

Chapter 4. Solid-State Properties of Polymers

No bulk polymer is completely crystalline

Semicrystalline polymers --- crystalline units are linked by unoriented chains

⇓ (morphology)

influence on physical, thermal & mechanical properties

4.1 Amorphous state

In the amorphous solid state,

chains assume unperturbed dimensions as in solution under θ conditions.

T_g : long-range segmental motions cease.

Below T_g : short-range motions can occur.

4.1.1 Chain entanglements and reptation

Entanglements --- important in viscoelastic properties, melt viscosity & mechanical properties such as stress relaxation, creep & craze formation

* Critical molecular weight

M_c : MW that forms stable chain entanglements

M_e (MW between entanglements) $M_c \approx 2M_e$

TABLE 4.1 ENTANGLEMENT MOLECULAR-WEIGHTS FOR LINEAR POLYMERS^a

Polymer	M_c	M_e
1,4-Polybutadiene	5,900	1,900
cis-Polyisoprene	10,000	5,800
Polyisobutylene	15,200	8,900
Polydimethylsiloxane	24,400	8,100
Poly(vinyl acetate)	24,500	12,000
Poly(methyl methacrylate)	27,500	5,900
Poly(α -methylstyrene)	28,000	13,500
Polystyrene	31,200	18,100

^a From Graessley.²

* Reptation

originally developed by de Gennes

movement as snakelike motion of the chain within a virtual tube

(See Fig. 4.2)

Reptation theory --- successful in developing a molecular theory for dynamics & viscoelastic properties of entangled polymers

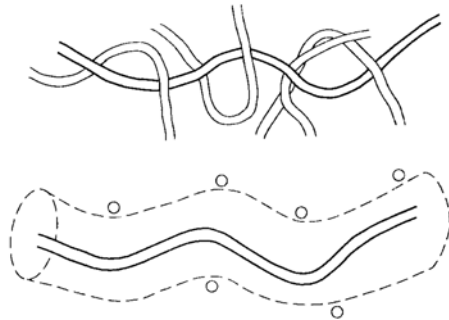


Figure 4.2. Reptation model of a polymer chain constrained in entangled network. A particular chain can be viewed as constrained to move within a virtual tube defined by neighboring entanglement sites. Circles pictured in the lower view represent cross sections of chains constituting the tube constraints. (Adapted with permission from J. Klein, *Nature*, **271**, 143 (1978). Copyright ©1978 by Macmillian Magazines Limited.)

4.1.2 Glass transition

T_g : transition temperature from the amorphous solid state to the melt state

공통적인 현상 : isoviscous state, isofree volume, isentropic state

Polymers with flexible backbones & small substituent groups ~ low T_g

" rigid backbones ~ high T_g

TABLE 4.2 REPRESENTATIVE VALUES OF THE GLASS-TRANSITION TEMPERATURE OF SOME AMORPHOUS POLYMERS

Polymer	T_g (°C)
Polydimethylsiloxane	-123
Poly(vinyl acetate)	28
Polystyrene	100
Poly(methyl methacrylate)	105
Polycarbonate	150
Polysulfone	190
Poly(2,6-dimethyl-1,4-phenylene oxide)	220

4.1.3. Secondary-relaxation processes

small-scale molecular motions

: limited motions of the main chain, rotations, vibrations

or flips of substituent groups.

"crankshaft rotation"

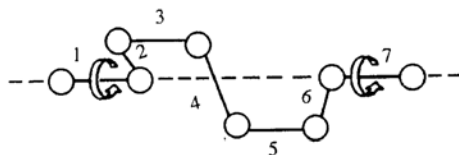


Figure 4.3. Schatzki model of crankshaft motion of a carbon-carbon backbone. The dashed line represents the virtual axis around which bonds 2-6 rotate.

4.2 Crystalline state

4.2.1 Ordering of polymer chains

Crystalline *lamellae* -- basic units of crystalline polymer morphology
(Polymers never crystallize to 100%)

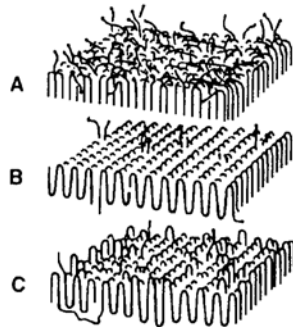


Figure 4.4. Three idealized models for chain folding in polymer crystallites. **A**, nonadjacent reentry; **B**, regular adjacent reentry; **C**, irregular adjacent reentry. (Reprinted from J. R. Fried, *Plast Eng.*, June, 1982, p. 52, with permission of the publisher.)

thickness of a typical crystallite : 10 - 20 nm

⇒ Each fold consists of 40 - 80 repeating units in case of PE.

Planar zigzag conformation : PE, syndiotactic vinyl polymers, PVAL, nylons

Helix conformation : PP, isotactic polymers, polyisobutylene

(PP : 3 monomer units form a single turn, i.e., a 3_1 helix)

Polymers crystallized from melt or concentrated solution

⇒ *spherulites* ("ball" or "globe") --- polycrystalline, 0.5 μm - mm size

Crystalline polymers exhibit both T_g & T_m

T_g : long-range segmental motions occur in the amorphous region

T_m : crystallites are destroyed & an amorphous, disordered melt is formed

For many polymers, $T_g \approx \frac{1}{2}$ or $\frac{2}{3}$ of T_m

TABLE 4.3 REPRESENTATIVE VALUES OF THERMAL TRANSITIONS FOR SEMICRYSTALLINE POLYMERS

Polymer	$T_g, ^\circ\text{C}$	$T_m, ^\circ\text{C}$
Polyethylene (high-density)	-120	135
Polycaprolactone	-60	61
Poly(vinylidene fluoride)	-45	172
Polyoxymethylene	-85	195
Poly(vinyl alcohol)	85	258
Poly(hexamethylene adipamide) (nylon-6,6)	49	265
Poly(ethylene terephthalate)	69	265

Crystallinity enhancement

. hydrogen bonds : nylon-6,6 ($T_m = 265^\circ\text{C}$) vs. PE ($T_m = 135^\circ\text{C}$)

. tacticity & geometric isomerism :

cis-PBD ($T_m = 2^\circ\text{C}$) vs. trans-PBD ($T_m = 145^\circ\text{C}$)

isotactic PS (crystalline) vs. atactic PS (amorphous)

4.2.2 Crystalline-melting temperature

Free energy of fusion per repeating unit,

$$\Delta G_u = \Delta H_u - T \Delta S_u$$

At equilibrium melting temperature, $\Delta G_u = 0$ (G of sol. = G of liq. at T_m)

$$\therefore T_m^0 = -\frac{\Delta H_u}{\Delta S_u}$$

TABLE 4.4 REPRESENTATIVE VALUES OF THE THERMODYNAMIC PARAMETERS FOR SOME SEMICRYSTALLINE AND CRYSTALLIZABLE POLYMERS

Polymer	T_m^0 °C	ΔH_u cal mol ⁻¹	ΔS_u cal K ⁻¹ mol ⁻¹
Polyethylene	146	960	2.3
Polyoxymethylene	180	1590	3.5
Polypropylene	200	1386	2.9
Poly(ethylene terephthalate)	280	6431	11.6
Polycarbonate ^a	335	6348	10.4

^a Solvent-induced crystallization.

T_m (observed melting temp.) < T_m^0 (equilibrium melting temp.)

Factors affecting the melting-point depression

- . kinetic effect of a finite heating or cooling rate
- . crystallite size (influenced by crystallization conditions
or by the presence of impurities)

. diluent (residual solvent or plasticizer)

: melting-point depression of high MW polymer by a diluent,

<--- Flory-Huggins theory

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \left(\frac{R}{\Delta H_u} \right) \left(\frac{V_u}{V_1} \right) (\phi_1 - \chi_{12} \phi_1^2)$$

where V_u : molar volume of repeating unit

V_1 : molar volume of diluent

ϕ_1 : volume fraction of diluent

4.2.3 Crystallization kinetics

Rate of crystallization affects the extent of crystallization

" depends on the crystallization temperature

ex) growth rate of spherulites in PET as a f'n of T

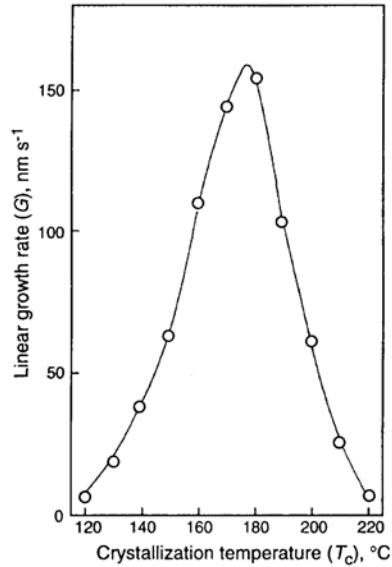


Figure 4.7. Plot of linear growth rate of spherulites in poly(ethylene terephthalate) (PET) as a function of temperature and at a pressure of 1 bar.⁸ The maximum growth rate is observed near 178°C. Values of T_g and T_m for PET are approximately 69° and 265°C, respectively.

The net rate of crystallization is zero at T_m (lamellae formation \cong destruction)

The large-scale segmental mobility required for chain folding ceases at T_g

$\implies T_g < T_{max} < T_m$ T_{max} : max. crystallization rate T

T_{max} --- optimum balance betw. chain mobility & lamellae growth independent of MW

$T_{max} \downarrow$ as MW \uparrow

Fractional crystallinity at time t

: Avrami equation, $\phi = 1 - \exp(-kt^n)$

where ϕ : fractional crystallinity

k : temperature-dependent growth rate parameter

n : temperature-independent nucleation index ($1 < n < 4$)

Measurement of fractional crystallinity

: IR, XRD, ρ measurement & calorimetric methods

. Density measurements, $\phi = \frac{\rho - \rho_a}{\rho_c - \rho_a}$

where ρ_c : density of totally crystalline sample

ρ_a : density of totally amorphous sample

TABLE 4.5 AMORPHOUS AND CRYSTALLINE DENSITIES

Polymer	ρ_a g cm ⁻³	ρ_c g cm ⁻³
Nylon 6	1.09	1.12-1.14
Nylon-6,6	1.09	1.13-1.145
Poly(ethylene terephthalate)	1.335	1.515
Poly(vinyl chloride)	1.385	1.44-1.53
Polycarbonate	1.196	1.316
Poly(<i>p</i> -phenylene sulfide)	1.32	1.43
Poly(2,6-dimethyl-1,4-phenylene oxide)	1.06	1.31

4.3 Thermal transitions and properties

4.3.1 Thermodynamic relationships

glass transition : second-order transition

2차 전이의 정의 : G (or μ) 의 T 에 대한 2계 미분이 불연속

V or H 의 T 에 대한 1계 미분이 불연속

cf.) 1차 전이(first-order transition) : G (or μ) 의 T 에 대한 1계 미분이 불연속

T 에 대한 V or H 자체가 불연속 (See Fig. 4.9)

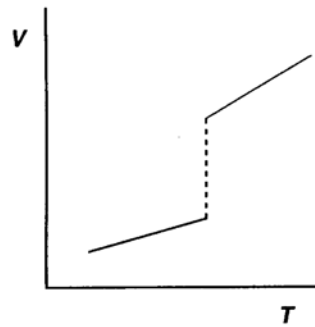


Figure 4.9. Thermodynamic first-order transition in volume at constant pressure.

$$dG = -S dT + V dp,$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S, \quad \left(\frac{\partial G}{\partial p}\right)_T = V$$

* Second-order transition

. Glass transition :

Ehrenfest second-order transition

Discontinuity in the second derivatives of the Gibbs free energy

. Experimental measurement of T_g

윗 식의 2 계 미분으로부터

$$-\left(\frac{\partial^2 G}{\partial T^2}\right)_p = \left(\frac{\partial S}{\partial T}\right)_p \quad \text{----- (A)}$$

$$\left(\frac{\partial^2 G}{\partial p^2}\right)_T = \left(\frac{\partial V}{\partial p}\right)_T \quad \text{----- (B)}$$

$$\left(\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial p}\right)_T\right)_p = \left(\frac{\partial V}{\partial T}\right)_p \quad \text{----- (C)}$$

From equation (A),

Entropy is not an experimentally measurable quantity.

Specific heat is easily measured by calorimetric techniques.

By using the relation between C_p and entropy,

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p = T \left(\frac{\partial S}{\partial T}\right)_p \quad \text{----} \quad dS = \frac{dQ}{T}, \quad dH = C_p dT, \quad dQ = dH \quad \text{at const } p.$$

$$\therefore -\left(\frac{\partial^2 G}{\partial T^2}\right)_p = -\frac{C_p}{T}$$

==> A second-order transition should occur as a discontinuity in C_p .

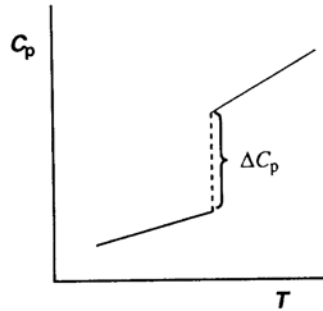


Figure 4.10. Thermodynamic second-order transition in specific heat at constant pressure.

From equations (B) & (C),

$$\beta = -\left(\frac{1}{V}\right) \left(\frac{\partial V}{\partial p}\right)_T \quad : \text{ isothermal compressibility coefficient}$$

$$\alpha = \left(\frac{1}{V}\right) \left(\frac{\partial V}{\partial T}\right)_p \quad : \text{ isobaric thermal-expansion coefficient}$$

Both coefficients may be obtained by dilatometric measurements.

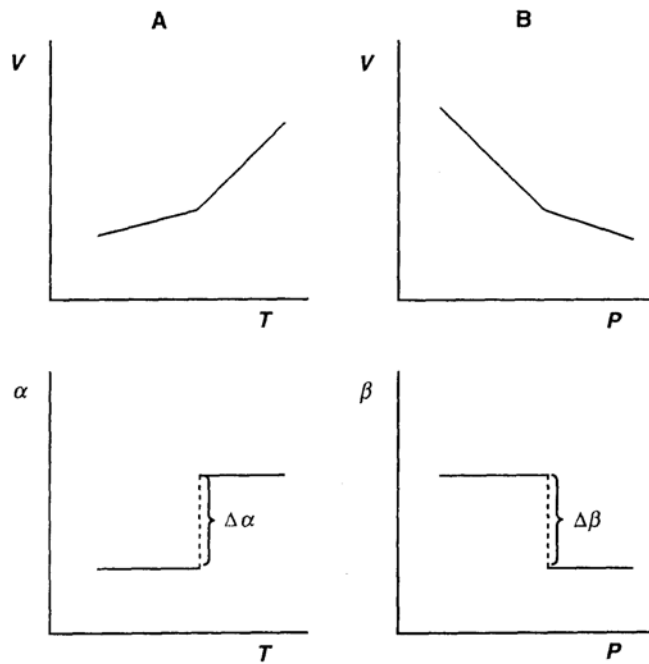


Figure 4.11. **A.** Thermodynamic second-order transition in volume as a function of temperature at constant pressure. **B.** Thermodynamic second-order transition in volume as a function of pressure at constant temperature.

4.3.2 Measurement techniques

- Measurements of thermal transitions : changes in refractive index, NMR line width, birefringence, dilatometry, differential scanning calorimetry(DSC), the response to cyclical strain(dynamic-mechanical analysis), or electric voltage(dielectric spectroscopy)
- Most commonly used techniques : dilatometry and DSC

Techniques capable of detecting different low-T secondary-relaxation processes

: dynamic-mechanical and dielectric measurements

* Dilatometry

: Specific volume of polymer sample is measured as a f'n of T.

(See Fig. 4.12)

At T_g , change in the slope of V-T curve (i.e., discontinuity in α)

At T_m , discontinuity in specific volume V

Approximation for the change in thermal-expansion coefficient at T_g (Simha & Boyer)

$$\Delta\alpha \approx -\frac{0.113}{T_g}$$

(See Table 4.6)

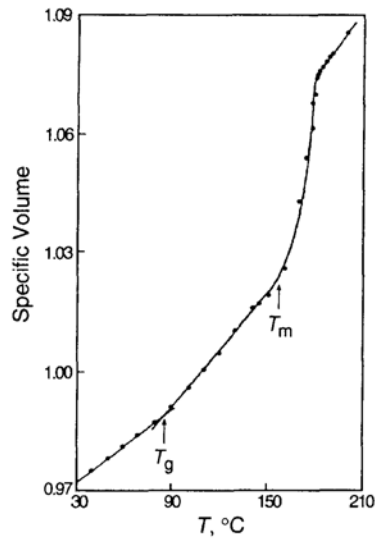


Figure 4.12. Dilatometric data of specific volume of a semicrystalline polymer, poly(*N,N'*-sebacoyl piperazine), plotted against temperature.¹¹ Results indicate a glass transition near 90°C and a crystalline-melting transition above 160°C.

TABLE 4.6 REPRESENTATIVE DILATOMETRIC DATA FOR POLYMERS¹²

Polymer	T_g (K)	$\alpha' (\times 10^{-4})$	$\Delta\alpha (\times 10^{-4})$
Polydimethylsiloxane	150	8.12–12	5.4–9.3
Poly(vinyl acetate)	302	5.98	3.9
Poly(vinyl chloride)	355	5.2	3.1
Polystyrene	373	5.5	3.0
Poly(methyl methacrylate)	378	4.6–5.0	2.45–3.05

* Calorimetry (DSC) --- most widely used techniques

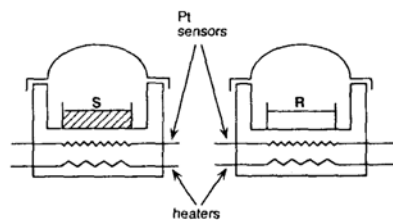


Figure 4.13. Schematic representation of a typical DSC sample cell showing the sample (S) and reference (R) pans, as well as the heating and temperature sensing elements.

The differential power needed to maintain both reference and sample pans at equal T during a programmed heating cycle is recorded as a function of T .

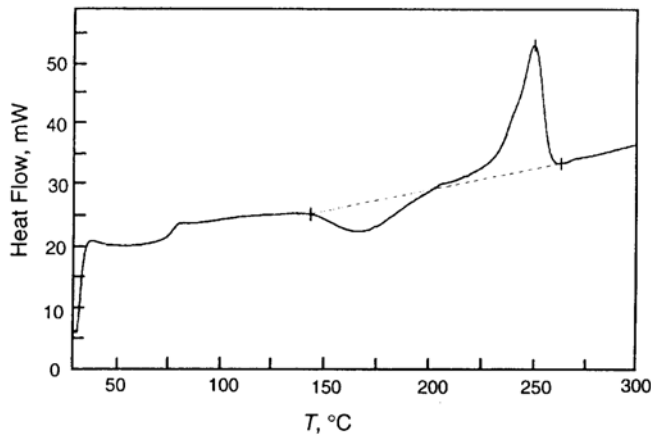


Figure 4.14. DSC thermogram of poly(ethylene terephthalate) crystallized at 200°C for 90 s showing a glass transition near 75°C, an excess crystallization peak above 143°C, and a crystalline-melting endotherm with a peak maximum near 250°C.

Fractional crystallinity ϕ of a polymer sample

$$\phi = \frac{-\Delta Q}{\Delta H_f}$$

where ΔQ : the heat of fusion of a semicrystalline polymer
(area under the melt endotherm)

ΔH_f : the heat of fusion at 100% crystallinity

or
$$\phi = 1 - \frac{\Delta C_p}{(\Delta C_p)_{am}}$$

where $(\Delta C_p)_{am}$: the specific heat increment in amorphous state

* Heat-distortion temperature (HDT) or Heat-deflection temperature

==> indicator of the temperature limit for structural (load-supporting) applications

A sample bar of standard dimension under a load of 455kPa placed at its center

---> Heating in an immersion bath at 2°C/min

. amorphous polymer : $HDT \leq T_g$

. semicrystalline polymer : $T_g \leq HDT \leq T_m$ (See Table 4.7)

4.3.3 Structure-property relationships

T_g, T_m --- strongly influenced by the chemical structure of the repeating unit

. T_g & T_m \uparrow as polymer chain flexibility \downarrow

← aromatic composition of the main chain \uparrow

← bulky substituent groups in the main chain \uparrow

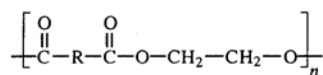
← nonrotational (i.e., unsaturated) groups the main chain \uparrow


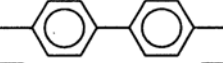
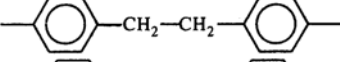
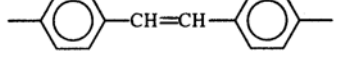
(See Table 4.8)

TABLE 4.7 THERMAL-TRANSITION TEMPERATURES

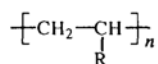
Polymer	HDT ^a (°C)	T _g (°C)	T _m (°C)
Polyethylene	29 to 126	-120 to -125	137
Polypropylene	40 to 152	-10 to -18	176
Nylon-6,6	62 to 261	49	265
Poly(vinyl chloride)	60 to 76	87	Low crystallinity
Polystyrene	63 to 112	100	Amorphous
Polycarbonate	39 to 148	150	Amorphous
Polysulfone	146 to 273	190	Amorphous


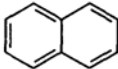
^a At 1.82 MPa (264 psi); HDT range indicates values reported for all commercial grades, including reinforced resins.

TABLE 4.8 EFFECT OF BACKBONE STRUCTURE ON THE CRYSTALLINE-MELTING TEMPERATURE OF POLYESTERS DERIVED FROM ETHYLENE GLYCOL (HOCH₂CH₂OH)

Compound	Main-Chain Unit, R	T _m (°C)
A	—(CH ₂) ₄ —	50
B		270
C		355
D		220
E		420

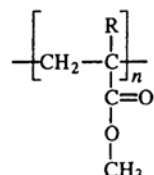
Bulky substituent groups --> hinder chain rotation --> T_g ↑

TABLE 4.9 GLASS-TRANSITION TEMPERATURES OF SELECTED VINYL POLYMERS

Polymer	Substituent Group, R	T _g (°C)
Polyethylene	H	-125
Polypropylene (atactic)	CH ₃	-20
Poly(vinyl chloride)	Cl	89
polyacrylonitrile	C≡N	100
Polystyrene		100
Poly(α-vinyl naphthalene)		135

- Polarity \uparrow \rightarrow intermolecular interactions \uparrow \rightarrow $T_g \uparrow$
 ex) PP ($T_g = -20^\circ\text{C}$), PVC ($T_g = 89^\circ\text{C}$), PAN ($T_g = 100^\circ\text{C}$)
- Flexibility of the side group \uparrow \rightarrow $T_g \downarrow$

TABLE 4.10 EFFECT OF INCREASING SIZE OF THE SUBSTITUENT GROUP ON THE GLASS-TRANSITION TEMPERATURE OF POLYMETHACRYLATES



Polymethacrylate	Substituent Group, R	T_g ($^\circ\text{C}$)
Poly(methyl methacrylate)	CH ₃	105
Poly(ethyl methacrylate)	CH ₂ CH ₃	65
Poly(propyl methacrylate)	CH ₂ CH ₂ CH ₃	35

- Syndiotactic \rightarrow $T_g \uparrow$
 ex) i-PMMA ($T_g = 45^\circ\text{C}$), s-PMMA ($T_g = 115^\circ\text{C}$)
- Trans geometric isomers \rightarrow $T_g \uparrow$
 ex) cis-PBD ($T_g = -108^\circ\text{C}$), trans-PBD ($T_g = -18^\circ\text{C}$)
 cis-polyisoprene ($T_g = -73^\circ\text{C}$), trans-polyisoprene ($T_g = -53^\circ\text{C}$)

4.3.4 Effect of MW, composition & pressure on T_g

* MW dependence

Fox-Flory equation :

$$T_g = T_g^\infty - \frac{K}{M_n} \quad \text{limiting-property relationship}$$

TABLE 4.11 FOX-FLORY PARAMETERS

Polymer	T_g^∞ (K)	K (K)
Polydimethylsiloxane	148	5.9×10^3
Poly(vinyl chloride)	351	8.1×10^4
Polystyrene	373	1.2×10^5
Poly(methyl methacrylate)	387	2.1×10^5
Poly(α -methylstyrene)	446	3.6×10^5

* Composition dependence

Blending the homogeneous mixture with a low MW additive or a second polymer

. Simple rule of mixture

$$T_g = w_1 T_{g,1} + w_2 T_{g,2} \Rightarrow T_g = \sum_{i=1}^N w_i T_{g,i}$$

where w_i : weight fraction of component I

; good for polymer blends,

but overpredicts T_g of polymers plasticized with low MW compound

. Kelly-Bueche eq'n <--- T_g 의 free volume 이론으로부터 나온 식

$$T_g = \frac{\alpha_1 \phi_1 T_{g,1} + \alpha_2 (1 - \phi_1) T_{g,2}}{\alpha_1 \phi_1 + \alpha_2 (1 - \phi_1)} \quad 1 : \text{diluent}, 2 : \text{polymer}$$

α : thermal expansion coeff.

ϕ : volume fraction

. Wood eq'n <--- random copolymer 의 T_g 예측 위해 개발된 식인데

plasticized polymer 의 T_g 예측에도 사용

$$T_g = \frac{T_{g,1} + (k T_{g,2} - T_{g,1}) w_2}{1 - (1 - k) w_2}$$

k : adjustable parameter

w : weight fraction

. Equation based on thermodynamics

$$\ln \left(\frac{T_g}{T_{g,1}} \right) = \frac{w_2 \ln(T_{g,2}/T_{g,1})}{w_1 (T_{g,2}/T_{g,1}) + w_2} \quad (\text{See Fig. 7.2})$$

$$\leftarrow \text{원 식 } \ln \left(\frac{T_g}{T_{g,1}} \right) = \frac{w_2 \Delta C_{p,2} \ln(T_{g,2}/T_{g,1})}{w_1 \Delta C_{p,1} (T_{g,2}/T_{g,1}) + w_2 \Delta C_{p,2}} \text{ 에서}$$

모든 polymers 에 대해 $T_g \Delta C_p$ 가 const.

Useful for a wide variety of polymer mixtures, including polymer blends,

for which the T_g of both components are roughly comparable, and plasticized

polymers, for which the T_g s of the polymer and plasticizer are widely apart.

이 식을 Taylor series expansion

(T_g s of polymer & diluent are not too different)

하면 다음의 식이 된다 (Fox equation).

. Fox eq'n

$$\frac{1}{T_g} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}} \quad (\text{Inverse rule of mixture})$$

. Logarithmic rule of mixture

$$\ln T_g = w_1 \ln T_{g,1} + w_2 \ln T_{g,2}$$

* Pressure dependence

--- insensitive, T_g increases at a rate of approximately 25K/kbar

$$\frac{dT_g}{dp} = \frac{\Delta \beta}{\Delta \alpha}$$

4.4 Mechanical properties

4.4.1 Mechanism of deformation

At low strain (i.e., <1%) --- elastic deformation

At high strain --- crazing(brittle polymers) or shear banding(ductile polymer)

* Crazing

: small cracks in a direction perpendicular to the principal direction of deformation

Typical values of critical strains ==> Table 4.12

TABLE 4.12 CRITICAL STRAINS FOR CRAZE INITIATION IN GLASSY POLYMERS

Polymer	Critical Strain (%)
Polystyrene	0.35
Styrene-acrylonitrile copolymer (SAN)	0.49
Poly(methyl methacrylate)	0.8-1.30
Poly(2,6-dimethyl-1,4-phenylene oxide)	1.5
Polycarbonate	1.8
Polysulfone	2.5

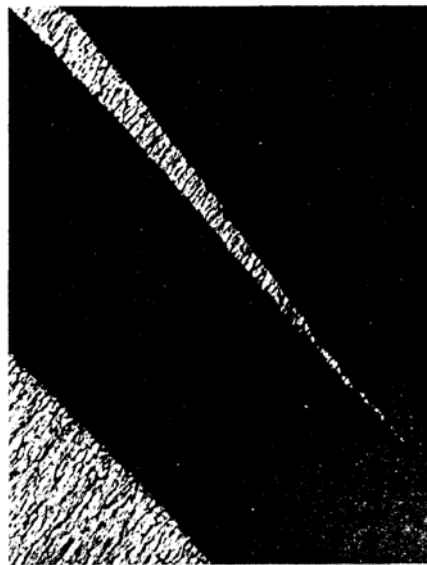


Figure 4.16. Micrograph of craze structures in poly(2,6-dimethyl-1,4-phenylene oxide).¹⁸ (Courtesy of R. P. Kambour.)

A craze -- a few nm to μm in thickness, with microfibrils (0.6 to 30nm in diameter)

90% of the total volume of the craze : void space

anisotropic morphology ---> scattering of light ---> stress whitening

* Shear banding

localized shear deformation at 45° angle to the stretch direction (ex. PC)

dominant mode of deformation during tensile yielding of ductile polymers

SAN --- exhibits crazing & shear banding

4.4.2 Methods of testing

static testing (deformation rate is steady in time) : tensile & shear, compressive tests

transient testing (time response) : creep & stress relaxation tests

impact testing --- Izod & Charpy tests

cyclic testing --- fatigue test

* Static testing

. Tensile deformation

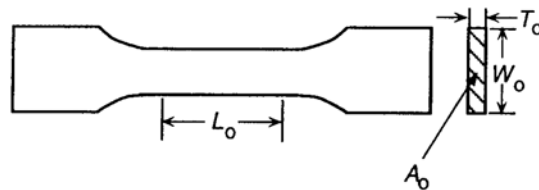


Figure 4.17. Illustration of a typical tensile-dogbone sample. The overall length of the specimens may vary from 63.5 to 246 mm. During tensile measurement, the sample is gripped at the wide ends. Specimen parameters include L_0 , gage length (distance between test marks or extensometer span, ca. 50 mm); W_0 , initial width (19 or 29 mm); T_0 , initial thickness (4 to 14 mm); and A_0 , initial cross-sectional area.

engineering (or nominal) stress σ ,

$$\sigma = \frac{F}{A_0}$$

engineering strain ϵ ,

$$\epsilon = \frac{\Delta L}{L_0}$$

true stress,

$$\sigma^T = \frac{F}{A} = \sigma \frac{L}{L_0} \quad (V = V_0 \text{ during deformation})$$

true strain,

$$\epsilon^T = \int_{L_0}^L \frac{1}{l} dl = \ln\left(\frac{L}{L_0}\right)$$

volume change,

$$\Delta V = V - V_0 = (1 - 2\nu)\epsilon V_0$$

Poisson's ratio,

$$\nu = -\frac{\epsilon_T}{\epsilon_L} = \frac{1}{2} \left[1 - \frac{1}{V} \left(\frac{\partial V}{\partial \epsilon} \right) \right]$$

$\nu = 0.5$ for incompressible materials

TABLE 4.13 POISSON'S RATIO OF SOME IMPORTANT POLYMERS

Polymer	Poisson's Ratio
Polyethylene (LD)	0.49
Poly(methyl methacrylate)	0.40
Polystyrene	0.38
Natural rubber	0.49
Poly(vinyl chloride)	0.4

Hooke's law (for ideal elastic solid) : $\sigma = E \epsilon$

cf.) $\epsilon = D \sigma$

E : tensile (or Young's) modulus

D : tensile compliance ($=1/E$)

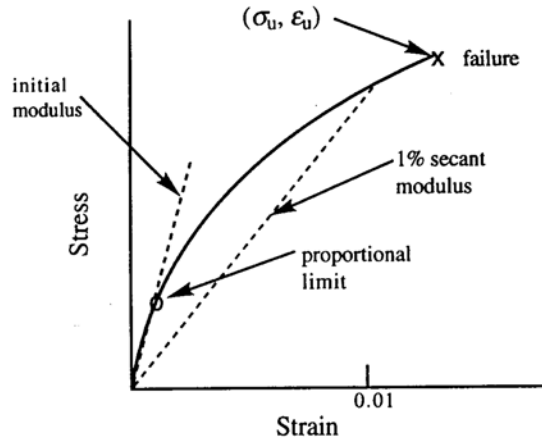


Figure 4.18. Representative stress-strain curve for a polymer undergoing brittle failure.

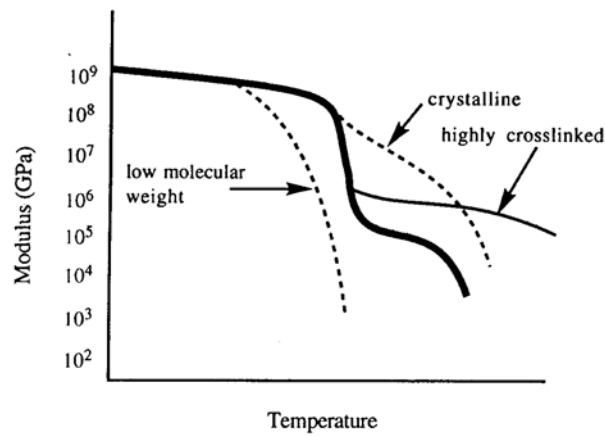


Figure 4.19. Plot of modulus versus temperature for a high-molecular-weight, amorphous polymer with variations for low-molecular-weight ($M < M_c$), cross-linked, and semicrystalline polymers.

$$E_p \text{ (rubbery plateau modulus)} \propto \frac{\rho RT}{M_e} \quad : \text{ inversely proportional to } M_e$$

M_e : MW between entanglements

. shear deformation

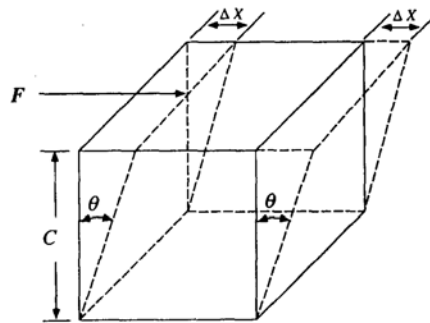


Figure 4.20. Illustration of the shear deformation of a solid with the shear force (F) acting on the top surface of the cube.

engineering shear stress $\tau = \frac{F}{A_0}$

shear strain $\gamma = \tan \theta = \frac{\Delta X}{c}$

$\tau = G \gamma$, G : shear modulus

$\gamma = J \tau$, J : shear compliance

For isotropic materials,

$E = 2(1 + \nu)G$

$J = 2(1 + \nu)D$

If $\nu = 0.5$ (incompressible), $E = 3G$, $J = 3D$

. $\sigma - \epsilon$ curve

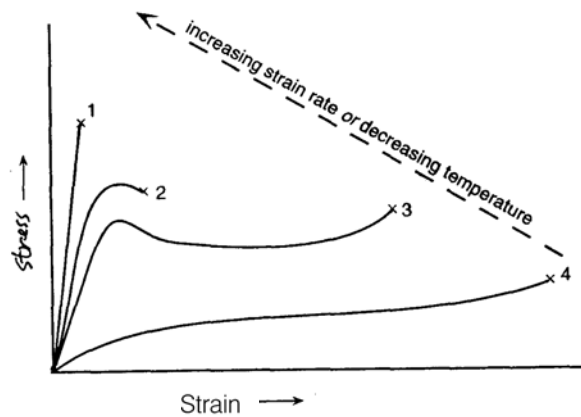


Figure 4.21. Typical stress–strain curves for samples exhibiting brittle failure (curve 1), ductile failure with neck formation (curve 2), ductile failure with cold drawing and orientational hardening (curve 3), and rubbery behavior with evidence of strain-induced crystallization (curve 4). Point of failure is indicated by the symbol x .

Curve 1 : brittle polymers

Curves 2&3 : ductile polymers

show yield stress σ_y (maximum stress at ϵ_y), strain softening, draw stress, cold drawing, and orientation hardening

Curve 4 : rubbery polymers
 shows strain-induced crystallization
 modulus of ductile polymers < modulus of brittle polymers
 toughness of " > toughness of "

TABLE 4.14 MECHANICAL PROPERTIES OF REPRESENTATIVE POLYMERS

Polymer	Elastic Modulus GPa ^a	Yield Strength MPa	Ultimate Strength MPa	Elongation to Break %
Polypropylene	1.0–1.6	23	24–38	200–600
Polystyrene	2.8–3.5	—	38–55	1–2.5
Poly(methyl methacrylate)	2.4–2.8	48–62	48–69	2–10
Polyethylene (low-density)	0.14–0.28	6.9–14	10–17	400–700
Polycarbonate	2.4	55–69	55–69	60–120
Poly(vinyl chloride) (rigid)	2.1–4.1	55–69	41–76	5–60
Polytetrafluoroethylene	0.41	10–14	14–28	100–350

^a To convert GPa to psi, multiply by 1.45×10^5 ; to convert MPa to psi, multiply by 145.

Factors to affect the mechanical properties

: chemical structure of polymer, conditions of sample preparation, MW, MW distribution, crystallization, extent of crosslinking or branching, T & rate of deformation

T ↑ → brittle to rubbery response

rate of deformation ↓ → brittle to rubbery response

* Transient testing

: creep & stress-relaxation

. creep tests

: measure ϵ at a constant load σ_0

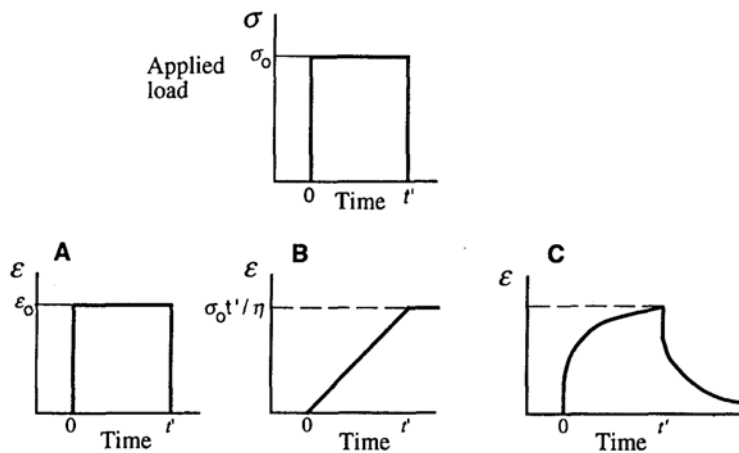


Figure 4.23. Response of different idealized materials to an instantaneous application of a stress at time $t = 0$. **A**, elastic; **B**, viscous; and **C**, viscoelastic.

$$D(t) = \frac{\varepsilon(t)}{\sigma_0} \quad : \text{ tensile compliance}$$

simple laboratory setup for creep testing

Plastic film or bar clamped at one end to a rigid support enclosed in a temperature controlled box. Weight is added to the opposite end.

⇒ measuring the relative movement of two marks

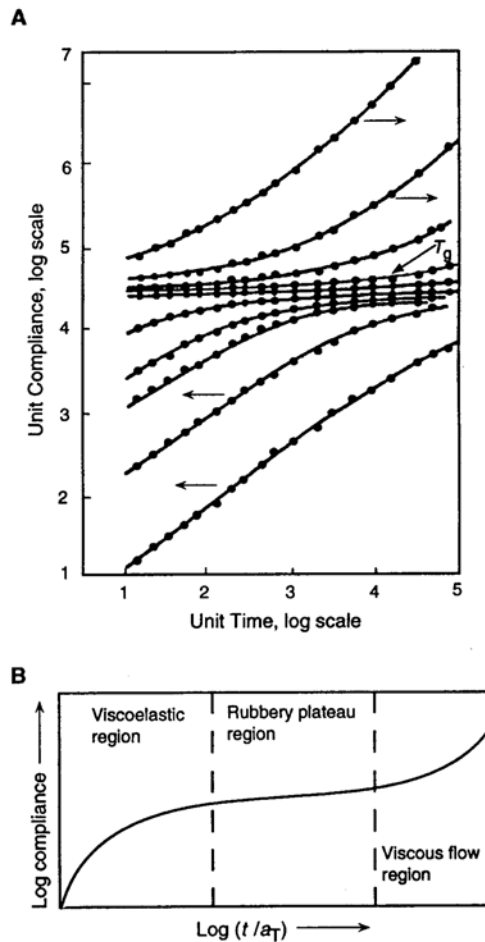


Figure 4.24. **A.** Representative plots of creep compliance as a function of time at different temperatures. Arrows show direction of the horizontal shift of data to obtain a master curve at a reference temperature taken as the T_g of the polymer. **B.** Creep master curve obtained by time-temperature superposition.

stress-relaxation tests

measure σ at a fixed ε_0 at const T.

$$E(t) = \frac{\sigma(t)}{\varepsilon_0}$$

(See Fig. 4.25)

⇒ Master curve (time-temperature superposition)

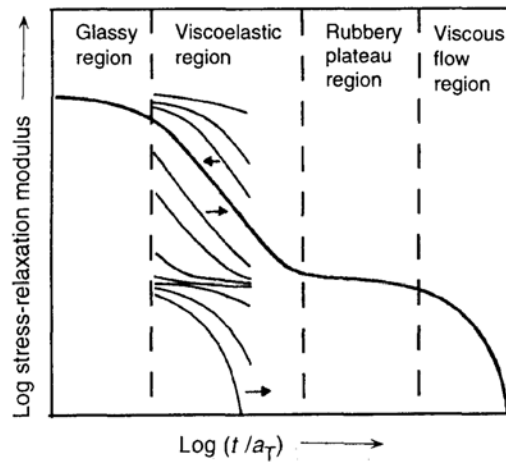


Figure 4.25. Stress-relaxation modulus as a function of time. Arrows show directions of shift to obtain master curve at reference temperature.

* Impact testing

Izod and Charpy tests --- widely used.

Energy-to-break is determined from the loss in kinetic E of the hammer.

TABLE 4.15 VALUES OF NOTCHED-IZOD IMPACT STRENGTH FOR SOME REPRESENTATIVE THERMOPLASTICS

Polymer	Impact Strength ^a J m ⁻¹
Polystyrene	13–21
Poly(vinyl chloride)	21–160
Polypropylene	27–107
Polystyrene (high-impact)	27–427
Polyethylene (high-density)	27–1068
ABS	53–534
Polysulfone	69–267
Polycarbonate	641–961
Polyethylene (low-density)	854

^a To convert J m⁻¹ to ft-lb_f in.⁻¹, divide by 53.38.

impact resistant polymers : HIPS & ABS

(dispersing small rubber particles within brittle polymers)

* Fatigue testing

"fatigue life"

endurance limit : max. value of stress for which failure will not occur.

--- important in load-bearing applications

(See Fig. 4.26)

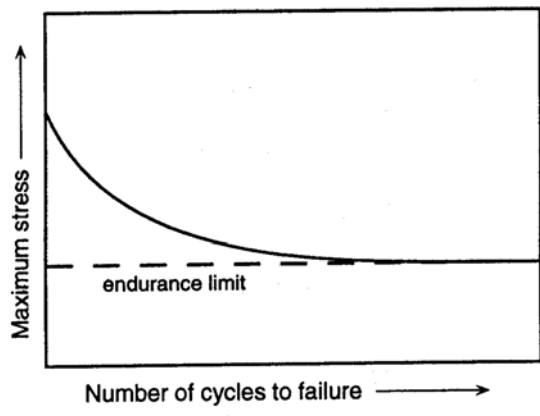


Figure 4.26. Representative fatigue curve.