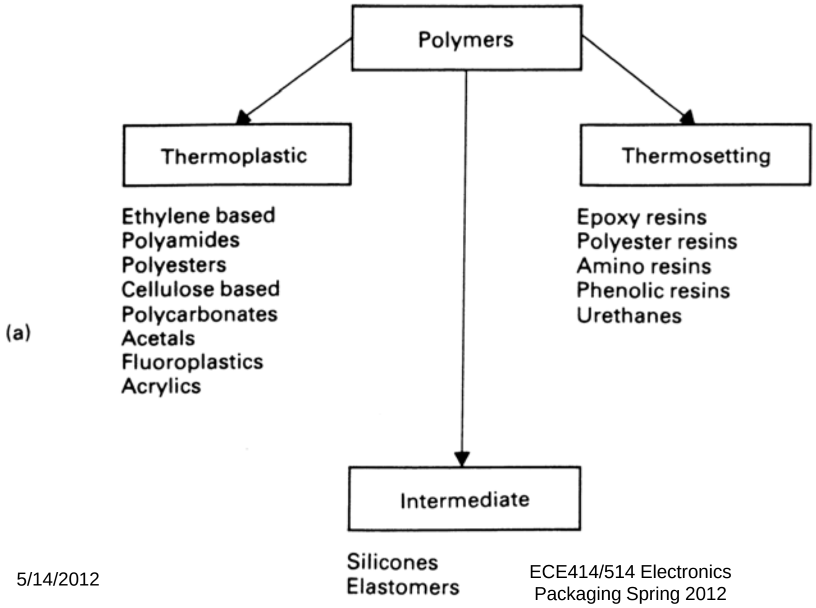
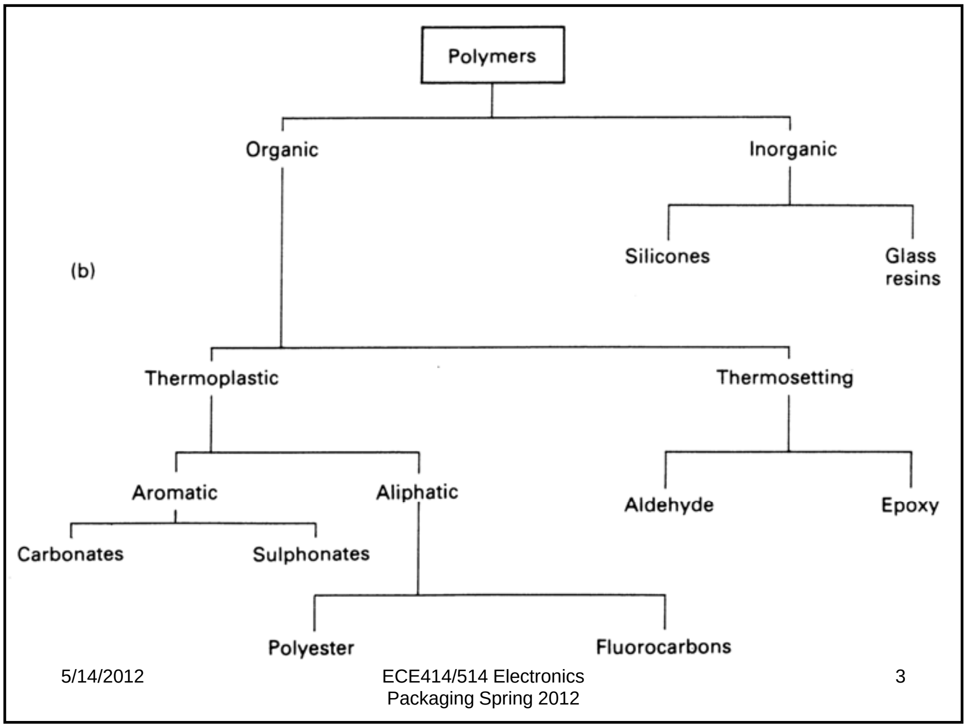
ECE414/514
Electronics Packaging
Spring 2012 Lecture 14
Materials B: Polymers

James E. Morris
Dept of Electrical & Computer Engineering
Portland State University

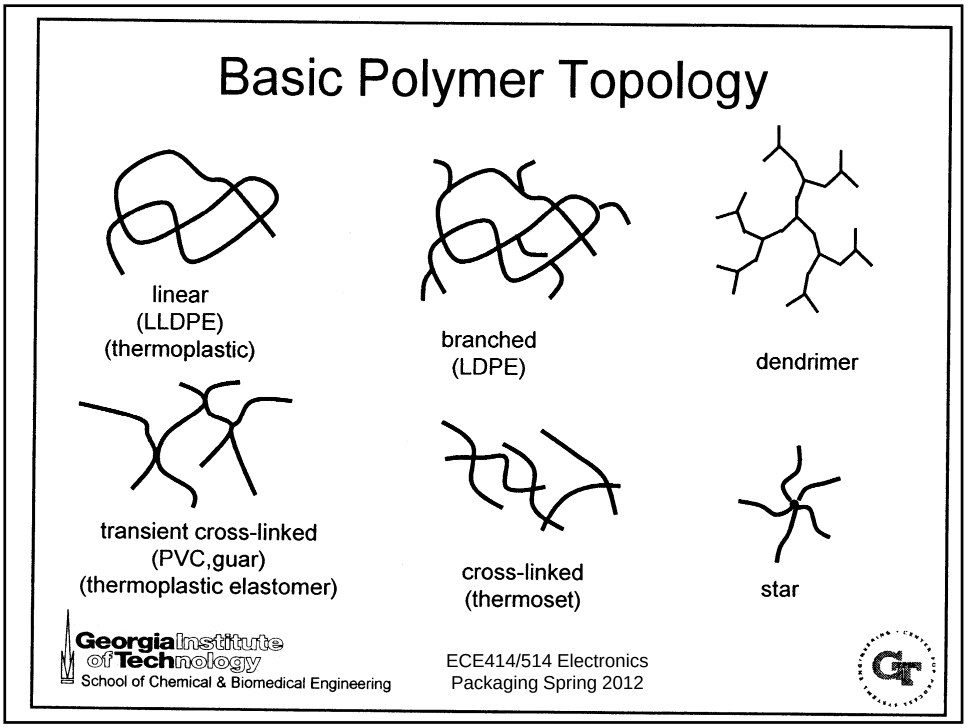
Introduction: Polymer types, chains, & cross-linking





(b)

- Polymers
  - Organic
    - Thermoplastic
      - Aromatic
        - Carbonates
        - Sulphonates
      - Aliphatic
        - Polyester
        - Fluorocarbons
    - Thermosetting
      - Aldehyde
      - Epoxy
  - Inorganic
    - Silicones
    - Glass resins



Basic Polymer Topology

linear
(LLDPE)
(thermoplastic)

branched
(LDPE)

dendrimer

transient cross-linked
(PVC,guar)
(thermoplastic elastomer)

cross-linked
(thermoset)

star

Georgia Institute of Technology
School of Chemical & Biomedical Engineering

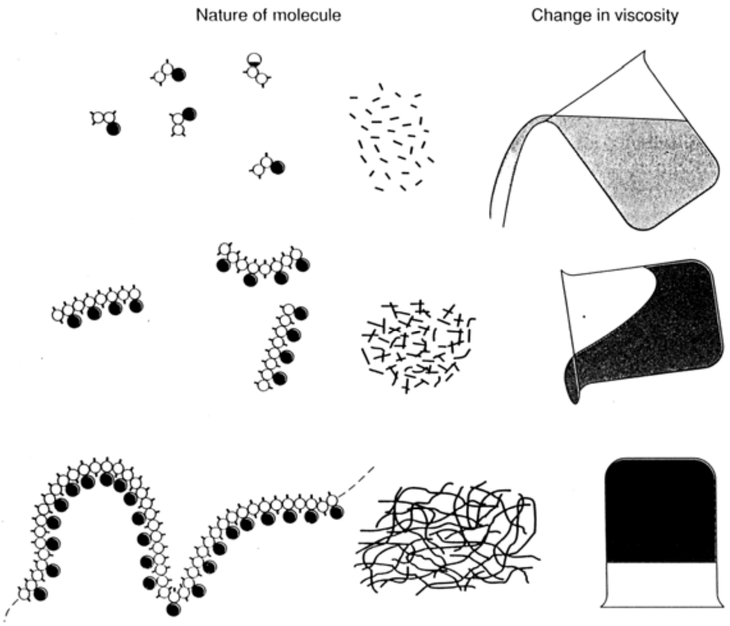


FIGURE 4-6 Stages in the polymerization of a vinyl polymer and the relative changes in viscosity they produce. From R. A. Higgins, *The Properties of Engineering Materials*, R. E. Krieger, Huntington, NY (1977).

Fabrication/curing (polyethylene)

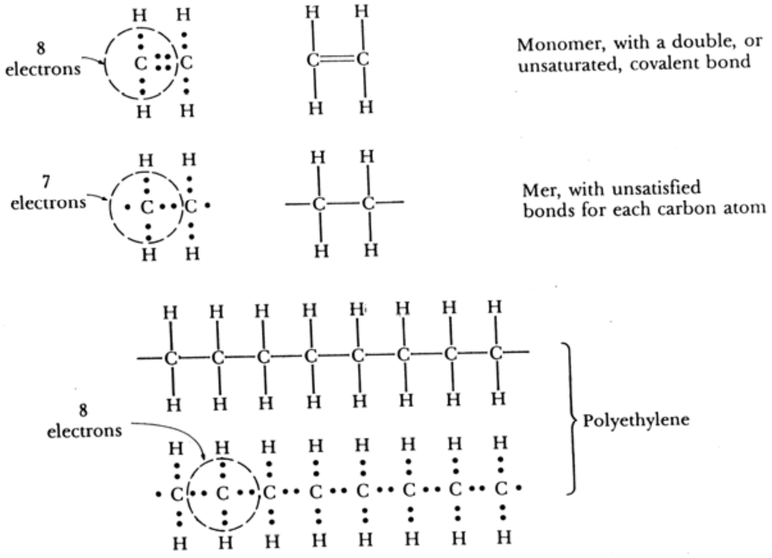


FIG. 15-3 The addition reaction for producing polyethylene from ethylene molecules. The unsaturated double bond in the monomer is broken to produce a mer, which can then attract additional mers to either end to produce a chain.

Variations on the basic polyethylene structure

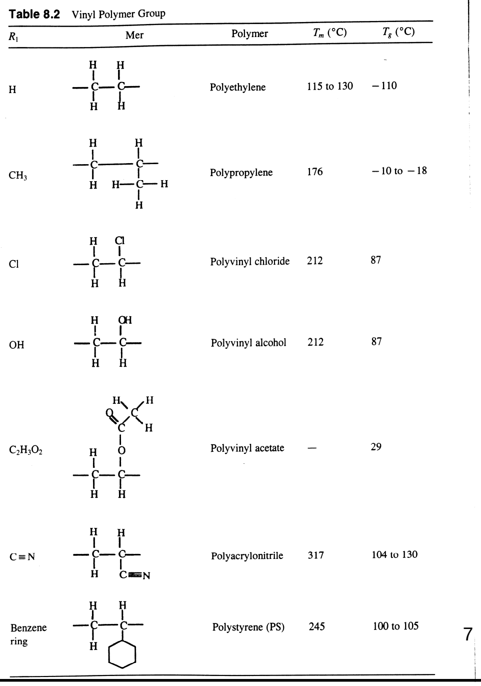


Table 8.2 Vinyl Polymer Group

R_1	Mer	Polymer	T_m (°C)	T_g (°C)
H		Polyethylene	115 to 130	−110
CH_3		Polypropylene	176	−10 to −18
Cl		Polyvinyl chloride	212	87
OH		Polyvinyl alcohol	212	87
$C_2H_3O_2$		Polyvinyl acetate	—	29
C≡N		Polyacrylonitrile	317	104 to 130
Benzene ring		Polystyrene (PS)	245	100 to 105

Epoxy

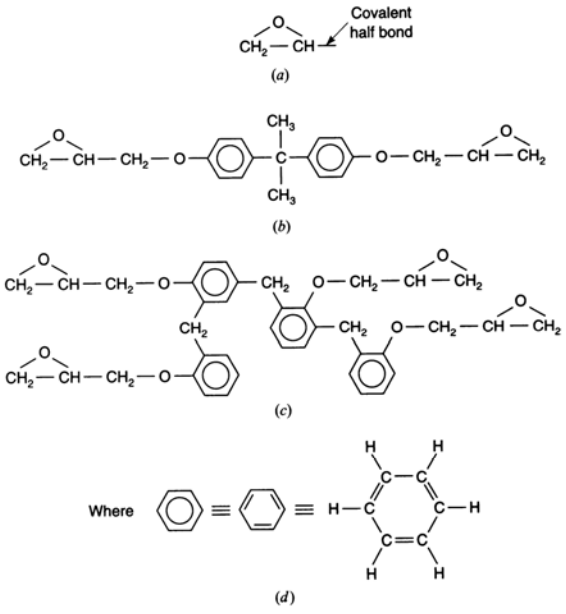
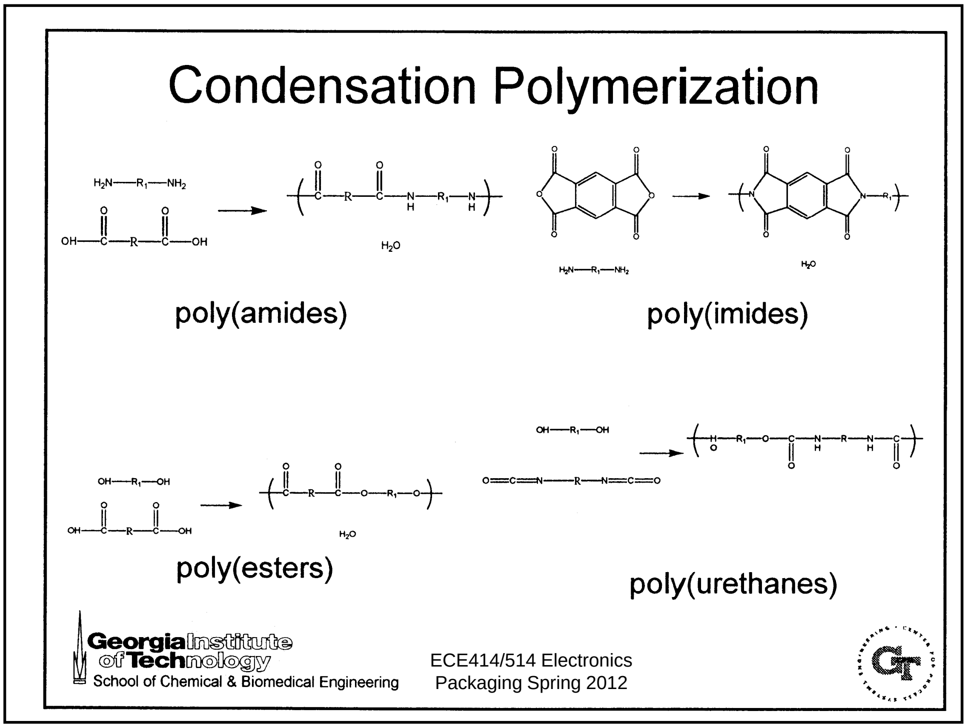


Figure 2.7 Chemical structures of (*a*) epoxide group, (*b*) diglycidyl ether of bisphenol-A (DGEBA), (*c*) epoxy novolar, and (*d*) the benzene structure.



Condensation Polymerization

poly(amides)

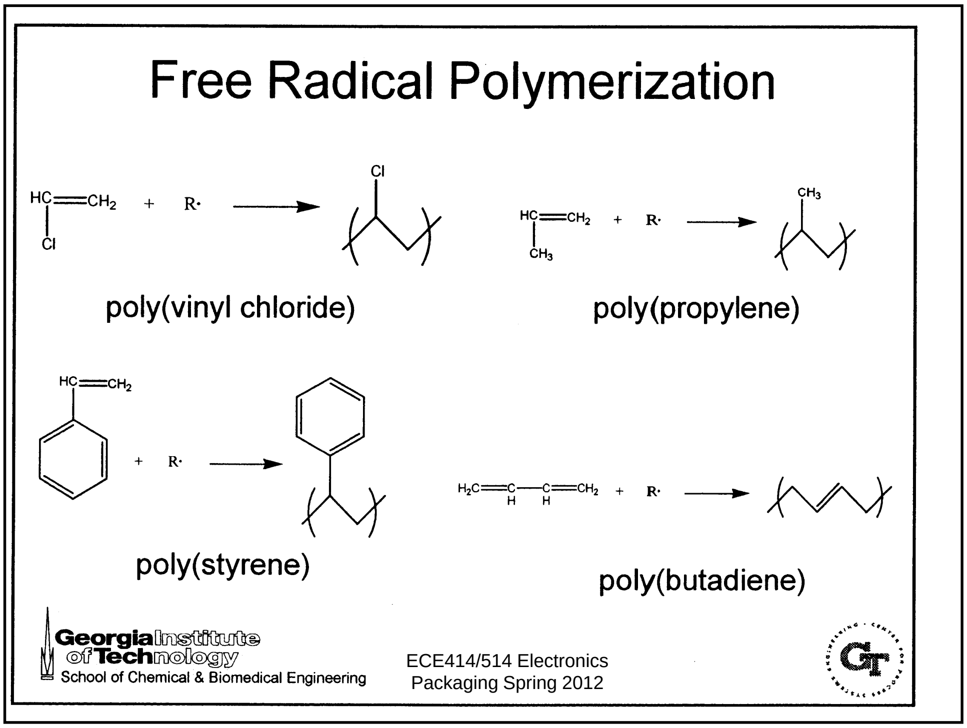
poly(imides)

poly(esters)

poly(urethanes)

Georgia Institute of Technology
School of Chemical & Biomedical Engineering

ECE414/514 Electronics
Packaging Spring 2012



Free Radical Polymerization

poly(vinyl chloride)

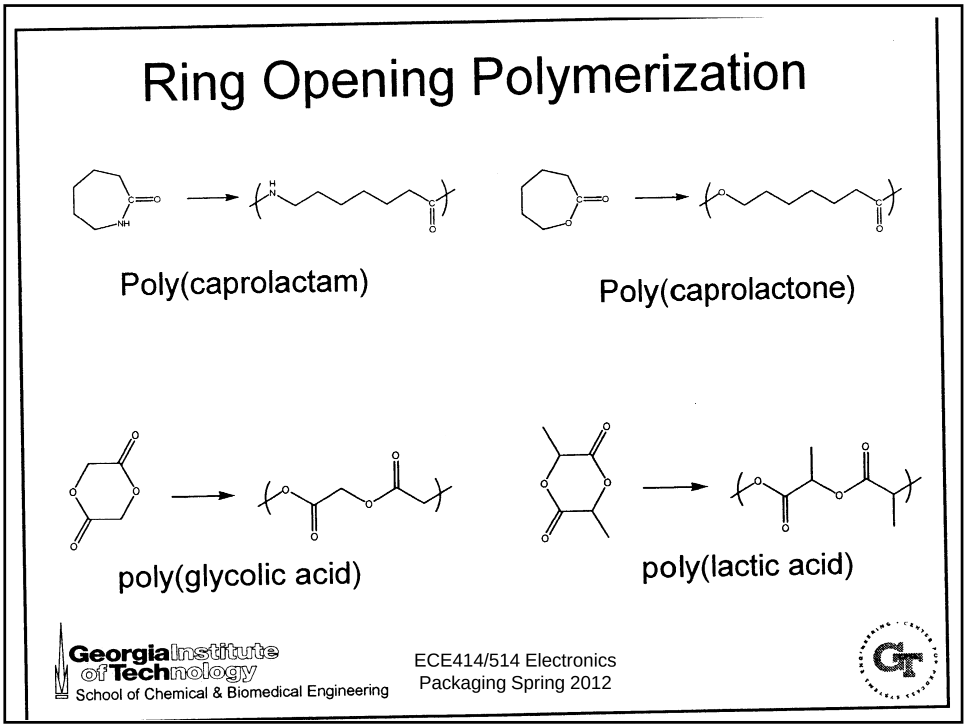
poly(propylene)

poly(styrene)

poly(butadiene)

Georgia Institute of Technology
School of Chemical & Biomedical Engineering

ECE414/514 Electronics
Packaging Spring 2012



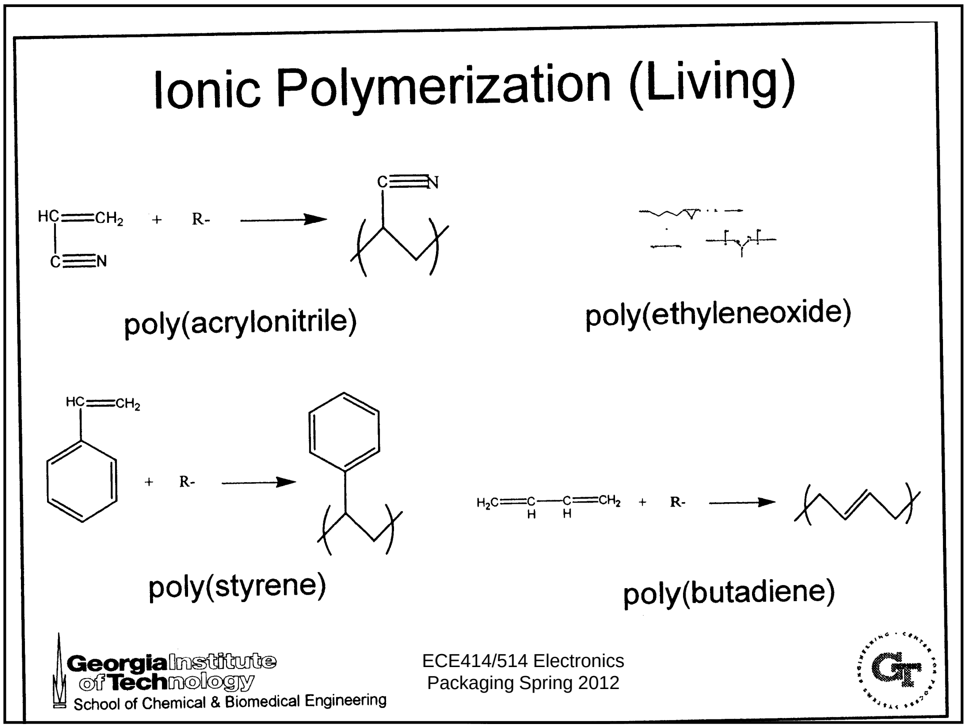
Ring Opening Polymerization

Poly(caprolactam)

Poly(caprolactone)

poly(glycolic acid)

poly(lactic acid)



Ionic Polymerization (Living)

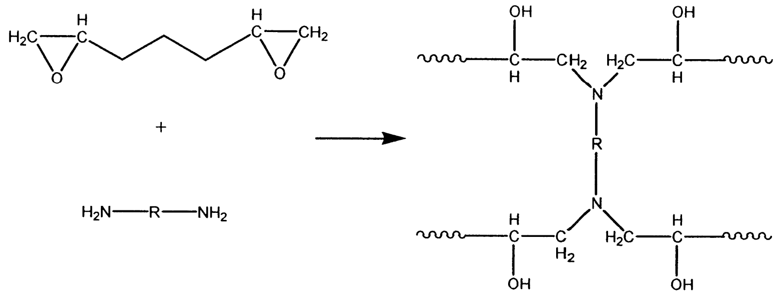
poly(acrylonitrile)

poly(ethyleneoxide)

poly(styrene)

poly(butadiene)

Polymer Combination Complications

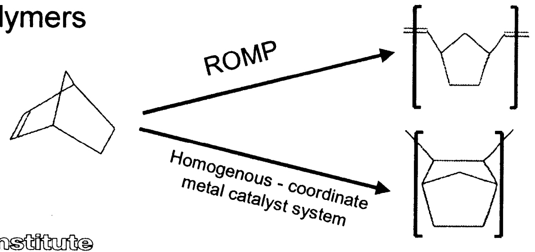


- Ring opening mechanism
- Condensation kinetics
- Cross-linked (gel) topology

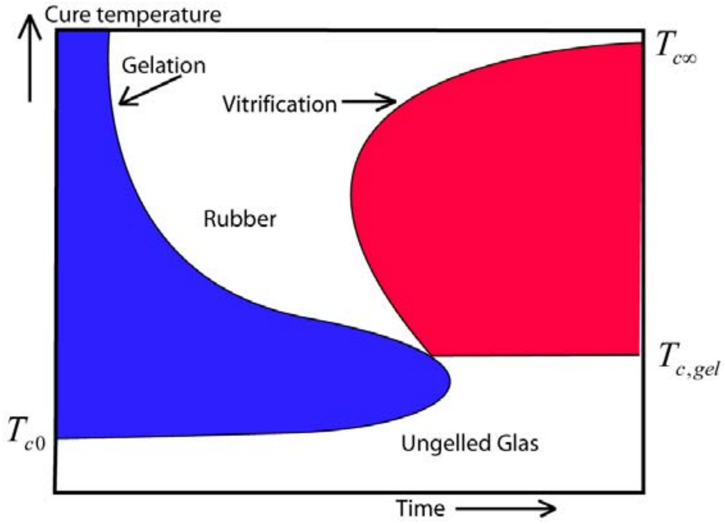
Epoxy Resins

Coordination-Insertion Polymerization

- Zeigler-Natta Catalysts
- Group Transfer Polymerization
- Metallocene Catalysts
- Ring Opening Metathesis Polymerization (ROMP)
- Various other homogeneous catalysts
- These catalysts can produce structurally regular polymers



Cure Modeling



Cure Models

- Reaction rate $d\alpha/dt = k\ f(\alpha)$, where $k = A\ \exp-(E/kT)$
  - k = chemical rate constant, $f(\alpha)$ reactant concn.
  - α = degree of cure
- N-th order model: $f(\alpha) = (1 - \alpha)^n$
- Calculate degree of cure:
  - 1st order: $d\alpha/dt = k(1- \alpha)$, $\therefore\ \alpha = 1-\exp(-kt)$
  - 2nd order: $\alpha = 1 - (1 + kt)^{-1}$
- Auto-catalyzed model:
  - $f(\alpha) = \alpha^m (1- \alpha)^n$
  - Linear combination: $d\alpha/dt=k\ f(\alpha)=(k_1+k_2\ \alpha^m)(1- \alpha)^n$

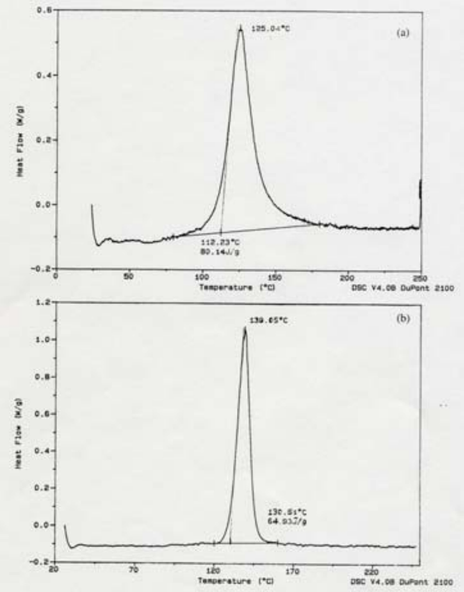


Figure 4.2: Typical DSC curves at 10°C/min. ramp run. (a) Adhesive A. (b) Adhesive B.

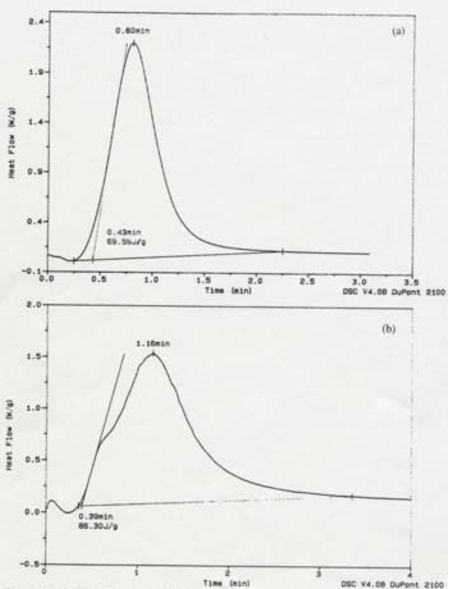


Figure 4.3: Typical DSC curves at isothermal runs. (a) Adhesive B. (b) Adhesive C.

Differential Scanning Calorimetry (DSC)

Cure Calculations

- k found for each T from E, A (experimental)
- E, A found from DSC, heating rates

$$\frac{d\alpha}{dt} = f(\alpha)\cdot A\cdot e^{-E/kT}, \quad \text{so} \qquad \int_0^{\alpha p}\frac{1}{f(a)}d(\alpha) = A\int_{t0}^{tp}e^{-E/RT}dt$$

$$= \left(\frac{A}{\phi}\right)\cdot\int_{T0}^{Tp}e^{-E/RT}dT, \quad \text{if} \quad T(t) = \phi t$$

$$\approx \left(\frac{A}{\phi}\right)\cdot\int_{0}^{Tp}e^{-E/RT}dT, \quad \text{if} \quad T_0 << T_p$$

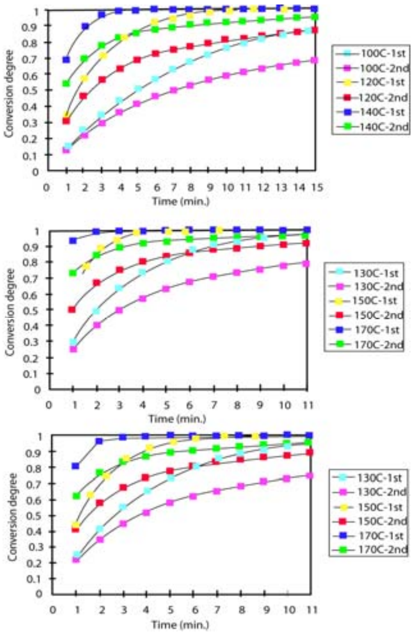
$$\approx \left(\frac{AE}{\phi R}\right)\cdot p\left(\frac{E}{RT_p}\right) \quad \text{for} \quad 20 < \frac{E}{RT_p} < 60$$

- Find: $E \approx -\left(\frac{R}{0.4567}\right)\cdot\left(\frac{\Delta\log\phi}{\Delta\left(1/T_p\right)}\right)$

  - ie var'n of peak exothermic temp with heat rate

- $A = \left(\frac{\phi E}{RT_p{}^2}\right)e^{E/RT_p}$

Calculation Results: Degree of Cure vs. Time for 3 Adhesives



Cure Optimization

- Removal of volatile organics
  - Organic liquids/solvents added
  - Viscosity control for printing
- Complete cure
- Polymer degradation
- Problems:
  - Bubbles
- Plasma polymerization

Structure (polyethylene

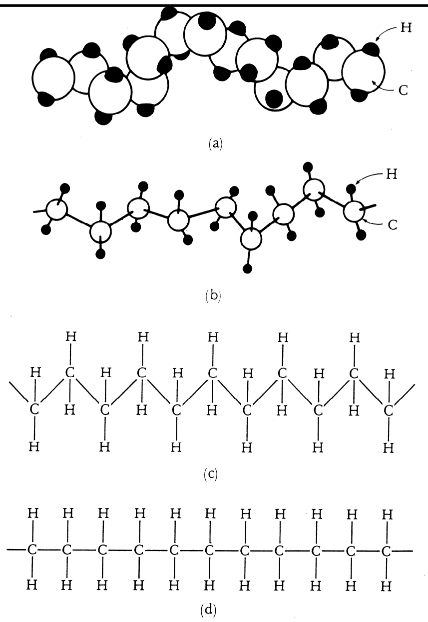
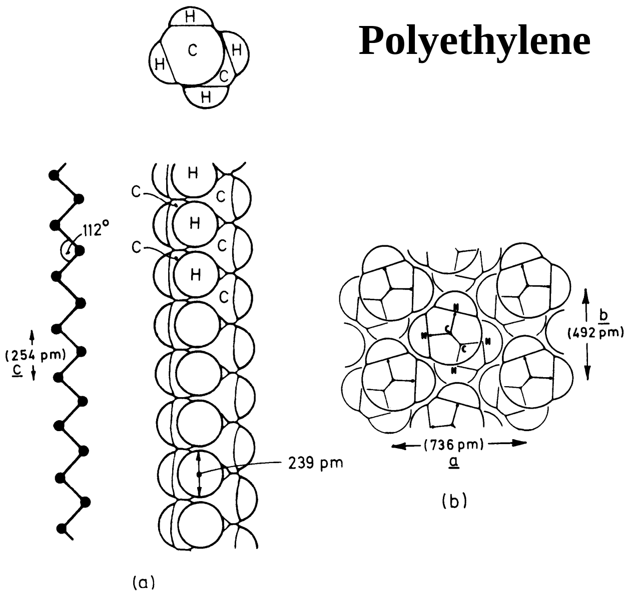


FIG. 15-1 Four ways to represent the structure of polyethylene. (a) Solid three-dimensional model, (b) three-dimensional "space" model, (c) two-dimensional model showing the kinked nature of the polymer chain, and (d) simple two-dimensional model.

Polyethylene



2.1 (a) Scale drawing of the conformation of a polyethylene molecule in the zigzag, crystalline conformation showing both the side and end view. (b) View of the crystal along the c axis in which the atoms have their correct external radii.

Copolymers: Alternating

Random

Block

Graft

Terpolymers

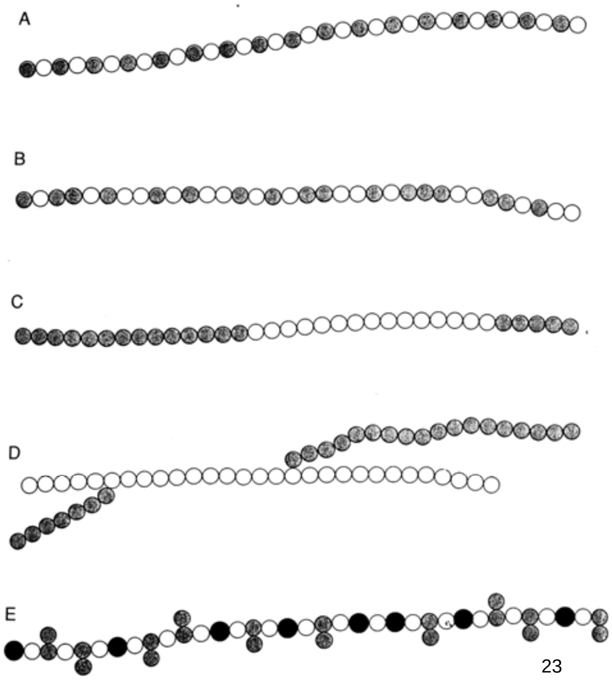


FIGURE 4-7 Types of copolymers: (A) Alternating. (B) Random. (C) Block. (D) Graft. (E) Terpolymers.

CHAPTER 15 POLYMERS 483

Alternating

Random

Block

Graft

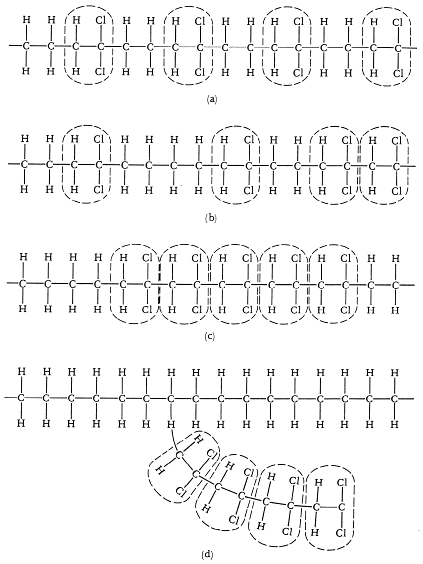


FIG. 15-22 Four types of copolymers. (a) Alternating monomers, (b) random monomers, (c) block copolymers, and (d) grafted copolymers.

Branching

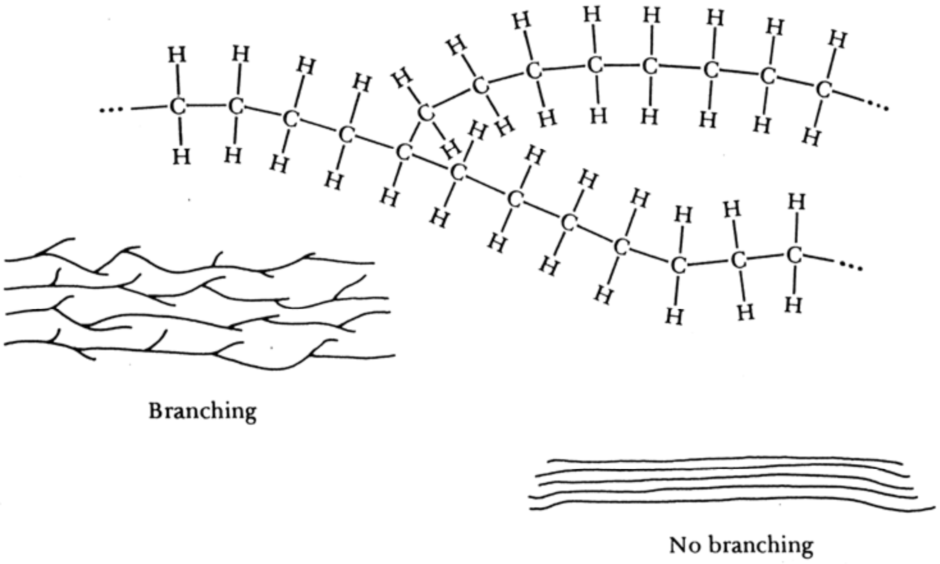


FIG. 15-19 Branching can occur in linear polymers. Branching makes crystallization more difficult

---

Van der Waals

Chains

&

Viscosity

CHAPTER 15 POLYMERS 471

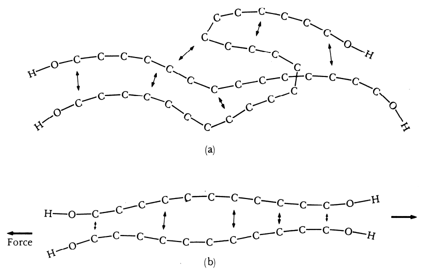


FIG. 15-10 (a) The individual chains are held together loosely by van der Waal's bonds and mechanical interlocking. (b) When the polymer is stretched, the chains are straightened out and eventually begin to slide past one another.

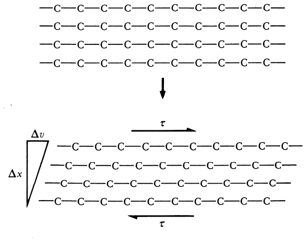


FIG. 15-11 A shear stress τ causes the polymer chains to slide over one another by viscous flow. The velocity gradient, $\Delta v/\Delta x$, produces a displacement of the chains that depends on the viscosity η of the polymer.

TABLE 2.5 Dissociation Energy for the Bond Types Present in Polymers

Bond Type	Dissociation Energy (kcal/mole)
Primary covalent	50–100
Ionic	10–20
Hydrogen bond	3–7
Dipole interaction	1.5–3
Van der Waals	0.5–2

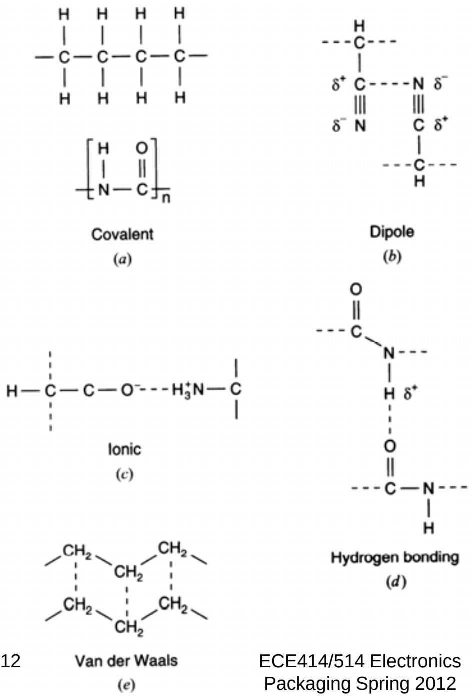
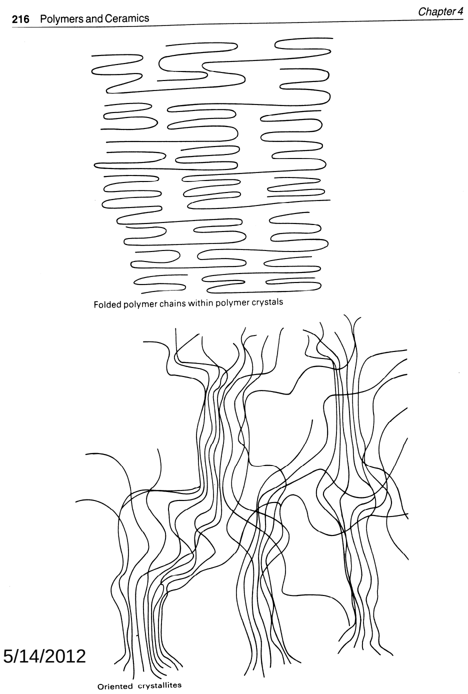


Figure 2.5 Illustrations of bonding forces present in polymers.

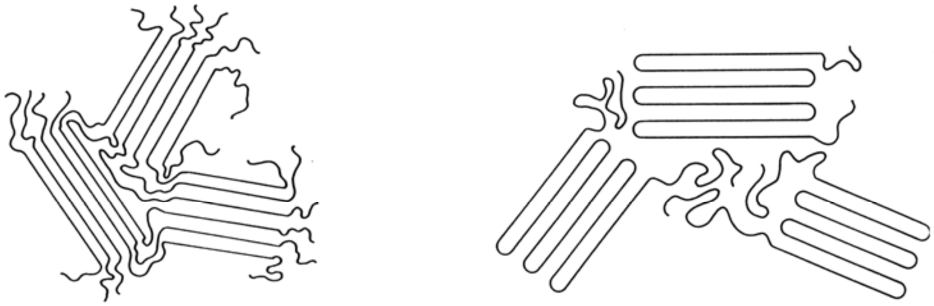
Crystals


216 Polymers and Ceramics

Chapter 4

Folded polymer chains within polymer crystals

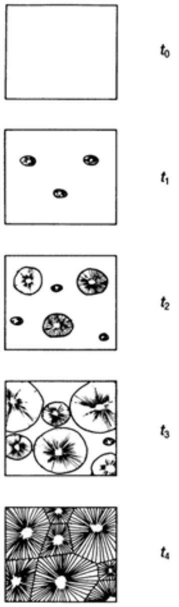
Oriented crystallites


(a)

(b)

FIG. 15-17 The fringed micelle (a) and folded chain (b) models for the structure of crystalline polymers.

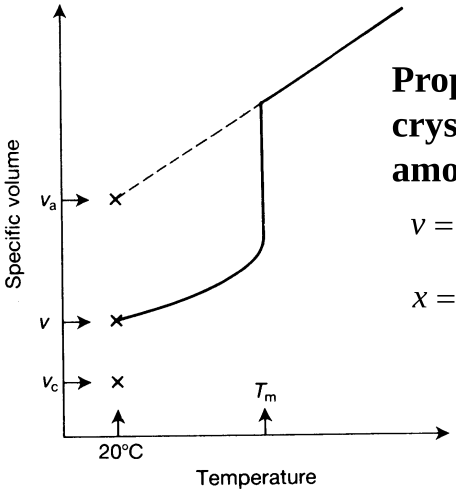
Crystallization



Nucleation & growth of spherulites

↓

2.7 Illustration of five stages in crystallization showing spherulite growth. At time t_0—the supercooled melt. At later times t_1 to t_3—the growth of spherulites. Finally, at time t_4—the specimen is composed completely of spherulites.



Proportion of crystalline and amorphous phases

$$v = xv_c + (1-x)v_a$$

$$x = \frac{v_a - v}{v_a - v_c}$$

2.6 Specific volume versus temperature for semicrystalline linear polyethylene showing the effect of heating a specimen from 20°C to above the melting point T_m. The specific volume of the specimen at 20°C is v. The specific volume of the amorphous fraction v_a is obtained by extrapolating the v–T curve for the liquid down to 20°C. The specific volume of the crystalline fraction v_c is obtained from the lattice constants of the unit cell (see Problem 2.1). The crystal fraction can be obtained using these quantities in eqn 2.2.

Glass Transition Temperature T_g

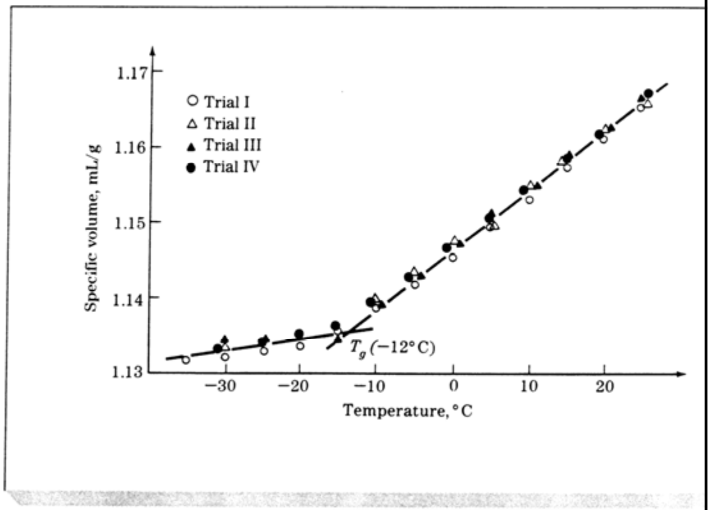
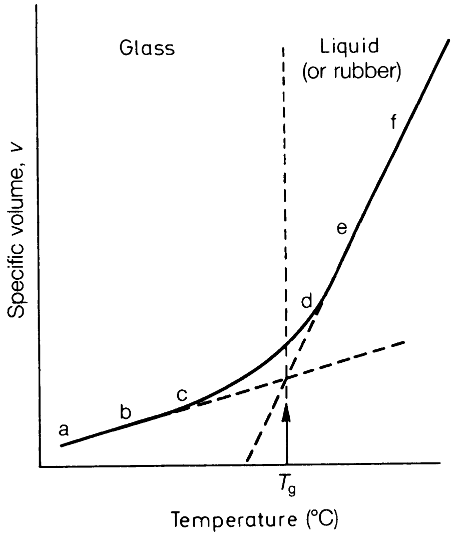


FIGURE 7.15 Experimental data of specific volume vs. temperature for the determination of the glass transition temperature of atactic polypropylene. T_g is at −12°C. [*After D. L. Beck, A. A. Hiltz, and J. R. Knox, Soc. Plast. Eng. Trans., 3:279(1963).*].



2.11 The glass transition temperature T_g is obtained from an experiment in which the specific volume v is measured whilst the specimen is cooled at a fixed rate, usually 1°C per minute. The construction for obtaining T_g from the data is shown. For polymer of low RMM, T_g marks the transition from glass to liquid; for high RMM, T_g marks the transition from glass to rubber.

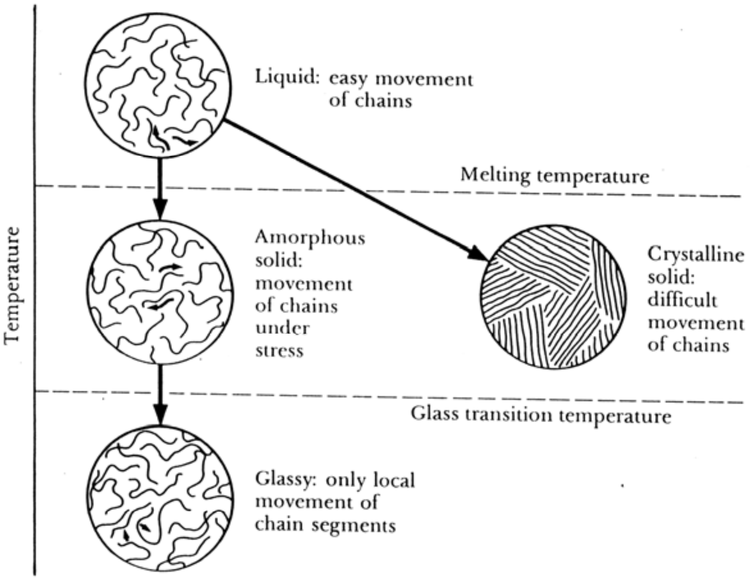
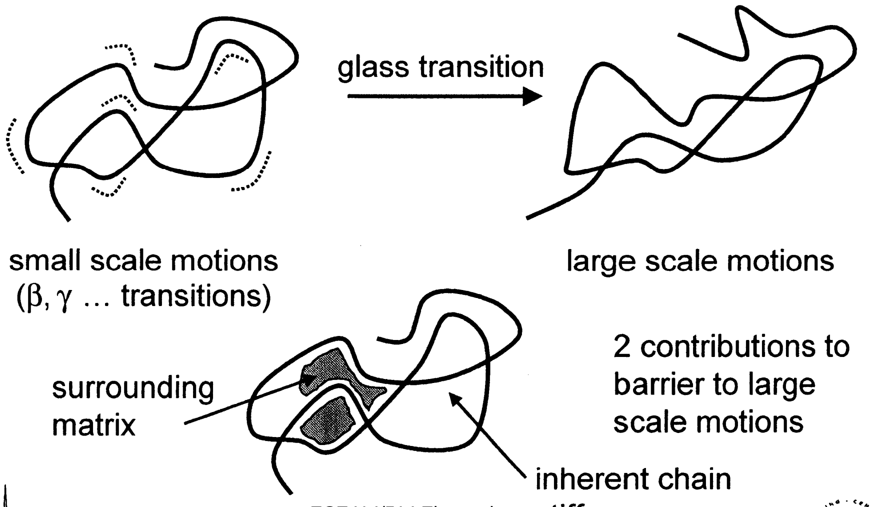


FIG. 15-13 The effect of temperature on the structure and behavior of thermoplastic polymers.

Origin of Glass Transition



glass transition

small scale motions
(β, γ … transitions)

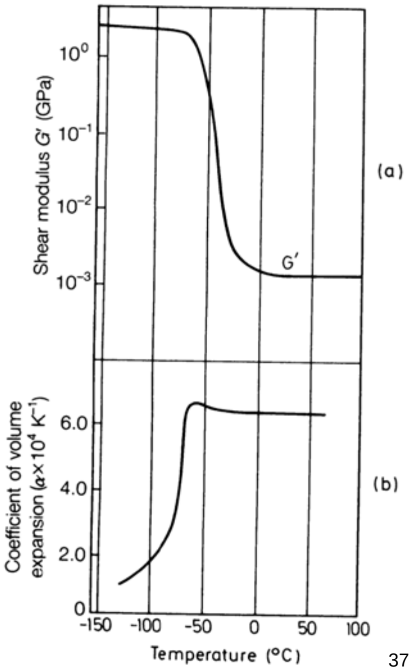
large scale motions

surrounding
matrix

2 contributions to
barrier to large
scale motions

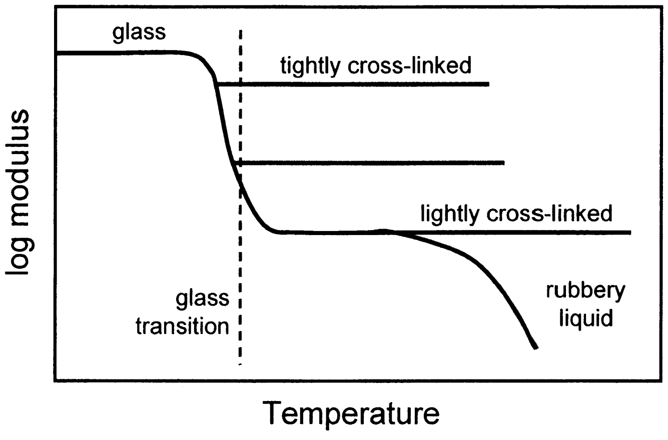
inherent chain
stiffness

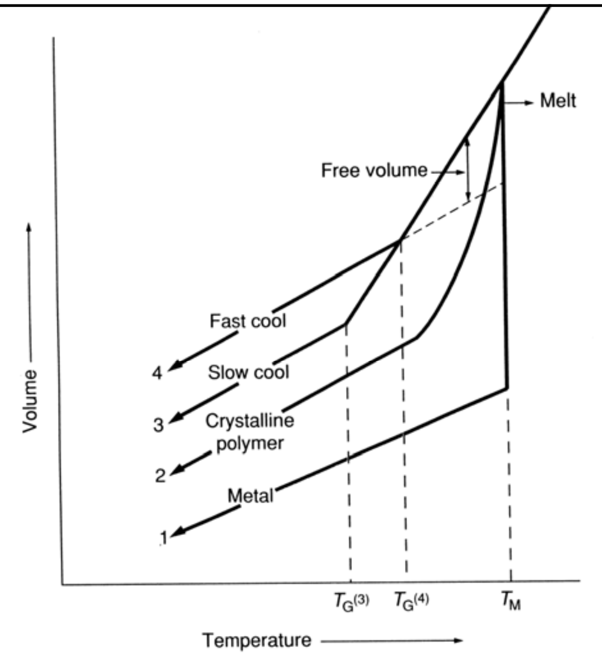
T_g effects



2.12 The glass–rubber transition in polyisobutylene:

Effect of Cross-linking





-12 Volume change as a function of temperature in (1) metals, (2) partially crystalline polymers, (3) amorphous polymers cooled at low rates, and, (4) amorphous polymers cooled at high rates.

FIGURE 7.14 Solidification and cooling of noncrystalline and partly crystalline thermoplastics showing change in specific volume with temperature (schematic). T_g is the glass transition temperature and T_m is the melting temperature. Noncrystalline thermoplastic cools along line *ABCD*, where *A* = liquid, *B* = highly viscous liquid, *C* = supercooled liquid (rubbery), and *D* = glassy solid (hard and brittle). Partly crystalline thermoplastic cools along line *ABEF*, where *E* = solid crystalline regions in supercooled liquid matrix and *F* = solid crystalline regions in glassy matrix.

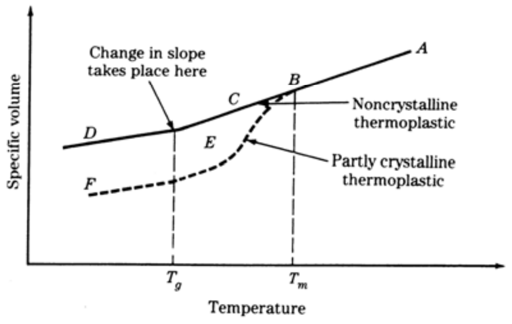
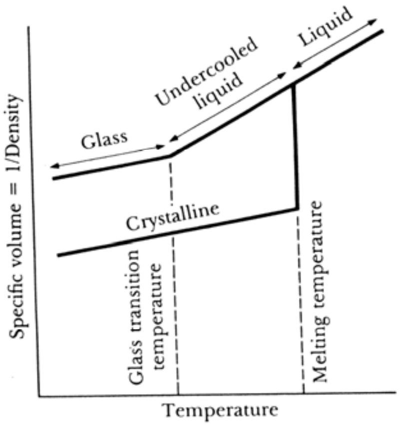


TABLE 7.1 **Glass Transition Temperature T_g*, °C, for Some Thermoplastics**

Polyethylene	−110	(nominal)
Polypropylene	−18	(nominal)
Polyvinyl acetate	29	
Polyvinyl chloride	82	
Polystyrene	75–100	
Polymethyl methacrylate	72	

* Note that the T_g of a thermoplastic is not a physical constant like the melting temperature of a crystalline solid but depends to some extent on variables such as degree of crystallinity, average molecular weight of the polymer chains, and rate of cooling of the thermoplastic.



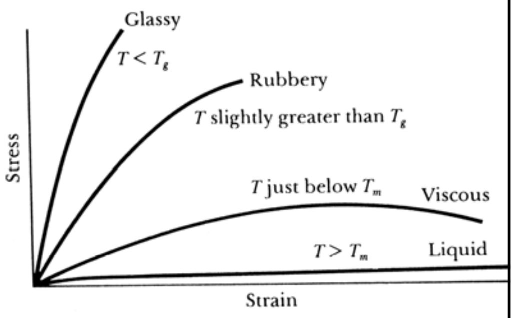
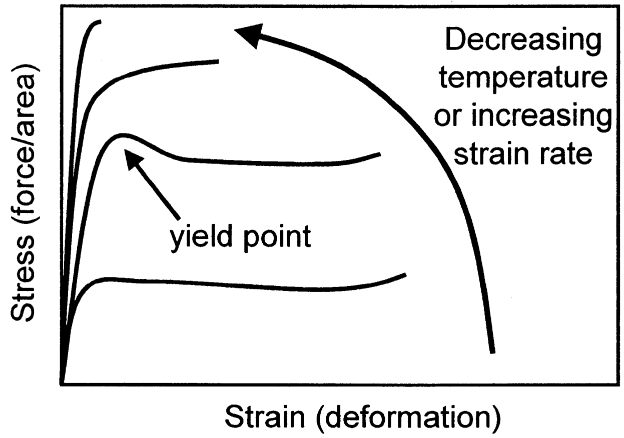


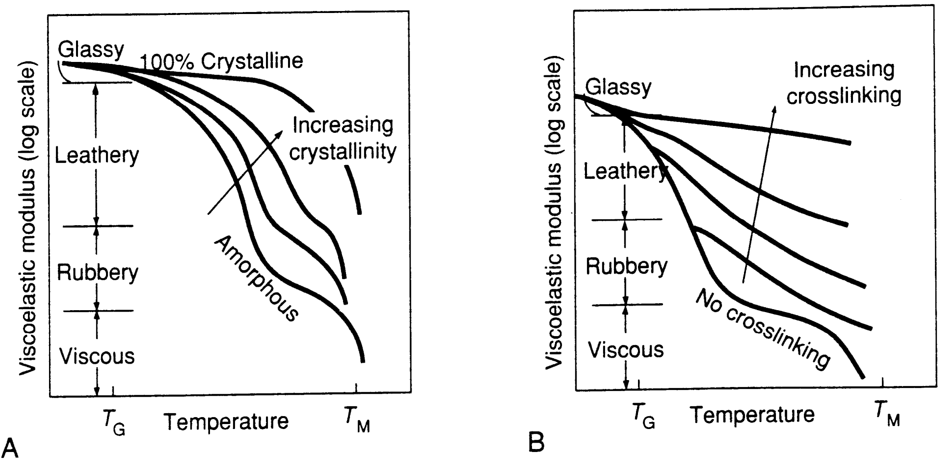
FIG. 15-14 The effect of temperature on the stress-strain behavior of the thermoplastic polymer.

FIG. 15-15 The relationship between the specific volume and the temperature of the polymer shows the melting and glass transition temperatures.

Plastic Deformation



"Time-temperature superposition"



Typical temperature-dependent changes in the viscoelastic modulus of long-chain polymers. (A) Effect of degree of crystallinity. (B) Effect of extent of crosslinking. From S. Kalpakjian, *Manufacturing Processes for Engineering Materials*, 2nd ed., Addison–Wesley, Reading, MA (1991).

Thermoset (epoxy) properties

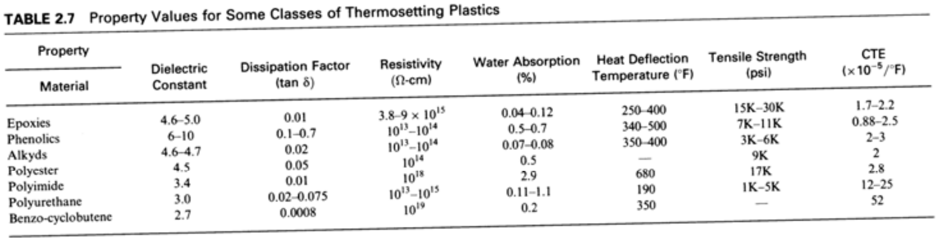


TABLE 2.7 Property Values for Some Classes of Thermosetting Plastics

Property / Material	Dielectric Constant	Dissipation Factor (tan δ)	Resistivity (Ω-cm)	Water Absorption (%)	Heat Deflection Temperature (°F)	Tensile Strength (psi)	CTE ($\times 10^{-5}$/°F)
Epoxies	4.6–5.0	0.01	3.8–9×10^{15}	0.04–0.12	250–400	15K–30K	1.7–2.2
Phenolics	6–10	0.1–0.7	10^{13}–10^{14}	0.5–0.7	340–500	7K–11K	0.88–2.5
Alkyds	4.6–4.7	0.02	10^{13}–10^{14}	0.07–0.08	350–400	3K–6K	2–3
Polyester	4.5	0.05	10^{14}	0.5	—	9K	2
Polyimide	3.4	0.01	10^{18}	2.9	680	17K	2.8
Polyurethane	3.0	0.02–0.075	10^{13}–10^{15}	0.11–1.1	190	1K–5K	12–25
Benzo-cyclobutene	2.7	0.0008	10^{19}	0.2	350	—	52

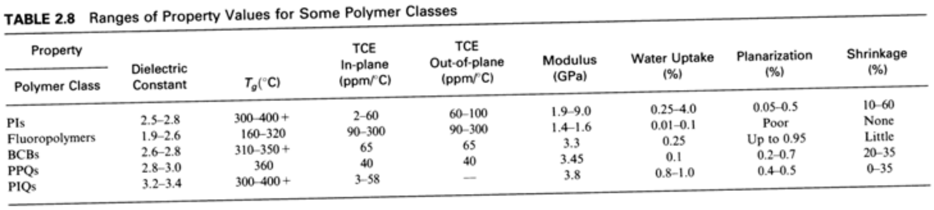


TABLE 2.8 Ranges of Property Values for Some Polymer Classes

Property / Polymer Class	Dielectric Constant	T_g(°C)	TCE In-plane (ppm/°C)	TCE Out-of-plane (ppm/°C)	Modulus (GPa)	Water Uptake (%)	Planarization (%)	Shrinkage (%)
PIs	2.5–2.8	300–400 +	2–60	60–100	1.9–9.0	0.25–4.0	0.05–0.5	10–60
Fluoropolymers	1.9–2.6	160–320	90–300	90–300	1.4–1.6	0.01–0.1	Poor	None
BCBs	2.6–2.8	310–350 +	65	65	3.3	0.25	Up to 0.95	Little
PPQs	2.8–3.0	360	40	40	3.45	0.1	0.2–0.7	20–35
PIQs	3.2–3.4	300–400 +	3–58	—	3.8	0.8–1.0	0.4–0.5	0–35

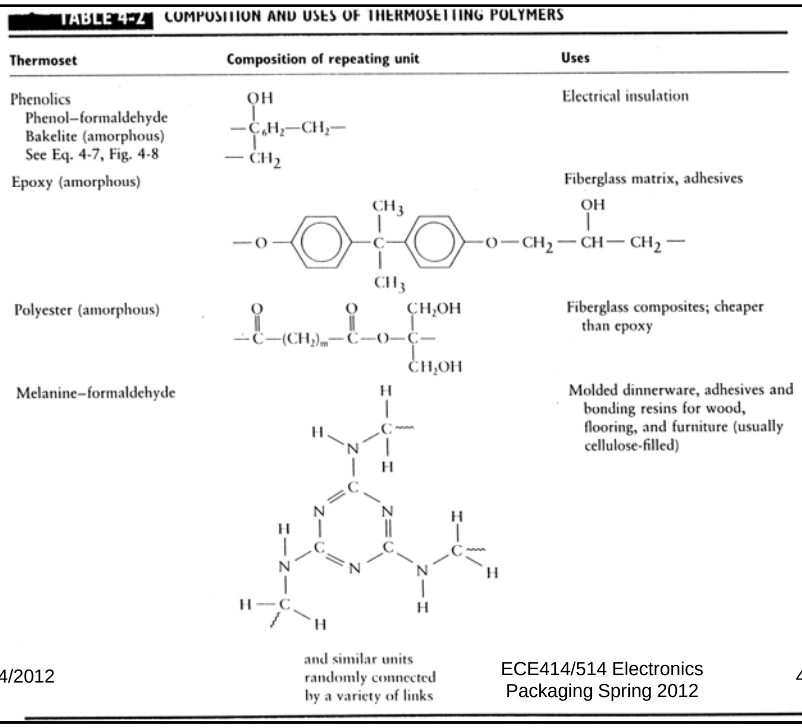
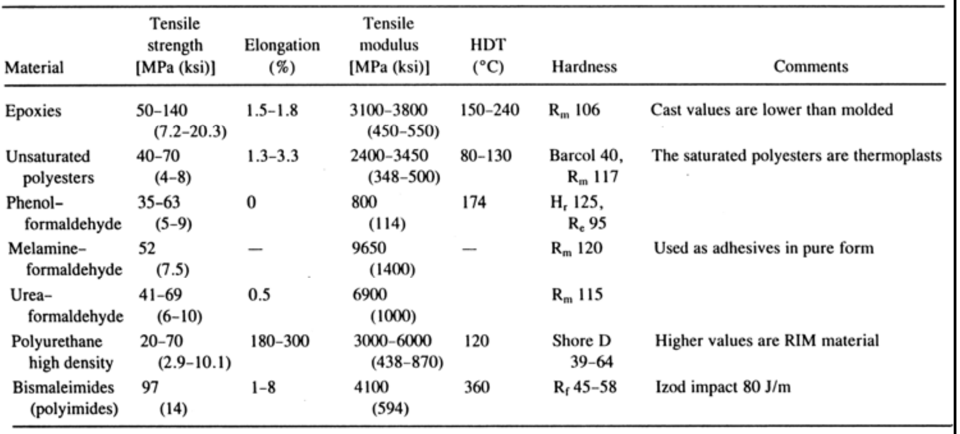


TABLE 4-2 COMPOSITION AND USES OF THERMOSETTING POLYMERS

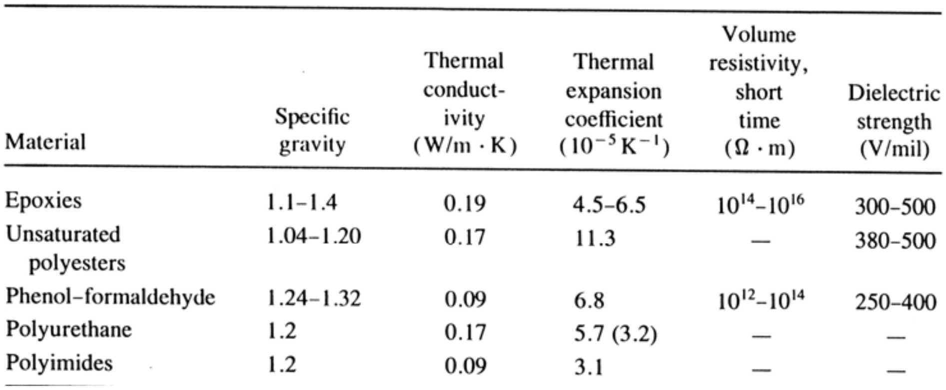
Thermoset	Composition of repeating unit	Uses
Phenolics Phenol–formaldehyde Bakelite (amorphous) See Eq. 4-7, Fig. 4-8	$-\underset{\underset{-CH_2}{\vert}}{\overset{\overset{OH}{\vert}}{C_6H_2}}-CH_2-$	Electrical insulation
Epoxy (amorphous)		Fiberglass matrix, adhesives
Polyester (amorphous)	$-\overset{\overset{O}{\Vert}}{C}-(CH_2)_m-\overset{\overset{O}{\Vert}}{C}-O-\underset{\underset{CH_2OH}{\vert}}{\overset{\overset{CH_2OH}{\vert}}{C}}-$	Fiberglass composites; cheaper than epoxy
Melanine–formaldehyde	and similar units randomly connected by a variety of links	Molded dinnerware, adhesives and bonding resins for wood, flooring, and furniture (usually cellulose-filled)

Table 8.8 Typical Mechanical Properties of Selected Thermoset Polymers at Room Temperature



Material	Tensile strength [MPa (ksi)]	Elongation (%)	Tensile modulus [MPa (ksi)]	HDT (°C)	Hardness	Comments
Epoxies	50–140 (7.2–20.3)	1.5–1.8	3100–3800 (450–550)	150–240	R_m 106	Cast values are lower than molded
Unsaturated polyesters	40–70 (4–8)	1.3–3.3	2400–3450 (348–500)	80–130	Barcol 40, R_m 117	The saturated polyesters are thermoplasts
Phenol–formaldehyde	35–63 (5–9)	0	800 (114)	174	H_r 125, R_e 95	
Melamine–formaldehyde	52 (7.5)	—	9650 (1400)	—	R_m 120	Used as adhesives in pure form
Urea–formaldehyde	41–69 (6–10)	0.5	6900 (1000)		R_m 115	
Polyurethane high density	20–70 (2.9–10.1)	180–300	3000–6000 (438–870)	120	Shore D 39–64	Higher values are RIM material
Bismaleimides (polyimides)	97 (14)	1–8	4100 (594)	360	R_f 45–58	Izod impact 80 J/m

Table 8.9 Typical Physical Properties of Selected Thermosets



Material	Specific gravity	Thermal conductivity (W/m · K)	Thermal expansion coefficient (10^{-5} K^{-1})	Volume resistivity, short time (Ω · m)	Dielectric strength (V/mil)
Epoxies	1.1–1.4	0.19	4.5–6.5	10^{14}–10^{16}	300–500
Unsaturated polyesters	1.04–1.20	0.17	11.3	—	380–500
Phenol–formaldehyde	1.24–1.32	0.09	6.8	10^{12}–10^{14}	250–400
Polyurethane	1.2	0.17	5.7 (3.2)	—	—
Polyimides	1.2	0.09	3.1	—	—

Thermoplastics

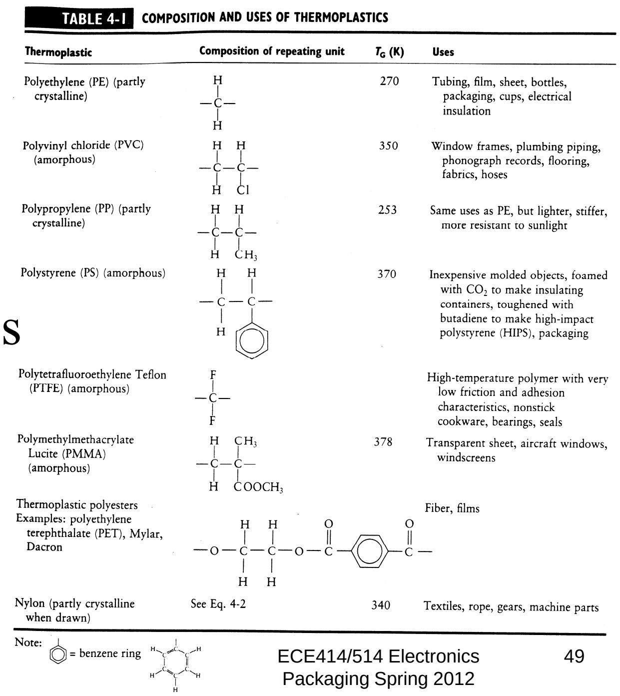


TABLE 4-1 COMPOSITION AND USES OF THERMOPLASTICS

Thermoplastic	Composition of repeating unit	T_G (K)	Uses
Polyethylene (PE) (partly crystalline)	$-\overset{H}{\underset{H}{C}}-$	270	Tubing, film, sheet, bottles, packaging, cups, electrical insulation
Polyvinyl chloride (PVC) (amorphous)	$-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{Cl}{C}}-$	350	Window frames, plumbing piping, phonograph records, flooring, fabrics, hoses
Polypropylene (PP) (partly crystalline)	$-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{CH_3}{C}}-$	253	Same uses as PE, but lighter, stiffer, more resistant to sunlight
Polystyrene (PS) (amorphous)		370	Inexpensive molded objects, foamed with CO_2 to make insulating containers, toughened with butadiene to make high-impact polystyrene (HIPS), packaging
Polytetrafluoroethylene Teflon (PTFE) (amorphous)	$-\overset{F}{\underset{F}{C}}-$		High-temperature polymer with very low friction and adhesion characteristics, nonstick cookware, bearings, seals
Polymethylmethacrylate Lucite (PMMA) (amorphous)	$-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{COOCH_3}{C}}-$	378	Transparent sheet, aircraft windows, windscreens
Thermoplastic polyesters Examples: polyethylene terephthalate (PET), Mylar, Dacron			Fiber, films
Nylon (partly crystalline when drawn)	See Eq. 4-2	340	Textiles, rope, gears, machine parts

Note: = benzene ring

Polyimide & silicone rubber are thermoplastics

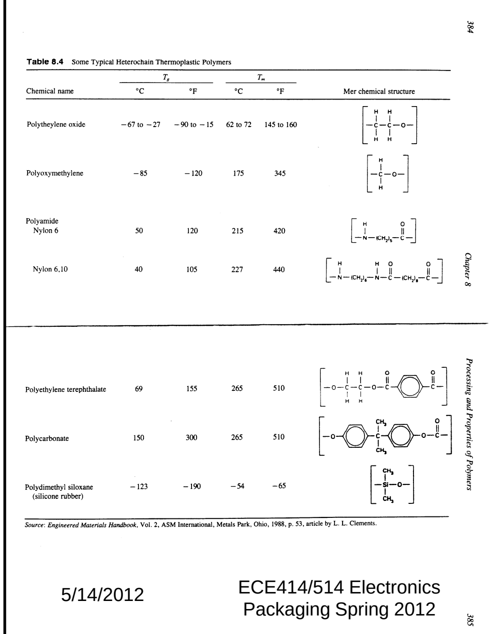


Table 8.4 Some Typical Heterochain Thermoplastic Polymers

Chemical name	T_g		T_m		Mer chemical structure
	°C	°F	°C	°F	
Polytheylene oxide	−67 to −27	−90 to −15	62 to 72	145 to 160	$\left[-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-O-\right]$
Polyoxymethylene	−85	−120	175	345	$\left[-\overset{H}{\underset{H}{C}}-O-\right]$
Polyamide Nylon 6	50	120	215	420	$\left[-\overset{H}{N}-(CH_2)_5-\overset{O}{\overset{\|}{C}}-\right]$
Nylon 6,10	40	105	227	440	$\left[-\overset{H}{N}-(CH_2)_6-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-\right]$
Polyethylene terephthalate	69	155	265	510	
Polycarbonate	150	300	265	510	
Polydimethyl siloxane (silicone rubber)	−123	−190	−54	−65	$\left[-\overset{CH_3}{\underset{CH_3}{Si}}-O-\right]$

Source: *Engineered Materials Handbook*, Vol. 2, ASM International, Metals Park, Ohio, 1988, p. 53, article by L. L. Clements.

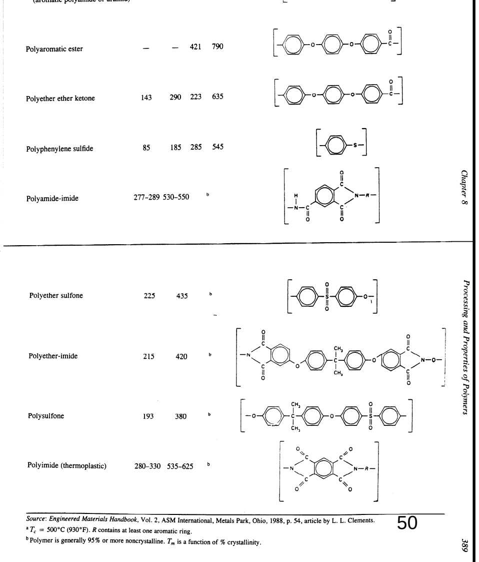


Table 8.5 Thermoplastic Polymers for High-Temperature Service

Chemical name	T_g		T_m		Mer chemical structure
	°C	°F	°C	°F	
Poly(*p*-phenylene terephthalamide) (aromatic polyamide or aramid)	375	705	~640[a]	~1185	
Polyaromatic ester	—	—	421	790	
Polyether ether ketone	143	290	223	635	
Polyphenylene sulfide	85	185	285	545	
Polyamide-imide	277–289	530–550	[b]		
Polyether sulfone	225	435	[b]		
Polyether-imide	215	420	[b]		
Polysulfone	193	380	[b]		
Polyimide (thermoplastic)	280–330	535–625	[b]		

Source: *Engineered Materials Handbook*, Vol. 2, ASM International, Metals Park, Ohio, 1988, p. 54, article by L. L. Clements.

[a] T_c = 500°C (930°F). *R* contains at least one aromatic ring.

[b] Polymer is generally 95% or more noncrystalline. T_m is a function of % crystallinity.

Table 8.6 Typical Mechanical Properties of Selected Thermoplastic Polymers at Room Temperature

Material	Tensile strength [MPa (ksi)]	Elongation (%)	Tensile modulus [MPa (ksi)]	Hardness	Izod impact energy [J (ft-lb)]	HDT (°C)[a]
Polyethylene						
High density	40–44 (3–5)	21–35	15–100 (100–200)	700–1400 R_r	65 (1–5)	1.4–6.8
Low density	7–21 (1–3)	50–800	100–250 (14.5–36.2)	R_r 10	21.6–33.7 (16–25)	—
Polypropylene	30–40 (4.5–5.8)	150–600	1150–1550 (166–225)	R_r 90	1.35–14.8 (1–11)	49–60
Polystyrene	33–55 (5.1–8.0)	1–4	2400–3350 (348–486)	R_r 75	0.15–0.54 (0.2–0.4)	76–94
Polyvinyl chloride	35–63 (5–9)	2–30	2000–4200 (286–600)	R_r 115	1.0–2.7 (0.7–2.0)	60–77
ABS	35–48 (5–7)	15–80	1750–2500 (250–357)	R_r 90–110	5.4–10.8 (4–8)	88–107
Polyamides						
Nylon 6,6	84 (12)	60–100	2070–3245 (300–470)	R_r 118	1.35–2.7 (1–2)	79–93
Nylon 6,12	62 (8.8)	150–340	2100 (3000)	R_r 114	1.35–2.7 (1–2)	58
Polycarbonates	63 (9)	110	2400 (348)	R_m 70–118	16–22 (11.7–16.2)	132
PMMA, acrylic	55–75 (8–10.9)	5	2400–3100 (348–450)	R_r 130	0.68 (0.5)	—
Polyesters	56 (8)	300	2400 (348)	R_m 117	1.63 (1.2)	50–85
Acetals						
Homopolymer	69 (10)	50	3588 (520)	R_m 92	1.89 (1.4)	154
Copolymer (celcon)	62 (9)	60	3105 (450)	R_m 85	1.75 (1.3)	128
Polyimides	97 (14)	8	2070 (300)	R_m 97	2.0 (1.5)	154
Polysulfones	70.3 (10.2)	5–6	2482 (360)	R_m 69	1.75 (1.3)	192
Poly ether ketone (PEEK)	100 (14.5)	>40	3900 (565)	—	2.15 (1.6)	1.67
Polyethylene terephthalate	45–145 (6.5–21.0)		2300–10300 (330–1500)	R_r 120	0.21–2.0 (0.4–1.5)	50–210
Polyvinylidene chloride (PVDC)	19 (2.8)	350	345–552 (50–80)	R_m 60–65	0.17–1.35 (0.13–1.0)	54–65

Table 8.7 Typical Physical Properties of Selected Thermoplasts

Material	Specific gravity	Thermal conductivity (W/m·K)	Thermal expansion coefficient [10^{-5}K^{-1} (10^{-5}°F^{-1})]	Volume resistivity short time[a] (Ω·m)	Dielectric strength[b] [V/cm (V/mil)]
Polyethylene					
High density	0.96	0.44	11–13 (6.1–7.2)	10^{15}–10^{16}	200–190 (510–480)
Low density	0.92	0.35	13–20 (7.2–11.1)	10^{15}–10^{16}	390–180 (990–460)
Polypropylene	0.9	0.12–0.14	6–10 (1.0–5.5)	10^{15}	260–200 (660–510)
Polyvinyl chloride	1.4	0.16	9–18 (5–10)	10^{13}	240 (610)
Nylon 6,6	1.14	0.24	8–9 (4.4–5)	10^{13}	160 (410)
Polycarbonates	1.2	0.20	6.8 (3.8)	2×10^{14}	160 (410)
PMMA (acrylic)	1.18	0.19	4.5 (2.5)	10^{13}–10^{14}	200–160 (510–410)
Acetal copolymer	1.4	0.23	8–10 (4.4–5.5)	—	—
Polyimides	1.43	—	5.4–8 (3–4.5)	10^{14}–10^{15}	220 (560)

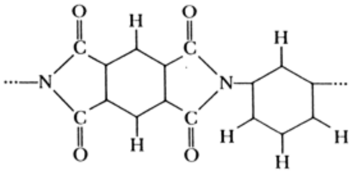
[a] Volume resistivity increases with time.

[b] From *Engineered Materials Handbook*, Vol. 2, ASM International, Metals Park, Ohio, 1988, p. 469.

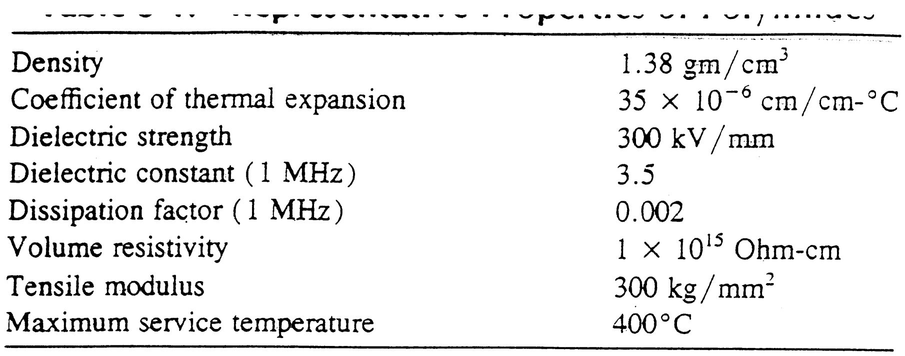
TABLE 2.6 Properties of Some Thermoplastic Polymers

Property Material	Dielectric Constant	Bulk Resistivity (Ω-cm)	Loss Tangent	Heat Distortion Temperature (°C)	Linear Expansion ($\times 10^5$/°F)	Tensile Strength (psi)
Silicone polyimide	3.0	10^{15}–10^{17}	0.007	300–475	40	300
Polystyrene	2.4–3.1	10^{18}	0.0002	180	4	4000
Polyetheylene	2.3	10^{16}	0.0005	—	9.5	3000
Fluorocarbon	2.1	10^{18}	0.0003	250	5.5	600

Polyimide

Polymer	Structure	Tensile Strength (psi)	% Elongation	Modulus of Elasticity (ksi)	Density (g/cm^3)
Polyimide		11,000–17,000	8–10	300	1.39

Polyimide properties



Density	1.38 gm/cm^3
Coefficient of thermal expansion	35×10^{-6} cm/cm-°C
Dielectric strength	300 kV/mm
Dielectric constant (1 MHz)	3.5
Dissipation factor (1 MHz)	0.002
Volume resistivity	1×10^{15} Ohm-cm
Tensile modulus	300 kg/mm^2
Maximum service temperature	400°C

Chemically cured (film) PI

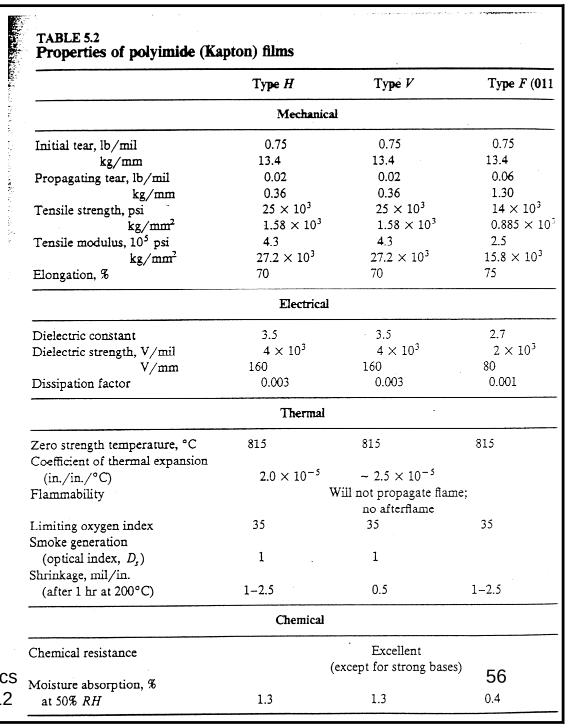
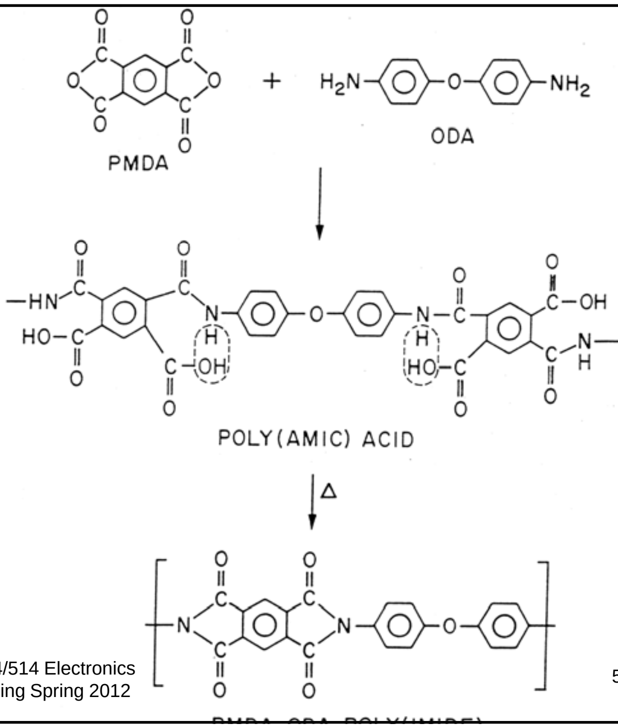


TABLE 5.2
Properties of polyimide (Kapton) films

	Type *H*	Type *V*	Type *F* (011
Mechanical			
Initial tear, lb/mil	0.75	0.75	0.75
kg/mm	13.4	13.4	13.4
Propagating tear, lb/mil	0.02	0.02	0.06
kg/mm	0.36	0.36	1.30
Tensile strength, psi	25×10^3	25×10^3	14×10^3
kg/mm^2	1.58×10^3	1.58×10^3	0.885×10^3
Tensile modulus, 10^5 psi	4.3	4.3	2.5
kg/mm^2	27.2×10^3	27.2×10^3	15.8×10^3
Elongation, %	70	70	75
Electrical			
Dielectric constant	3.5	3.5	2.7
Dielectric strength, V/mil	4×10^3	4×10^3	2×10^3
V/mm	160	160	80
Dissipation factor	0.003	0.003	0.001
Thermal			
Zero strength temperature, °C	815	815	815
Coefficient of thermal expansion (in./in./°C)	2.0×10^{-5}	$\sim 2.5 \times 10^{-5}$	
Flammability		Will not propagate flame; no afterflame	
Limiting oxygen index	35	35	35
Smoke generation (optical index, D_s)	1	1	
Shrinkage, mil/in. (after 1 hr at 200°C)	1–2.5	0.5	1–2.5
Chemical			
Chemical resistance		Excellent (except for strong bases)	
Moisture absorption, % at 50% *RH*	1.3	1.3	0.4

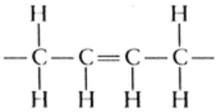
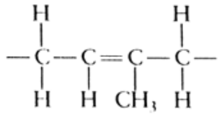
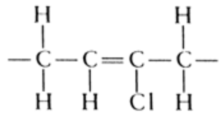
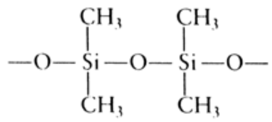
Thermally cured PMDA-ODA

Interface properties:
Metal on PI
PI on metal



Elastomers (category & application)

COMPOSITION AND USES OF ELASTOMERS (RUBBERS)

Elastomer	Composition of repeating unit	Uses
Polybutadiene	 $-\underset{H}{\overset{H}{C}}-\underset{H}{C}=\underset{H}{C}-\underset{H}{\overset{H}{C}}-$	Tires, moldings; amorphous except when stretched
Polyisoprene (natural rubber)	 $-\underset{H}{\overset{H}{C}}-\underset{H}{C}=\underset{CH_3}{C}-\underset{H}{\overset{H}{C}}-$	Tires, gaskets; amorphous except when stretched
Neoprene	 $-\underset{H}{\overset{H}{C}}-\underset{H}{C}=\underset{Cl}{C}-\underset{H}{\overset{H}{C}}-$	Oil-resistant rubber used for seals
Silicone rubber *	 $-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-$	Thermal and electrical insulation components and coatings, foam rubber

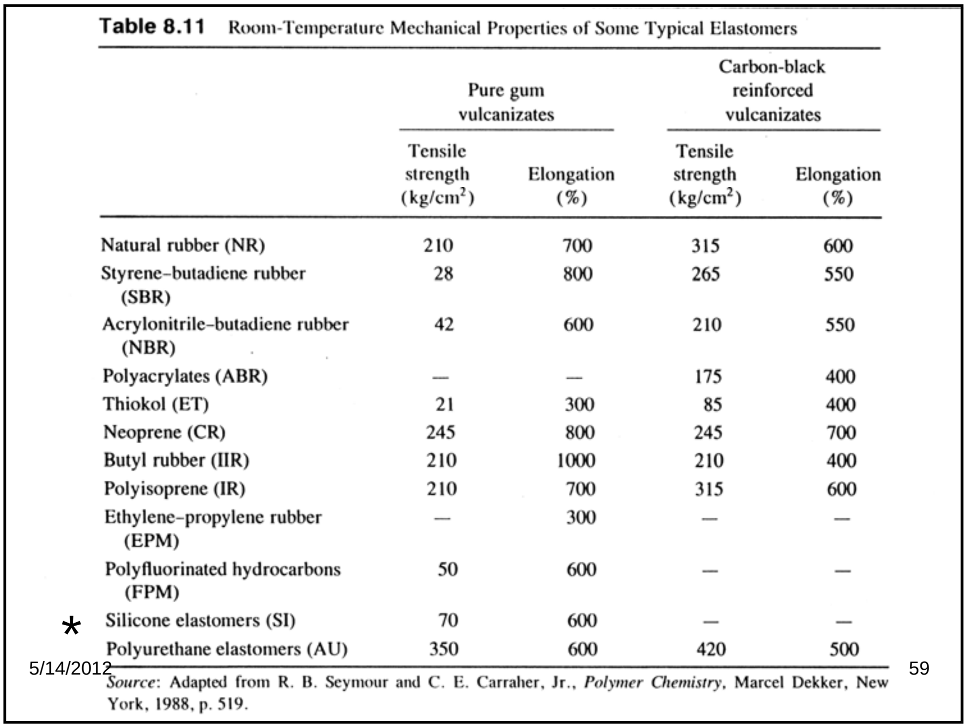


Table 8.11 Room-Temperature Mechanical Properties of Some Typical Elastomers

	Pure gum vulcanizates		Carbon-black reinforced vulcanizates	
	Tensile strength (kg/cm^2)	Elongation (%)	Tensile strength (kg/cm^2)	Elongation (%)
Natural rubber (NR)	210	700	315	600
Styrene–butadiene rubber (SBR)	28	800	265	550
Acrylonitrile–butadiene rubber (NBR)	42	600	210	550
Polyacrylates (ABR)	—	—	175	400
Thiokol (ET)	21	300	85	400
Neoprene (CR)	245	800	245	700
Butyl rubber (IIR)	210	1000	210	400
Polyisoprene (IR)	210	700	315	600
Ethylene–propylene rubber (EPM)	—	300	—	—
Polyfluorinated hydrocarbons (FPM)	50	600	—	—
* Silicone elastomers (SI)	70	600	—	—
Polyurethane elastomers (AU)	350	600	420	500

Source: Adapted from R. B. Seymour and C. E. Carraher, Jr., *Polymer Chemistry*, Marcel Dekker, New York, 1988, p. 519.

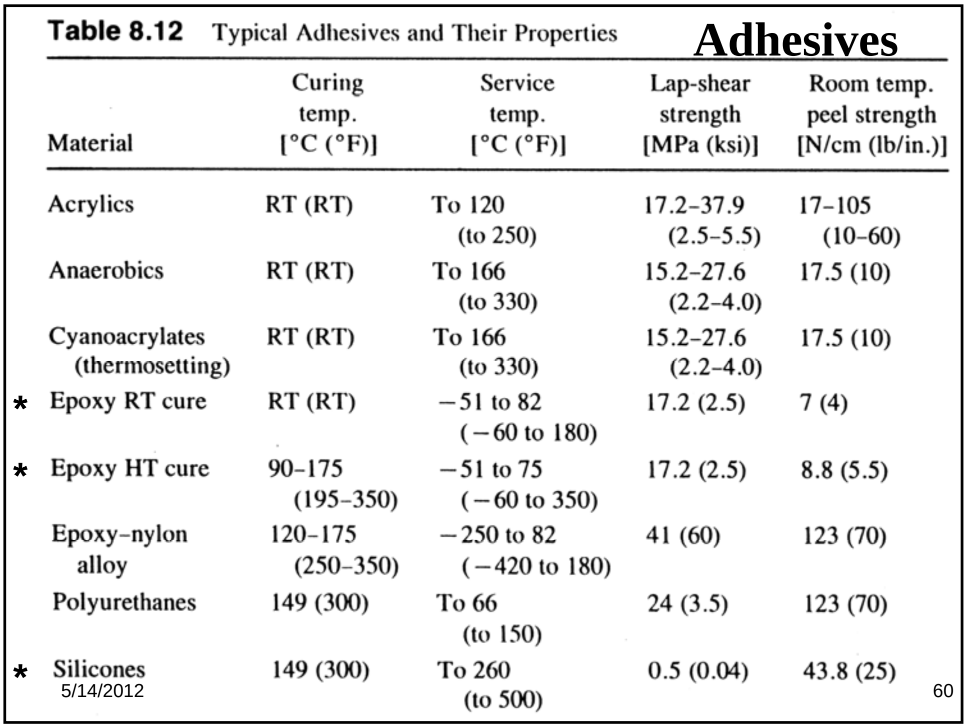


Table 8.12 Typical Adhesives and Their Properties

Adhesives

Material	Curing temp. [°C (°F)]	Service temp. [°C (°F)]	Lap-shear strength [MPa (ksi)]	Room temp. peel strength [N/cm (lb/in.)]
Acrylics	RT (RT)	To 120 (to 250)	17.2–37.9 (2.5–5.5)	17–105 (10–60)
Anaerobics	RT (RT)	To 166 (to 330)	15.2–27.6 (2.2–4.0)	17.5 (10)
Cyanoacrylates (thermosetting)	RT (RT)	To 166 (to 330)	15.2–27.6 (2.2–4.0)	17.5 (10)
* Epoxy RT cure	RT (RT)	−51 to 82 (−60 to 180)	17.2 (2.5)	7 (4)
* Epoxy HT cure	90–175 (195–350)	−51 to 75 (−60 to 350)	17.2 (2.5)	8.8 (5.5)
Epoxy–nylon alloy	120–175 (250–350)	−250 to 82 (−420 to 180)	41 (60)	123 (70)
Polyurethanes	149 (300)	To 66 (to 150)	24 (3.5)	123 (70)
* Silicones	149 (300)	To 260 (to 500)	0.5 (0.04)	43.8 (25)

Encapsulants

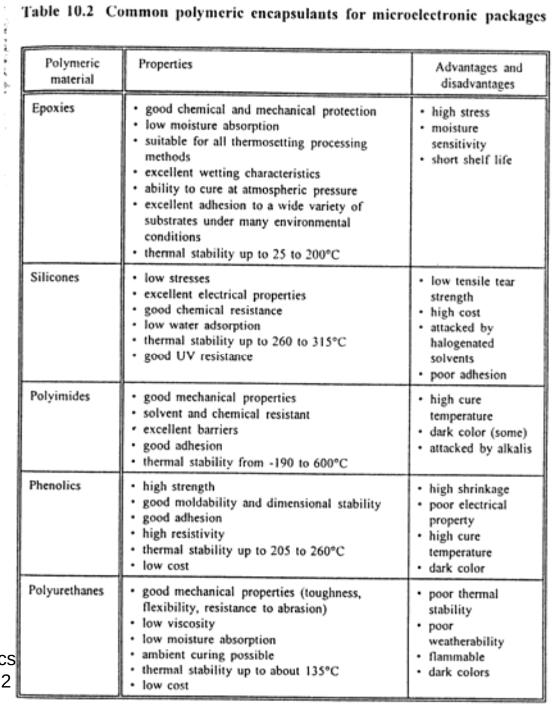
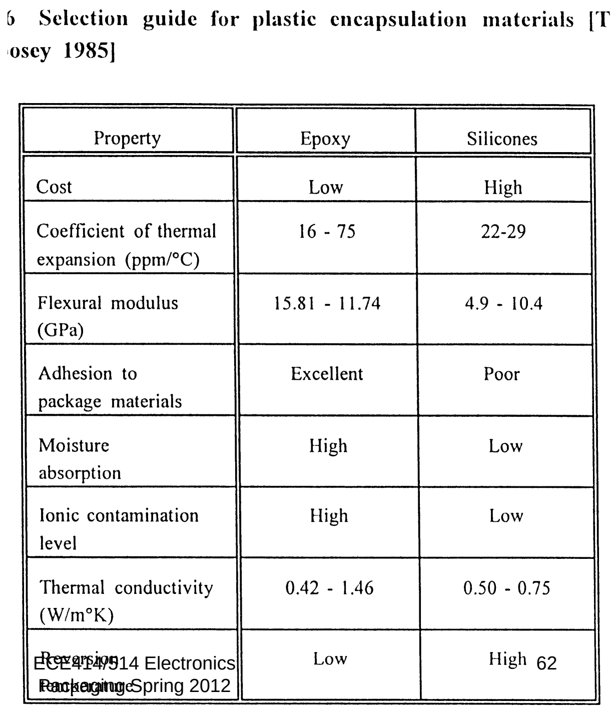


Table 10.2 Common polymeric encapsulants for microelectronic packages

Polymeric material	Properties	Advantages and disadvantages
Epoxies	• good chemical and mechanical protection • low moisture absorption • suitable for all thermosetting processing methods • excellent wetting characteristics • ability to cure at atmospheric pressure • excellent adhesion to a wide variety of substrates under many environmental conditions • thermal stability up to 25 to 200°C	• high stress • moisture sensitivity • short shelf life
Silicones	• low stresses • excellent electrical properties • good chemical resistance • low water adsorption • thermal stability up to 260 to 315°C • good UV resistance	• low tensile tear strength • high cost • attacked by halogenated solvents • poor adhesion
Polyimides	• good mechanical properties • solvent and chemical resistant • excellent barriers • good adhesion • thermal stability from -190 to 600°C	• high cure temperature • dark color (some) • attacked by alkalis
Phenolics	• high strength • good moldability and dimensional stability • good adhesion • high resistivity • thermal stability up to 205 to 260°C • low cost	• high shrinkage • poor electrical property • high cure temperature • dark color
Polyurethanes	• good mechanical properties (toughness, flexibility, resistance to abrasion) • low viscosity • low moisture absorption • ambient curing possible • thermal stability up to about 135°C • low cost	• poor thermal stability • poor weatherability • flammable • dark colors

---



6 Selection guide for plastic encapsulation materials [T
osey 1985]

Property	Epoxy	Silicones
Cost	Low	High
Coefficient of thermal expansion (ppm/°C)	16 - 75	22-29
Flexural modulus (GPa)	15.81 - 11.74	4.9 - 10.4
Adhesion to package materials	Excellent	Poor
Moisture absorption	High	Low
Ionic contamination level	High	Low
Thermal conductivity (W/m°K)	0.42 - 1.46	0.50 - 0.75
Reversion resistance	Low	High

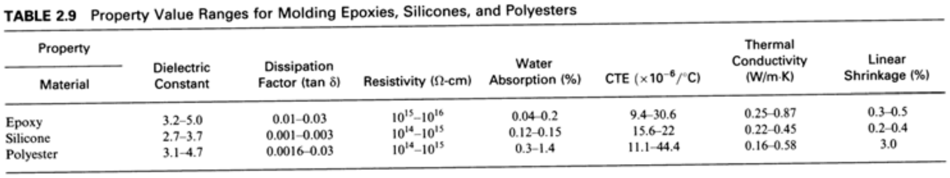


TABLE 2.9 Property Value Ranges for Molding Epoxies, Silicones, and Polyesters

Property / Material	Dielectric Constant	Dissipation Factor (tan δ)	Resistivity (Ω-cm)	Water Absorption (%)	CTE (×10^{-6}/°C)	Thermal Conductivity (W/m·K)	Linear Shrinkage (%)
Epoxy	3.2–5.0	0.01–0.03	10^{15}–10^{16}	0.04–0.2	9.4–30.6	0.25–0.87	0.3–0.5
Silicone	2.7–3.7	0.001–0.003	10^{14}–10^{15}	0.12–0.15	15.6–22	0.22–0.45	0.2–0.4
Polyester	3.1–4.7	0.0016–0.03	10^{14}–10^{15}	0.3–1.4	11.1–44.4	0.16–0.58	3.0

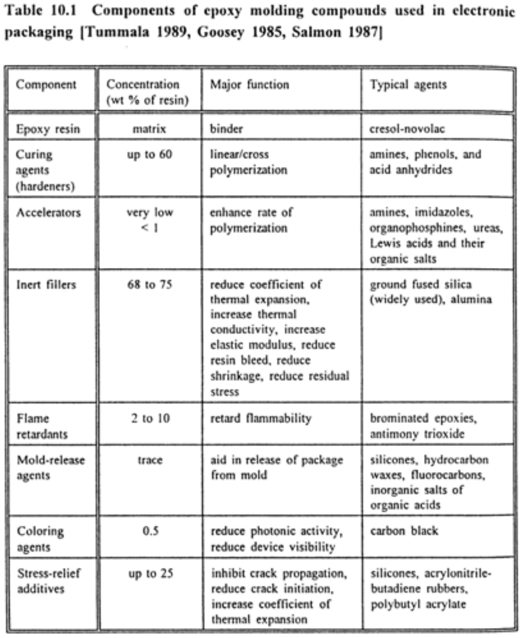


Table 10.1 Components of epoxy molding compounds used in electronic packaging [Tummala 1989, Goosey 1985, Salmon 1987]

Component	Concentration (wt % of resin)	Major function	Typical agents
Epoxy resin	matrix	binder	cresol-novolac
Curing agents (hardeners)	up to 60	linear/cross polymerization	amines, phenols, and acid anhydrides
Accelerators	very low < 1	enhance rate of polymerization	amines, imidazoles, organophosphines, ureas, Lewis acids and their organic salts
Inert fillers	68 to 75	reduce coefficient of thermal expansion, increase thermal conductivity, increase elastic modulus, reduce resin bleed, reduce shrinkage, reduce residual stress	ground fused silica (widely used), alumina
Flame retardants	2 to 10	retard flammability	brominated epoxies, antimony trioxide
Mold-release agents	trace	aid in release of package from mold	silicones, hydrocarbon waxes, fluorocarbons, inorganic salts of organic acids
Coloring agents	0.5	reduce photonic activity, reduce device visibility	carbon black
Stress-relief additives	up to 25	inhibit crack propagation, reduce crack initiation, increase coefficient of thermal expansion	silicones, acrylonitrile-butadiene rubbers, polybutyl acrylate

Assignment #7

Dally et al:

(1) 5.16
(2) 5.17
(3) 5.18
(4) 7.26

[Read Dally, Sections:

6.7 Plating
6.8 Solder mask
7.3 Soldering
7.5 Solder paste]

(5) Describe the composition of 70/30 Sn/Pb solder at room temperature following rapid cooling from the melt.

(6) List the five things you like the most about the course and the five things you dislike the most