\sigma(t)}{\varepsilon_0}$$





From A. V. Tobolsky, Properties and Structures of Polymers. Copyright © 1960 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.

15.5 Fracture of Polymers

- **The mode of fracture in thermosetting polymers (heavily crosslinked networks) is brittle.**
- **For thermplastic polymers, both ductile and brittle modes are possible.**
- **Craze formation prior to cracking in thermoplastic polymers**
  - during crazing, plastic deformation of spherulites
  - and formation of microvoids and fibrillar bridges

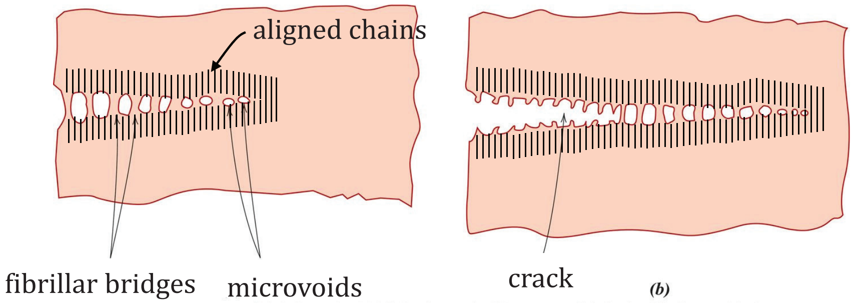
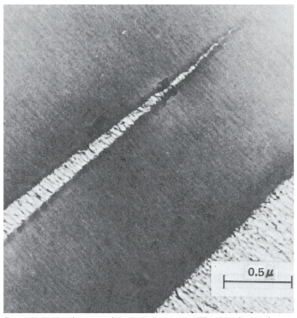


Fig. 15.9, *Callister & Rethwisch 9e.*
(From J. W. S. Hearle, *Polymers and Their Properties*, Vol. 1, *Fundamentals of Structure and Mechanics*, Ellis Horwood, Ltd., Chichester, West Sussex, England, 1982.)

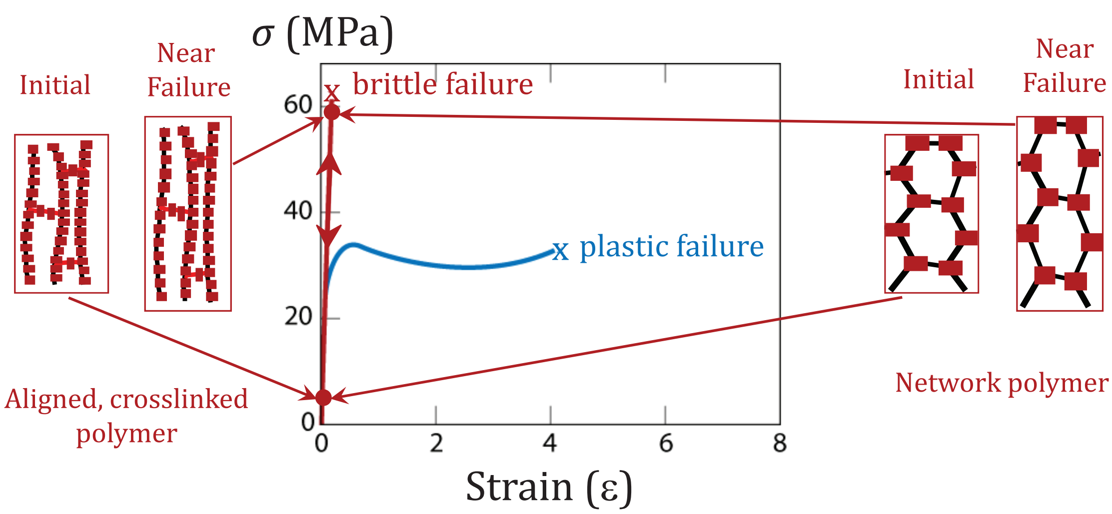


From R. P. Kambour and R. E. Robertson, "The Mechanical Properties of Plastics," in Polymer Science, A Materials Science Handbook, A. D. Jenkins, Editor. Reprinted with permission of Elsevier Science Publishers.

Fig. 15.10, *Callister & Rethwisch 9e.*

Mechanisms of Deformation

- **Brittle Crosslinked and Network Polymers**

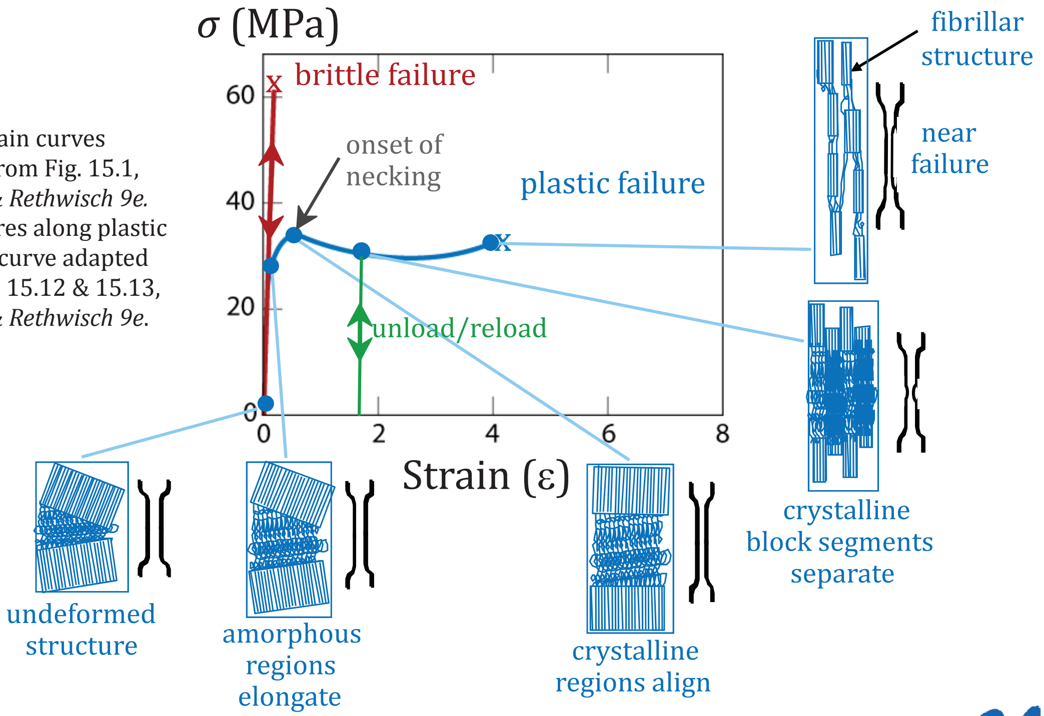


Stress-strain curves adapted from Fig. 15.1, *Callister & Rethwisch 9e.*

Mechanisms of Deformation

- **Semicrystalline (Plastic) Polymers**

Stress-strain curves adapted from Fig. 15.1, *Callister & Rethwisch 9e.* Inset figures along plastic response curve adapted from Figs. 15.12 & 15.13, *Callister & Rethwisch 9e.*



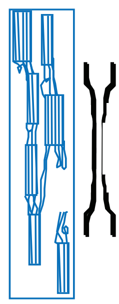
Predeformation by Drawing

- **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 chain alignment
  - reverses effects of drawing (reduces E and TS, enhances %EL)

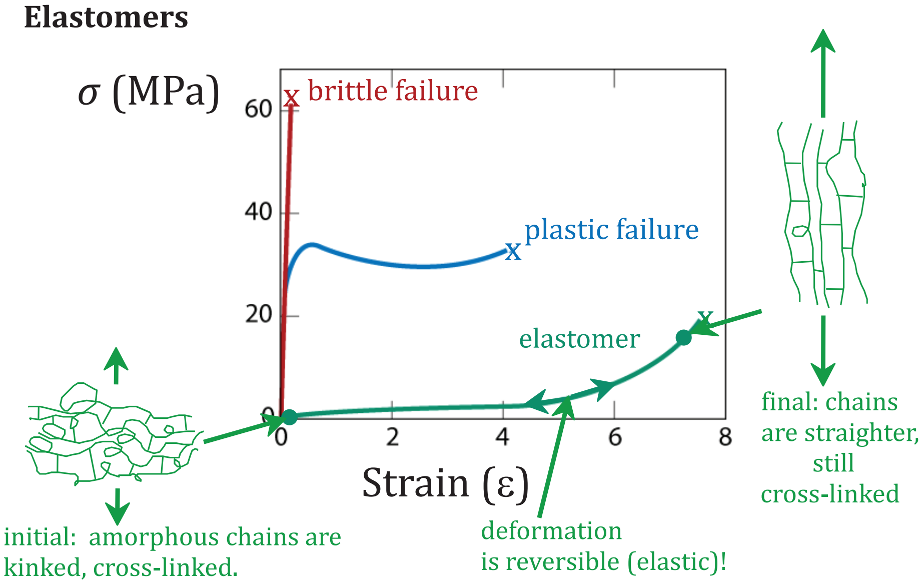
- **Contrast to effects of cold working in metals!**



Adapted from Fig. 15.13, *Callister & Rethwisch 9e.* (From Schultz, *Polymer Materials Science*, 1st Edition, © 1974. Reprinted by permission of Pearson Education, Inc., Upper Saddle River, NJ.)1974, pp 500-501.)

Mechanisms of Deformation

- **Elastomers**



Stress-strain curves adapted from Fig. 15.1, *Callister & Rethwisch 9e.* Inset figures along elastomer curve (green) adapted from Fig. 15.15, *Callister & Rethwisch 9e.*

- **Compare elastic behavior of elastomers with the:**
  - brittle behavior (of aligned, crosslinked & network polymers), and
  - plastic behavior (of semicrystalline polymers) (as shown on previous slides)

15.13 & 14 Melting & Glass-Transition Temperatures

- **What factors affect T_m and T_g?**
- **Both T_m and T_g increase with increasing chain stiffness.**
- **Chain stiffness increased by presence of**
  - Bulky sidegroups
  - Polar groups or sidegroups
  - Chain double bonds and aromatic chain groups
- **Regularity of repeat unit arrangements – affects T_m only**

Material	*Glass Transition Temperature (°C)*	*Melting Temperature (°C)*
Polyethylene (low density)	−110	115
Polytetrafluoroethylene	−97	327
Polyethylene (high density)	−90	137
Polypropylene	−18	175
Nylon 6,6	57	265
Poly(ethylene terephthalate) (PET)	69	265
Poly(vinyl chloride)	87	212
Polystyrene	100	240
Polycarbonate	150	265

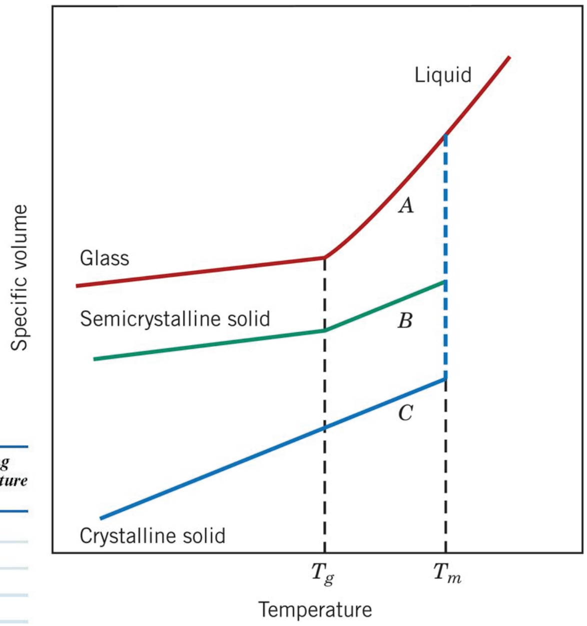


Fig. 15.18, *Callister & Rethwisch 9e.*

15.15 Plastics

Table 15.3 Trade Names, Characteristics, and Typical Applications for a Number of Plastic Materials

Material Type	*Trade Names*	*Major Application Characteristics*	*Typical Applications*
		Thermoplastics	
Acrylonitrile-butadiene-styrene (ABS)	Abson, Cycolac, Kralastic, Lustran, Lucon, Novodur	Outstanding strength and toughness, resistant to heat distortion; good electrical properties; flammable and soluble in some organic solvents	Under-the-hood automotive applications, refrigerator linings, computer and television housings, toys, highway safety devices
Acrylics [poly(methyl methacrylate)]	Acrylite, Diakon, Lucite, Paraloid, Plexiglas	Outstanding light transmission and resistance to weathering; only fair mechanical properties	Lenses, transparent aircraft enclosures, drafting equipment, bathtub and shower enclosures
Fluorocarbons (PTFE or TFE)	Teflon, Fluon, Halar, Hostaflon TF, Neoflon	Chemically inert in almost all environments, excellent electrical properties; low coefficient of friction; may be used to 260°C; relatively weak and poor cold-flow properties	Anticorrosive seals, chemical pipes and valves, bearings, wire and cable insulation, antiadhesive coatings, high-temperature electronic parts
Polyamides (nylons)	Nylon, Akulon, Durethan, Fostamid, Nomex, Ultramid, Zytel	Good mechanical strength, abrasion resistance, and toughness; low coefficient of friction; absorbs water and some other liquids	Bearings, gears, cams, bushings, handles, and jacketing for wires and cables, fibers for carpet, hose, and belt reinforcement

15.15 Plastics

Material Type	*Trade Names*	*Major Application Characteristics*	*Typical Applications*
Polycarbonates	Calibre, Iupilon, Lexan, Makrolon, Novarex	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, automobile battery cases
Polyethylenes	Alathon, Alkathene, Fortiflex, Hifax, Petrothene, Rigidex, Zemid	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, automotive gas tanks
Polypropylenes	Hicor, Meraklon, Metocene, Polypro, Pro-fax, Propak, Propathene	Resistant to heat distortion; excellent electrical properties and fatigue strength; chemically inert; relatively inexpensive; poor resistance to ultraviolet light	Sterilizable bottles, packaging film, automotive kick panels, fibers, luggage
Polystyrenes	Avantra, Dylene, Innova, Lutex, Styron, Vestyron	Excellent electrical properties and optical clarity; good thermal and dimensional stability; relatively inexpensive	Wall tile, battery cases, toys, indoor lighting panels, appliance housings, packaging

15.15 Plastics

Material Type	Trade Names	Major Application Characteristics	Typical Applications
Vinyls	Dural Formolon Geon Pevikon Saran Tygon Vinidur	Good low-cost, general-purpose materials; ordinarily rigid, but may be made flexible with plasticizers; often copolymerized; susceptible to heat distortion	Floor coverings, pipe, electrical wire insulation, garden hose, shrink wrap
Polyesters (PET or PETE)	Crystar Dacron Eastapak HiPET Melinex Mylar Petra	One of the toughest of plastic films; excellent fatigue and tear strength, and resistance to humidity, acids, greases, oils, and solvents	Oriented films, clothing, automotive tire cords, beverage containers
		Thermosetting Polymers	
Epoxies	Araldite Epikote Lytex Maxive Sumilite Vipel	Excellent combination of mechanical properties and corrosion resistance; dimensionally stable; good adhesion; relatively inexpensive; good electrical properties	Electrical moldings, sinks, adhesives, protective coatings, used with fiberglass laminates
Phenolics	Bakelite Duralite Milex Novolac Resole	Excellent thermal stability to more than 150°C; may be compounded with a large number of resins, fillers, etc.; inexpensive	Motor housings, adhesives, circuit boards, electrical fixtures

15.17 Fibers

- **Fibers: length/diameter >100**
- **Primary use is in textiles.**
- **Fiber characteristics:**
  - high tensile strengths
  - high degrees of crystallinity
  - structures containing polar groups

- **Formed by spinning**
  - extrude polymer through a spinneret (a die containing many small orifices)
  - the spun fibers are drawn under tension
  - leads to highly aligned chains - fibrillar structure

15.18 Miscellaneous Applications

- **Coatings – thin polymer films applied to surfaces – i.e., paints, varnishes**
  - protects from corrosion/degradation
  - decorative – improves appearance
  - can provide electrical insulation
- **Adhesives – bonds two solid materials (adherands)**
  - bonding types:
    - Secondary – van der Waals forces
    - Mechanical – penetration into pores/crevices
- **Films – produced by blown film extrusion**
- **Foams – gas bubbles incorporated into plastic**

15.19 Advanced Polymeric Materials

- **Ultrahigh Molecular Weight Polyethylene (UHMWPE)**
- **Molecular weight ca. 4 x 106 g/mol**
- **Outstanding properties**
  - high impact strength
  - resistance to wear/abrasion
  - low coefficient of friction
  - self-lubricating surface
- **Important applications**
  - bullet-proof vests
  - golf ball covers
  - hip implants (acetabular cup)

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

15.19 Advanced Polymeric Materials

- Thermoplastic Elastomers
- Example: Styrene-butadiene block copolymer

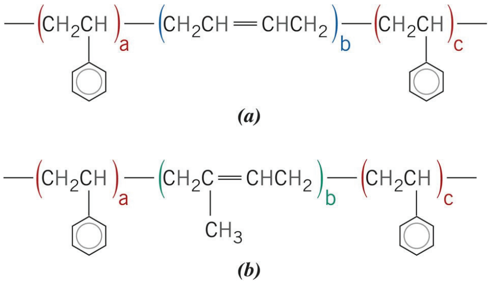


Fig. 15.21 Representations of the chain chemistries for (a) styrene-butadiene-styrene (S-B-S), and (b) styrene-isoprene-styrene (S-I-S) thermoplastic elastomer, *Callister & Rethwisch 9e.*

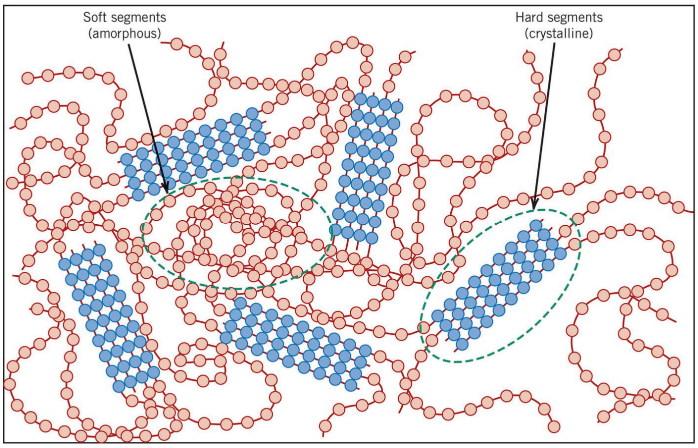
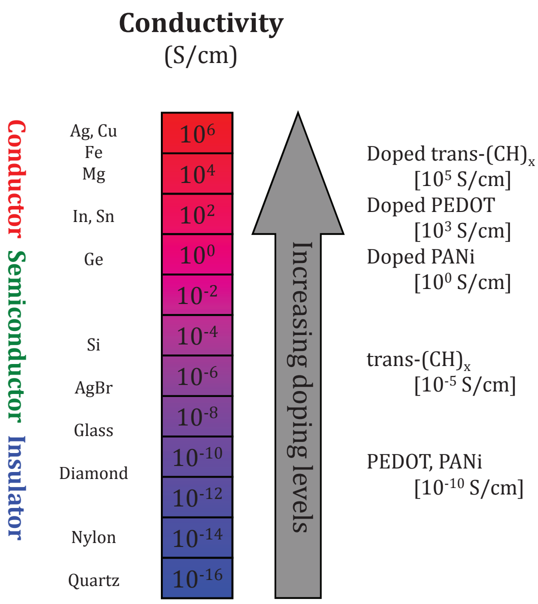
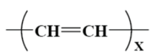


Fig. 15.22 Schematic representation of the molecular structure for a thermoplastic elastomer. This structure consists of "soft" (i.e., butadiene or isoprene) repeat unit center-chain segments and "hard" (i.e., styrene) domains (chain ends), which act as physical crosslinks at room temperature, *Callister & Rethwisch 9e.*

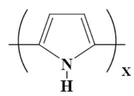
Conducting Polymer Electrodes



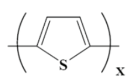
Conducting polymers



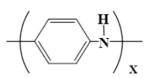
Polyacetylene



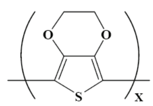
Polypyrrole



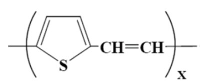
Polythiophene



Polyaniline



PEDOT [poly(3,4-ethylenedioxythiophene)]

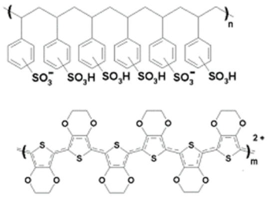


Poly(thienylenevinylene)

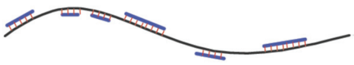
PEDOT:PSS & Polyaniline

PEDOT:PSS

[Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)]

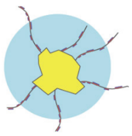


Secondary-and tertiary structures

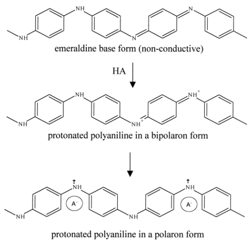


PSS-chain with PEDT-oligomers

Gel particle

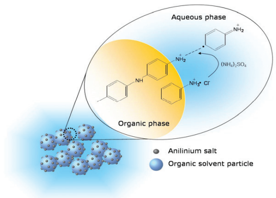


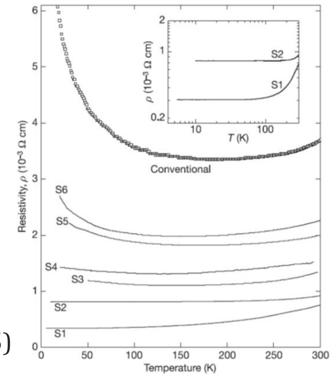
PANi (Polyaniline)



Self-Stabilized Dispersion Polymerization (SSDP)

(Lee et al., Adv. Func. Mat. 15, 2005)





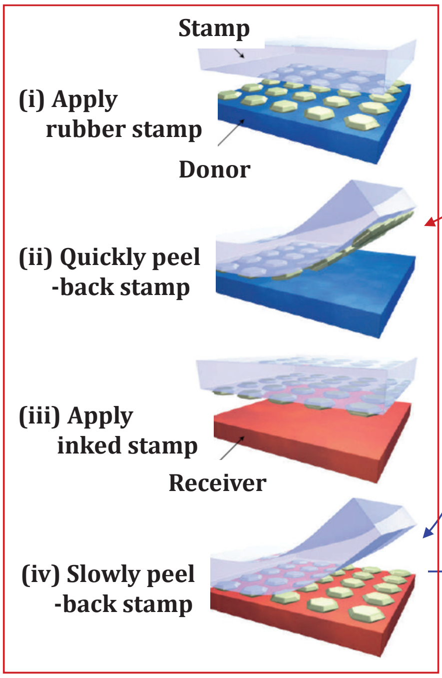
Temperature dependence of the resistivity, ρ(T), shows the metallic transport in polyaniline.

(Lee et al., Nature, 2006)

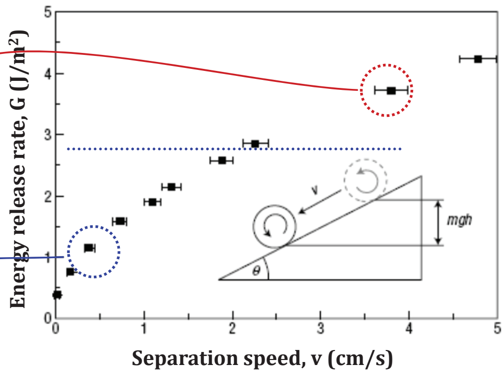
Time-Dependent Adhesion

Transfer printing

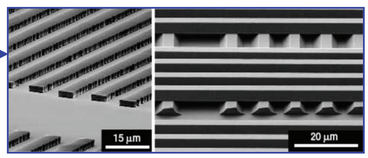
Meitl et al., Nature Materials, 5, 33 (2006)



Kinetically-controlled adhesion



Heterogeneous integration based on kinetically controlled switching between adhesion and release of solid objects to and from an elastomeric stamp

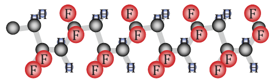


Functional Polymer Films

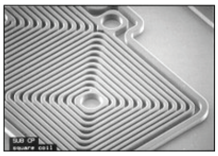
Key features of polymer films

- Photosensitive characteristics for lithography
- Thermo-mechanical behavior
- Viscoelastic and viscoplastic properties
- Time-dependent adhesion
- Electromechanical behavior
- Optical & electrical properties

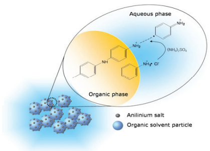
P(VDF-TrFE-CFE)
Relaxor ferroelectric polymer for sensors and actuators



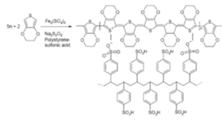
SU-8
Negative photoresist for MEMS
High aspect ratio lithography



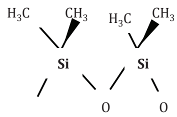
Polyaniline (PANi)
Conducting polymer



PEDOT:PSS
Conducting polymer



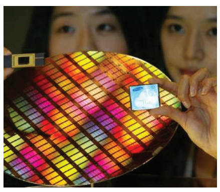
PDMS (polydimethylsiloxane)
Dow Corning: SYLGARD® 184 silicone elastomer
Composition: base : curing agent = 10 : 1



Future of functional polymers

Passive materials

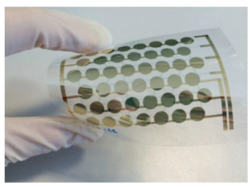
Plastic containers



Passivation, dielectrics, etc.
(Samsung, 30 nm 64 Gb NAND Flash Memory)

Sony's flexible color OLED

Electroactive polymers



Active elements

Micromechanics for Flexible Macroelectronics

Stretchable & flexible polymers
Electroactive polymers
Permeation barriers
Mechanical reliability of polymers

Bioactive polymers