

# Rheological Properties of Polymers

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## 2. Introduction

- 1). Rheology: response of materials due to small deformation
- 2). The characteristics of the materials response as function of the following factors: shear rate, the method and the magnitude of the imposing stress, the physical and chemical structure and measuring method, external environmental factors such as temperature.
- 3). Rheological properties affect on the characteristics of production/fabrication characteristics, the quality of the fabricated products.
- 4). Rheological properties are important: the structure/physical properties → processing /fabrication → product characteristics.
- 5). For predicted molecular design searching for hardness, impact resistance, and thermal properties, the rheological properties are necessary characteristics.
- 6). Instruments for rheological properties: capillary rheometer, rotational rheometer, extensional rheometer, Slit die rheometer.
- 7). Difference between polymers and molecules: high molecular materials, molecular weight (MW) and its distribution (MWD).
- 8). Macroscopic and Microscopic characteristics of Polymers: MW, MWD, time, molecular structure and composition, orientation, solvent, pressure, filler, temperature, and morphology.

## 3. Terminology

1. stress
2. strain
3. modulus ( $E, E^*, E', E''$ ), ( $G, G^*, G', G''$ )
4. compliance ( $D, D^*, D', D''$ ), ( $J, J^*, J', J'', J_0, J_e^0$ )
5. viscosity ( $\eta, \eta^*, \eta', \eta'', \eta_0, \eta_e^0$ )

## 4. Basic Concepts in Rheology

### 4-1. Sorts of Deformation:

1) extension: Deformation due to extension (tensile elongation):  $ABC \rightarrow A'B'C'$

- stress:  $F/AB = \sigma$  (engineering stress), (true stress:  $\sigma_t = F/A'B'$ )

- strain(dimensionless):  $\Delta C/C = (C'/C) - 1 = \epsilon$

- incompressible: no variance in volume) between the before and after measurements. ( $V'/V = A'B'C'/ABC = 1$ )

- poisson's ratio:  $\mu = \Delta A/A/\epsilon = \Delta B/B/\epsilon$  ( $\Delta A/A = \Delta B/B$ )

$$\mu = 1/2[1 - (1/V)dV/d\epsilon]$$

e.g. PS; 0.325, PET; 0.37-0.4, Nylon6 ; 0.3-0.4 , ideal rubber:0.5

- modulus:  $E = \sigma/\epsilon = 1/D$  ( $D$ = tensile compliance)

- tensile strain, uniaxial stress

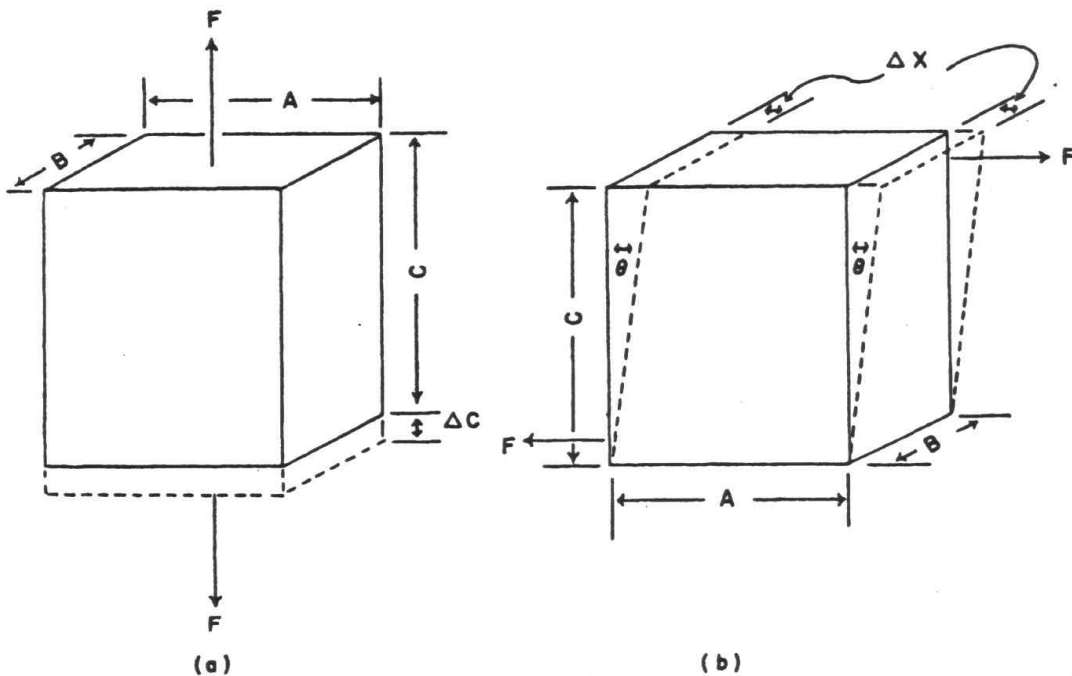


Figure1. Deformations upon extension and shear

2) Shear: deformation due to shear:

- shear stress:  $\sigma_s = F/AB$

- shear strain:  $\gamma = \Delta X/C = \tan \theta$

- strain rate:  $\dot{\gamma} = d\gamma/dt$

- shear compliance :  $G = \sigma_s / \gamma = 1/J$  ( $J$  = shear modulus)

-  $E = 3G, 3D = J$

## 5. Materials by Rheological Properties

### 1) Linear elastic material(Hookean solid):

- $\sigma = E\varepsilon$  (E; Young's modulus; tensile modulus)
- $\sigma = G\gamma$  (G; shear modulus)
- modulus: deformation에 대해 저항하는 척도
- dimension:  $\text{dyne/cm}^2 = \text{N/m}^2(\text{Pa})$
- for linear elastic material: modulus is independent regardless of the imposed stress.
- Polymers under small deformation behave like a linear elastic material :  
(Markovitz, 1980)
  - ① Polymers under the temperature range below the  $T_g$  or  $T_m$  region.
  - ② Crosslinked polymers except the  $T_g$  region.
  - ③ Linear or branched polymers with isotropic compression state beyond  $T_g$ .
  - ④ Polymers under initial stress.
  - ⑤ Concentrated suspension under small stress

### 2) Linear viscous material (Newtonian fluid)

- $\sigma = \eta(dy/dt)$
- viscosity  $\eta$ : 유동에 대한 저항의 척도
- Newtonian flow(linear viscous fluid) : constant  $\eta$  independent of flow rate.
- Newtonian fluid characteristics of polymers:
  - ① dilute solution of suspension
  - ② concentrated suspension as low shear rate
  - ③ linear or branched polymers, or their solution with low shear rate at much higher than the  $T_g$  and  $T_m$ .
- dimension:  $\text{dyne} \cdot \text{sec/cm}^2$  ( $\text{g/sec/cm} = \text{poise}$ ),  $\text{N} \cdot \text{sec/m}^2$  ( $\text{Pa} \cdot \text{sec}$ ),  
 $1 \text{ Pa} \cdot \text{sec} = 10 \text{ Poise}$
- kinematic viscosity ( $\nu$ ):  $\eta/d(\text{density})$  ( $\text{cm}^2/\text{sec} = \text{stokes}$ )

### 3) Rubber or non-linear elastic materials

- Like rubbers, some materials have large recoverable deformation, but the stress is not proportional to the deformation.
- The characteristics of elastomeric rubber;
  - ① almost perfect recovery to the original length after 5-10 times of elongation.
  - ② temperature raise upon rapid extension.
  - ③ decreased length upon heating under stress.
  - ④ need only small stress for deformation.
  - ⑤ normal stress effect.
- For polymers, characteristics of elastomeric rubber show at equilibrium deformation ( deformation characteristics: function of time)

- ① low crosslinking density material: higher temperature than  $T_g$
- ② block copolymers at  $T_g < T < T_m$
- ③ polymer gel having crystallite
- Statistical mechanics: small deformation upon small stress, modulus  $E$   
 $E = 3\rho RT/M_c$   
 ( $M_c$  is the molecular weight)

4) Viscoelastic material (Polymers)

- ① high molecular weight, MWD
- ② chain segmental response against external stress varies upon time, temperature, and velocity: at short time and low temperature, short segmental motion like solid, but long time and high temperature, long segmental motion like fluid.  
 $\Rightarrow \Rightarrow \Rightarrow$  **polymers behave elastomeric material or viscous liquid depending on the condition.**

③ Representative characteristics of viscoelastic materials:

- rheological properties are a function of time;
  - ⊙ low stress or deformation; linear viscoelastic material.
  - ⊙ high stress or deformation; non-linear viscoelastic material.
- characteristics of non-linear viscoelastic material;
  - ⊙ deformation higher than the limited value  $\Rightarrow$  modulus decrease with strain.
- viscosity varies with increased shear rate; polymer melt, concentrated polymer solution, high molecular weight solution.
- At high stress or shear rate, polymer melts show die swell, even melt fracture.
- When non-linear viscoelastic fluid is stirred  $\Rightarrow$  Weissenberg effect.
- non-linear viscoelastic material outside of the rotating sphere: rotates the same direction as the sphere.

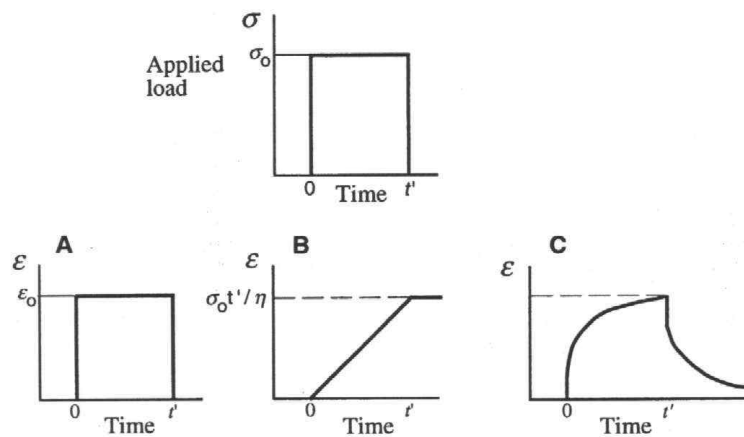


Figure 2. Response of different idealized materials to an instantaneous application of a stress at time  $t$ . **A**, elastic; **B**, viscous; and **C**, viscoelastic

## 6. Experimental Techniques for Rotational Rheometry

### 1) Basic structure of rotational rheometer

- ① stress controlled rheometer; measurement of deformation or shear rate upon controlled stress.
- ② strain controlled rheometer; measurement of stress upon controlled deformation or shear rate.

### 2) Test geometry

#### (1) Cone and plate(원추평판);

- ⊙ 1-4 degree of cone angle.
- ⊙ the height of the specimen varies with the cone angle.
- ⊙ useful for non-Newtonian fluid
- ⊙ the same shear rate is imposed on the entire material under no inertia and edge effect
- ⊙ no good for large particle reinforced polymer composite

#### (2) Parallel plate(평행평판);

- ⊙ shear rate is varied. the edge of the plate is the highest.
- ⊙ shear rate of the specimen: the rate at the edge of the specimen.
- ⊙ variable specimen thickness, easy to handle the specimen (mounting and cleaning), used for crosslinkable material.

#### (3) Concentric cylinder(동심축 원통관);

- ⊙ large contact area with the specimen.
- ⊙ relatively high torque for the same shear rate.
- ⊙ useful for very low viscosity material.
- ⊙ rotating the inside cylinder; Searl geometry; secondary flow at high shear rate.  
rotating the outside cylinder; Couette geometry; safe flow.
- ⊙ outside cylinder; strain increased
- ⊙ narrow distance between inside and outside cylinder  $\Rightarrow$  constant shear rate  
 $\Rightarrow$  requested geometry:  $R_0/R_i = 1.01$ ,  $h/R = 100$ .

#### (4) Rectangular bar(직육면체);

- ⊙ The above geometries: used for fluids such as polymer melts, solution, suspension, emulsion
- ⊙ Polymers or rubbers below the  $T_g$  or  $T_m$ ; the same shape of the specimens; specimen having the length  $L$ , thickness  $a$ , width  $b$  is rotated by the angle  $\psi$ : Torque  $T \Rightarrow$  shear modulus  $G \propto LT/\psi a^3 b$  (the thickness  $a$  is important)

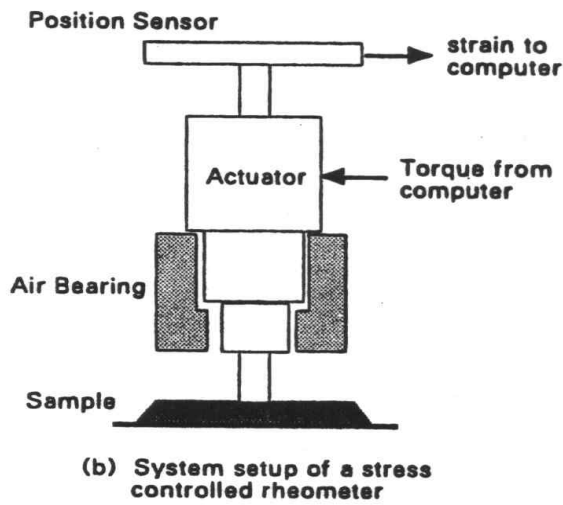
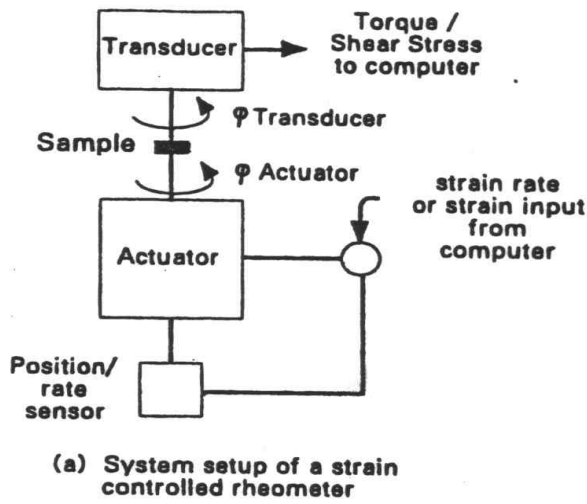


Figure 3. The basic structure of rotational rheometer

	Cone & Plate	Parallel Plate	Concentric cylinder
$\eta$ 조			
Shear rate	$\dot{\gamma} = \frac{\Omega}{\alpha}$	$\dot{\gamma} = \frac{\Omega}{h} R$ (edge shear rate)	$\dot{\gamma} = \frac{R_i(\Omega_o - \Omega_i)}{R_o - R_i}$
Viscosity	$\frac{3 \alpha T}{2 \times R^3 \Omega}$	$\frac{3 \alpha T}{2 \times R^3 \Omega} \left( 3 + \frac{d \ln T}{d \ln \dot{\gamma}_R} \right)$	$\frac{T(R_o - R_i)}{2 \times R_i^3 (\Omega_o - \Omega_i)}$

Figure 4. Test geometry used for fluid specimens



### 3) Experimental techniques and the rheological properties

#### (1) Constant shear rate experiment;

- measures the variance of the stress upon constant rotation of the geometry.
- ① Linear elastic material: stress increased with time. For constant strain rate, it needs increased stress.
- ② Newtonian fluid; constant shear rate upon constant stress.
- ③ Viscoelastic material; at low shear rate  $\Rightarrow$  stress increases with time, then saturated. But if the shear rate is higher than the critical point  $\Rightarrow$  it behaves like non-linear viscoelastic material, thus the stress reaches to the maximum, then saturated "steady state viscosity". For Newtonian or non-Newtonian fluids at low shear rate, viscosity is constant, it is called the "zero shear viscosity".

#### (2) Stress relaxation experiment;

- measures the shear stress after giving a constant strain.
- $\sigma(t) = G(t)\gamma$        $G(t) = \sigma(t)/\gamma_c$
- For longer period of time, measures the  $G(t)$  at various temperatures, then shifts the modulus at different temperatures based on the modulus at reference temperature.  $\Rightarrow$  The "master curve" by the "time-temperature superposition principle" [Fig. 12]. working only for amorphous polymers  $\Rightarrow$  "called "Rheologically simple"
- For crystalline polymers, this is not applicable because the morphology changes with temperature.
- By plotting the modulus versus temperature, the transition region between the glassy and rubbery region, the temperature where the  $\tan \delta$  is maximum,  $\Rightarrow T_g$ .
- dimension of modulus;  $\text{dyne/cm}^2$ ,  $\text{N/cm}^2$ .

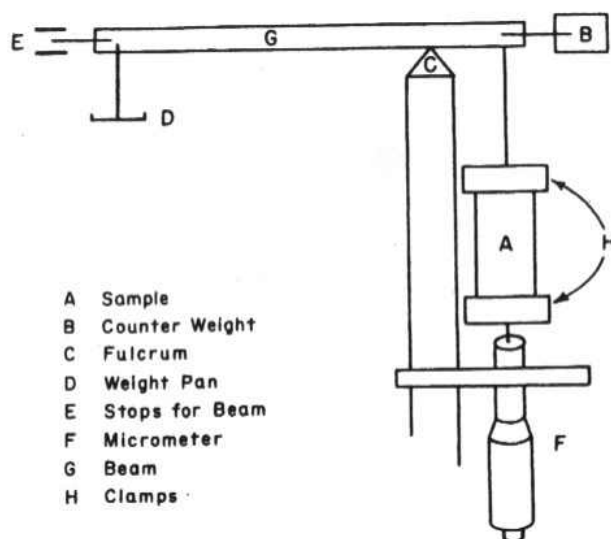


Figure 5. Experimental equipment for stress relaxation.

(3) Creep and Recovery Experiment

- measures the variance of strain upon imposed constant stress. (creep)  
 $\gamma(t) = J(t) \sigma_c$ , creep compliance;  $J(t)$
- measures the recovery of the deformation after the stress released when the deformation is reached the steady state. recovery compliance;  $R(t)$
- modulus,  $E = 1/\text{compliance}, J$ , but  $E(t) \neq 1/J(t)$ .
- dimension of compliance;  $\text{cm}^2/\text{dyne}, \text{m}^2/\text{N}$ .
- steady state compliance: measures the recoverable deformation(elasticity).
- viscosity: measures the energy loss.
- steady state compliance:  $\odot$  sensitive to MWD  
 $\odot$  multiply by the zero shear viscosity =  $\eta J_e^0$   
characteristic relaxation time( $\tau_c$ )
- for viscoelastic material; at  $t \ll \tau_c$ , behaves like solid, but  $t \gg \tau_c$ , behaves like fluid, thus  $\tau_c$  is important for determining the transition period.

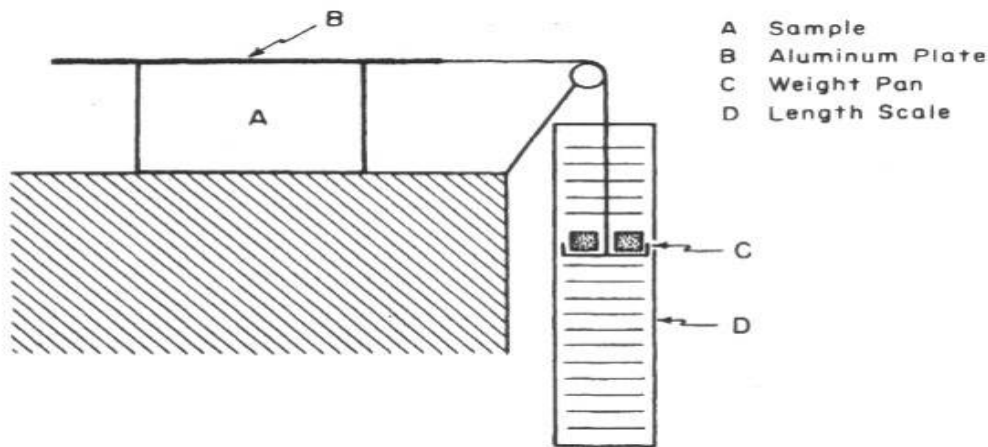


Figure 6. A simple apparatus to measure shear creep.

(4) Dynamic shear or oscillatory shear experiment

- deformation(strain) or stress is expressed in sine function.
- For strain-controlled rheometer:  $\gamma(t) = \gamma_0 \sin \omega t$
- For linear elastic material;  $\sigma = k(\text{sine})$ , since stress linearly varies with strain.
- For linear-viscoelastic material;  $\sigma = k(\text{shear rate})$ , stress is a function of cosine.  
stress is delayed 90 degree with strain. it is "out of phase".
- For viscoelastic material; between stress and strain,  $\delta$  ( $0^\circ < \delta < 90^\circ$ )  $\Rightarrow$   
 $\delta \rightarrow 0$ , dominate elasticity,  $\delta \rightarrow 90^\circ$  viscous material.
- $\sigma(t) = \sigma_0 \sin(t + \delta) = \sigma_0 \cos \delta \sin \omega t + \sigma_0 \sin \delta \cos \omega t$   
 $= G'(\omega) \sin \omega t + G''(\omega) \cos \omega t$   
 $\odot G'(\omega)$ ; storage shear modulus) ; in-phase of the stress upon strain.

©  $G''(\omega; \text{loss shear modulus})$  ; out of-phase. viscosity characteristics.

- The position difference ;  $\tan \delta$  is a function ;

$$\tan \delta = \sin \delta / \cos \delta = G''/G' = \text{점성특성/탄성특성} = E''(\text{손실특성})/E'(\text{저장특성})$$

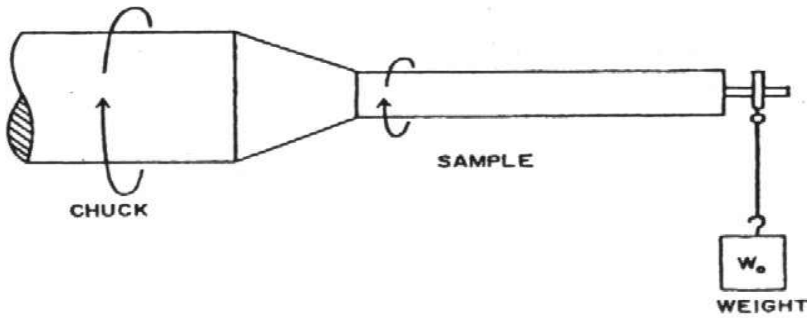
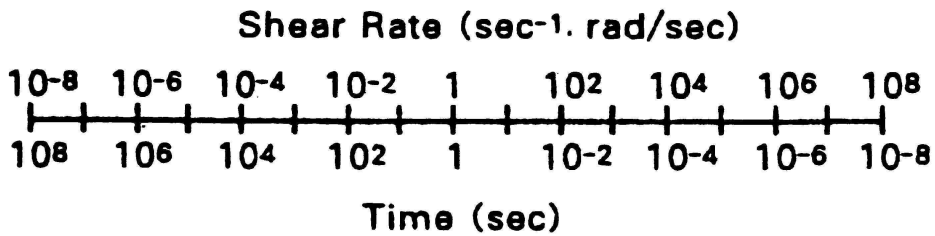
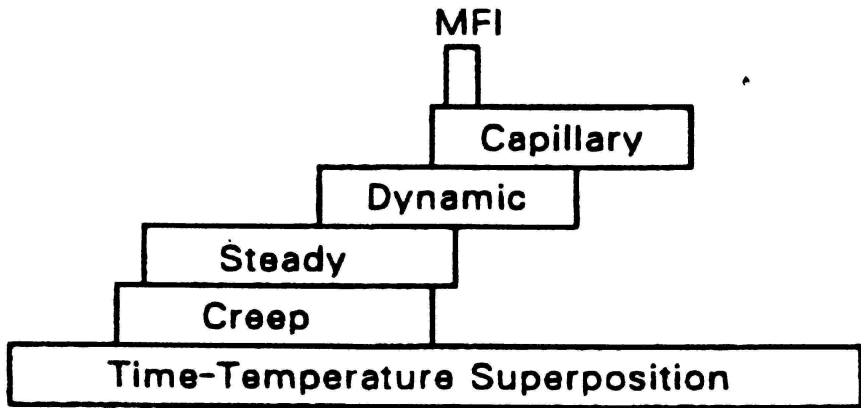


Figure 7. A novel dynamic experiment.

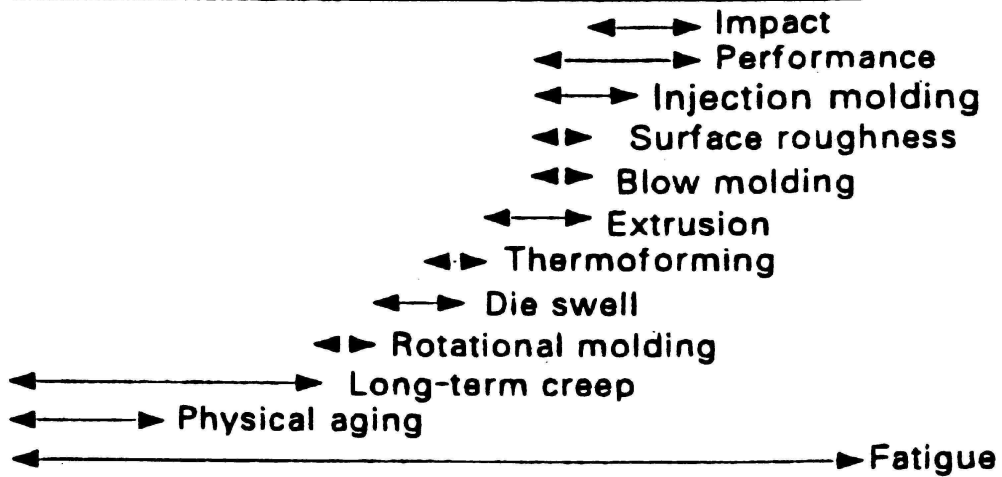
★ Shear rate region for different phenomena

phenomena	shear rate (1/sec)	application
sedimentation of fine powder	$10^{-6} \sim 10^{-4}$	medicin, paints
levelling due to surface tension	$10^{-2} \sim 10^{-1}$	paints, printing inks
draining under gravity	$10^{-1} \sim 10^{-1}$	painting, coating, toilet bleaches
extruders	$10^0 \sim 10^2$	polymers
chewing and swallowing	$10^1 \sim 10^2$	foods
dip coating	$10^1 \sim 10^2$	paints, confectionary
mixing and stirring	$10^1 \sim 10^3$	manufacturing liquids
pipe flow	$10^0 \sim 10^2$	pumping, blood flow
spraying and brushing	$10^3 \sim 10^4$	spraying-drying, painting
rubbing	$10^4 \sim 10^5$	application on cream and lotion
milling pigments in fluid base	$10^3 \sim 10^5$	paints, printing inks
high speed coating	$10^6 \sim 10^6$	paper
lubrication	$10^3 \sim 10^7$	gasoline engines

★ Relationships between process/property and time/rate in experimental technique.



years	days	min	sec	msec	μ sec
Molecular structure			Entanglement		Local motion



## 7. Relationship between Polymer Structure and Rheological Properties.

- How do the rheological properties vary depending on the molecular structure, morphology and chemical structure of the polymeric materials?

1) Structural factors affecting the rheological properties:

(1) Molecular weight ( $M_w$ ) and molecular weight distribution(MWD)

① number average molecular weight( $M_n$ ), weight average molecular weight( $M_w$ ), polydispersity index(PDI:  $M_w/M_n$ ) (Figure 8)

② polymer viscosity and elastic property vs. molecular structure and process condition(temp. shear rate); zero shear viscosity( $\eta_0$ )  $\leftrightarrow$   $M_w$ . (Figure 9)

amorphous linear polymer  $\leftrightarrow$   $\eta_0$ ; molecular dependency at the region of  $M_c$ .

-  $M_w < M_c$ ;  $\eta_0 \propto M_w^{1.0}$  (2 times of  $M_w$  gives 2 times of viscosity)

-  $M_w > M_c$ ;  $\eta_0 \propto M_w^{3.4}$  (2 times of  $M_w$  gives 10 times of viscosity)

$\Rightarrow$   $M_w$  higher than the  $M_c$ , an entanglement with reduced flow,  $M_c = 2 \times M_e$ .

- increased entanglement induces improved mechanical properties.  $\Rightarrow$  needs of combination of processibility and physical properties

- steady state compliance( $J_e^0$ ); when  $t \rightarrow \infty$ , the final recovery, or  $J'$  at  $\omega \rightarrow 0$   
 $J_e^0$  increased with molecular weight, then saturated above  $M'c$ .

( $M'c > 2M_c \Leftrightarrow$  for narrow MWD polymers,  $M'c = 1.8 M_c$ )

③ The same molecular weight polymers with different MWD exhibit different rheological properties.

- For broad MWD HDPE compared narrow one, the difference in viscosity increases with shear rate.

- shear thinning effect; at high shear rate, the broad MWD one dramatically decrease the viscosity.  $\Rightarrow$  polymers with high  $M_w$  with suitable  $M_n$  give improved mechanical properties and processibility with reduced viscosity.

- broad MWD (increased  $M_w$ ); improving the elasticity.

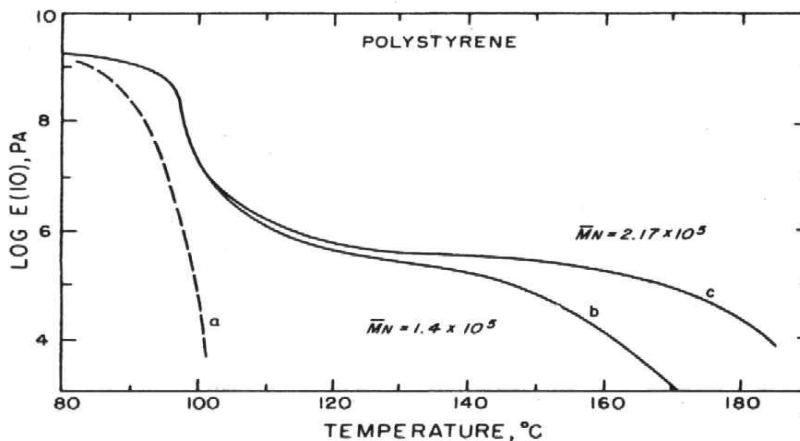


Figure 8. Ten-second modulus versus temperature curve for polystyrene of various molecular weight

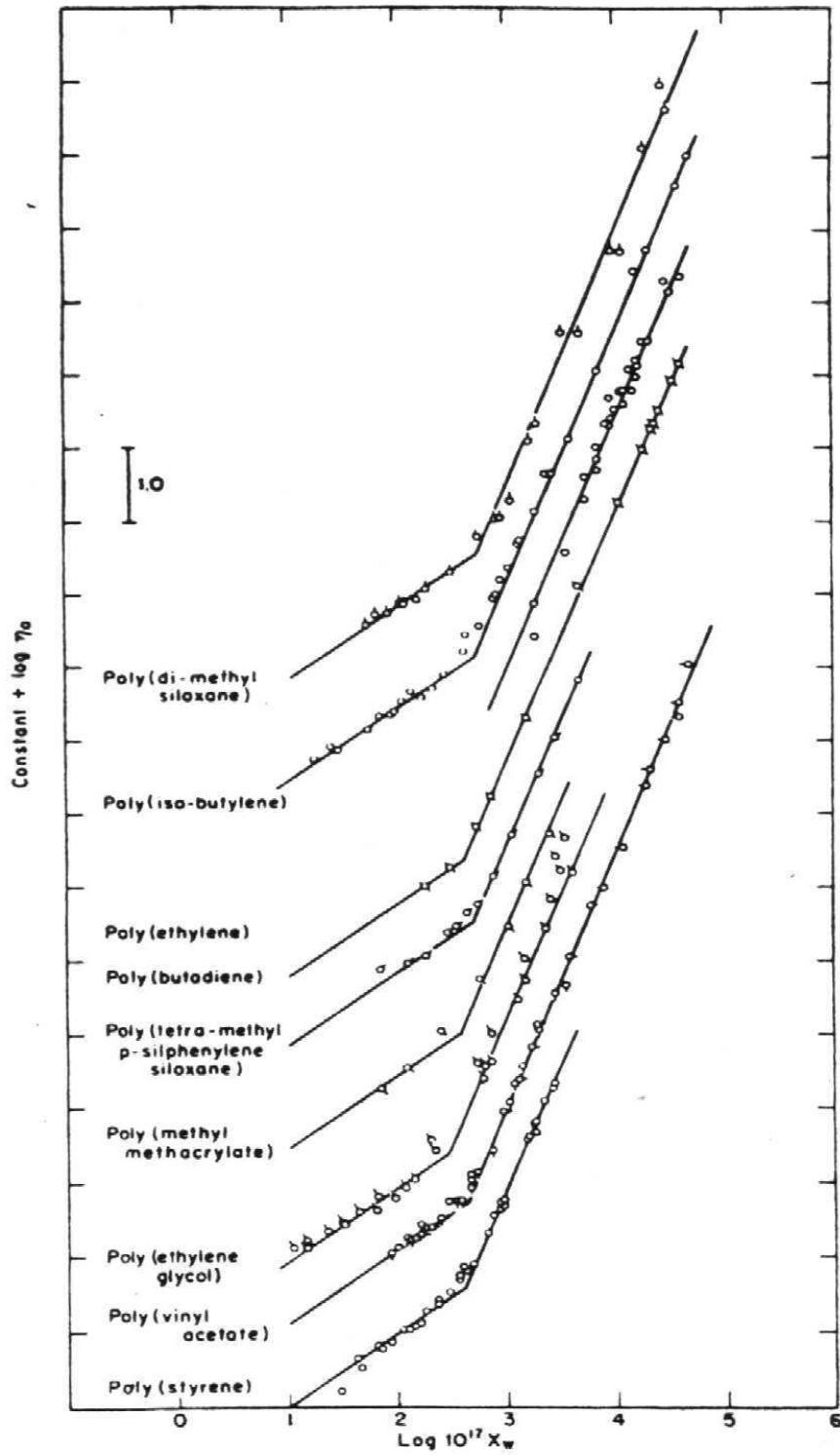


Figure 9.  $\log \eta_0$  plotted against an abscissa which for each polymer is  $\log M + \text{const.}$  for nine different polymers (Berry and Fox)

(2) Side chain structure

- ①  $T_g$  of polymers decreases with increased aliphatic side chain (decrease with aromatic side chain).
- ② Since polymers processed 50 degree above the  $T_g$ , viscosity dose not affect on short side chain unless long side chain or rigid liquid crystalline polymers.
- ③ internal plasticization (external plasticization)

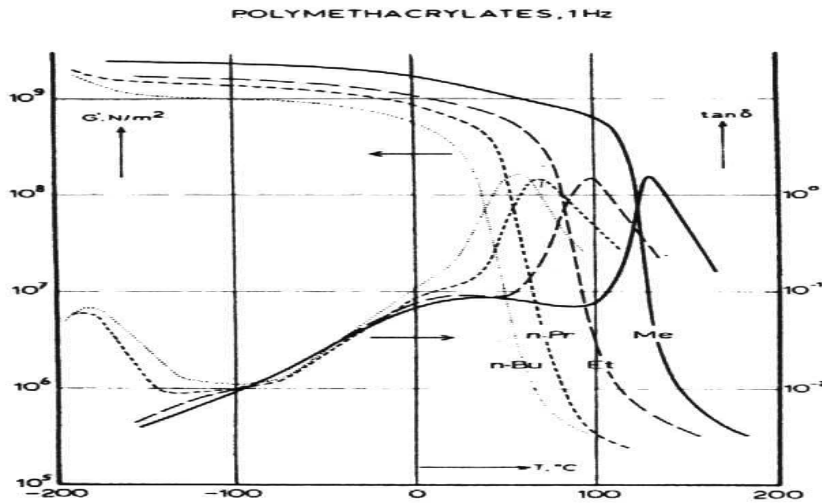


Figure 10. Shear modulus  $G'$  and loss  $\tan \delta$  at 1 Hz for poly(n-alkyl methacrylate).  
Me = methyl, Et=ethyl, n-Pr= n-propanol, n-Bu=n-butyl

(3) Branching

- ① long side chain branched linear polymers compared to the same molecular weight linear polymers; decrease in chain dimension, viscosity and steady state compliance.
- ② long side chain branch with increased number of branch; decreased chain mobility, affected by entanglement  $\Rightarrow \eta$  and  $J_e^0$  increase compared to the same MW linear polymers. relatively large shear thinning is obtained.

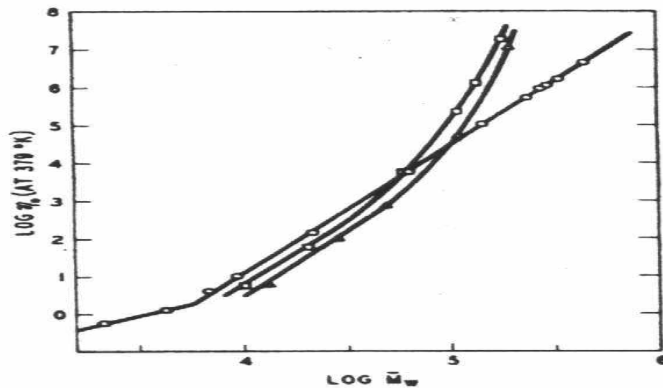


Figure 11. Logarithmic plot of steady-state viscosity at 379K. circle; linear, square; three-arm star, trianlgr; four arm star.

(4) Temperature

- Amorphous polymer: glassy state  $\Rightarrow$  glass transition region  $\Rightarrow$  rubbery state  $\Rightarrow$  flow state
- At different temperature, various type of specimens are used for rheological properties  $\Rightarrow$  **master curve** by the **time-temperature superposition principle**  $\Rightarrow$  shift factor ( $a_T$ ).
- shift factor gives information physical properties at ambient temperature

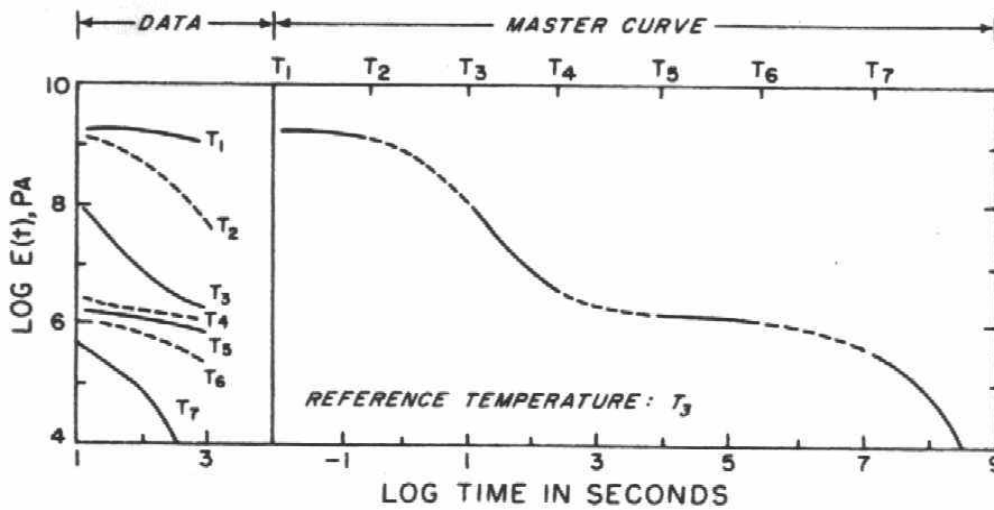


Figure 12. Preparation of a stress relaxation master curve from experimentally measured modulus-time curves at various temperature.

(5) Crystallinity

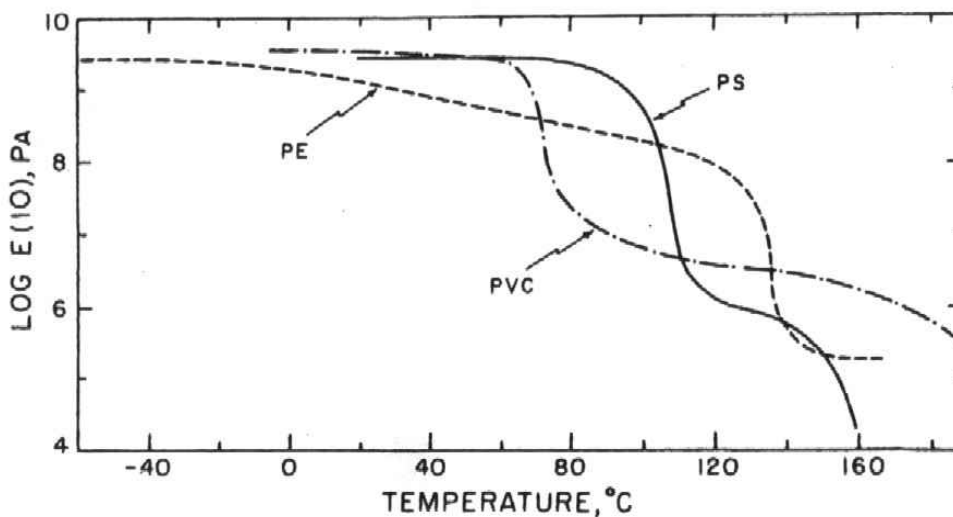


Figure 13. Comparison of ten-second modulus versus temperature curves for PS, PVC, and PE



- For crystalline polymers such as polyacetal, HDPE, and PP, the crystallinity can be controlled by changing the cooling rate from melt, sorts and concentration of nuclear agent, and MW.
- high crystallinity: improved chemical resistance and physical properties  $\Rightarrow$  needs controlling the crystallinity.
- comparison of modulus of various materials.

(6) Liquid crystalline polymers(LCP)

- ① LCP; - fluids with constant orientation(keeps crystallinity)  $\Rightarrow$  ordered state.
  - molecular structure: rigid rod
  - aspect ratio(length of the rod/diameter)  $> 6.4$  (Flory)
  - isotropic state(irregular configuration) at dilute or high temperature.
  - meso phase at low temperature and concentrated solution.
  - rigid backbone or side chain.

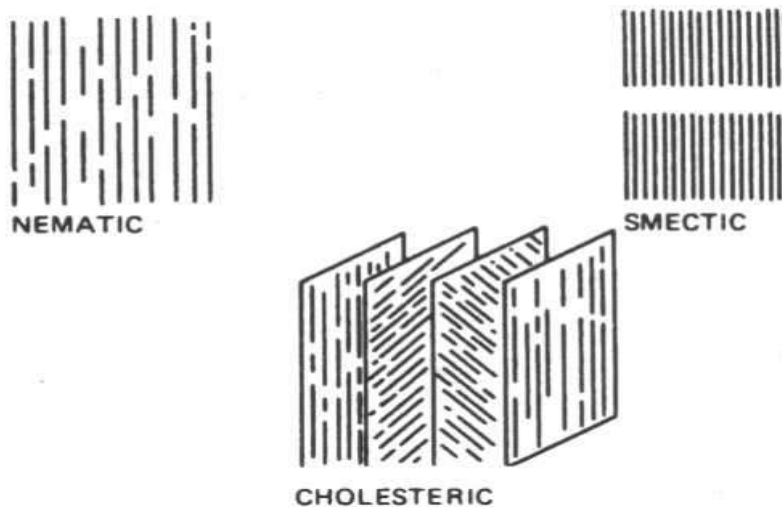


Figure 14. Schematic representation of the types of molecular order in the three basic types of liquid crystals.

(7) Crosslinking

- ① crosslinked polymers; increased modulus in the rubbery region with crosslinking density.
- ② for further crosslinking  $\Rightarrow$  increased  $T_g$ , the physical properties of rubber is lost, and turns out to thermosetting material(high E at high temperature). $\Leftrightarrow$  large amount of crosslinking agent, high temperature of crosslinking, augmented reaction sites of crosslinking agent.

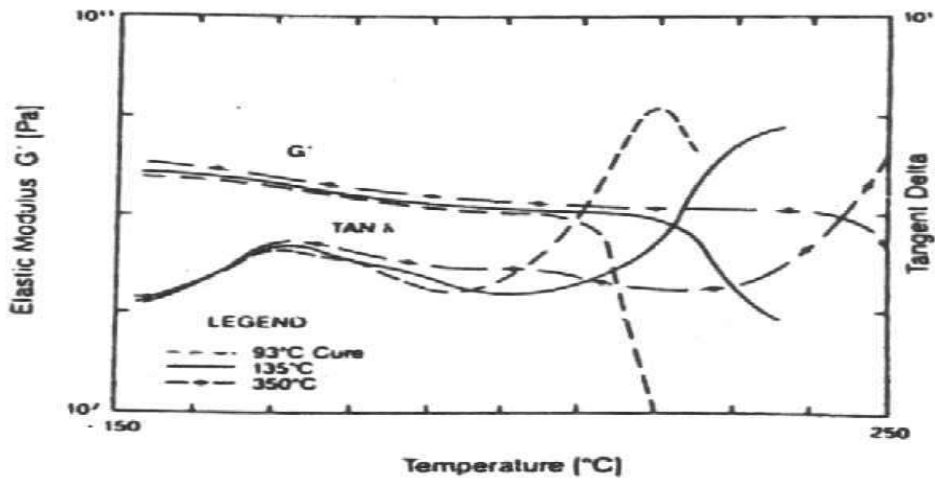


Figure 15. Effect of cure temperature on the modulus and glass transition of epoxy neat resin.

(8) Plasticizer

- ① PVC;  $T_g$ 가  $78^\circ\text{C}$ 인 thermoplastic. By the amount of added plasticizer, it is used as synthetic leather, wall-paper, PVC pipe, etc. Thus PVC can be used in various purposes from hard PVC to soft PVC.
- ② Due to the amount of added plasticizer, the  $T_g$  of the material varies.

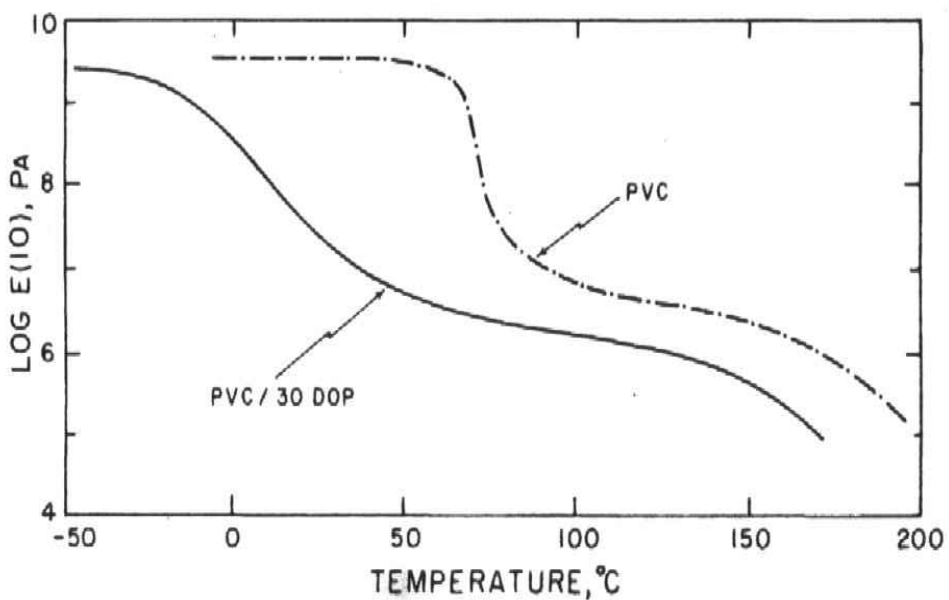


Figure 16. The effect of plasticization on a modulus-temperature curve.(American Chemical Chemistry)

(9) Copolymer

- ① To understand and control the characteristics of the products, copolymers are often synthesized using suitable molecular design.
- ② For example, methylmethacrylate(MMA)- methacrylate(MA) copolymer:
  - compare the  $T_g$  of each polymer  $\rightarrow T_g$  of PMMA  $>$   $T_g$  of PMA
  - single  $T_g \rightarrow$  homogeneous system  $\rightarrow$  random copolymer
  - double  $T_g \rightarrow$  heterogenous system(no compatibility)  $\rightarrow$  block copolymer  $\rightarrow T_g$  of the each component
- ③ Storage modulus  $G'$  and loss modulus  $G''$  at 1 Hz as a function of temperature for a copolymer of CHMA and MMA and for the same copolymer plasticized by 20 parts of DBP to 100 parts of copolymer.

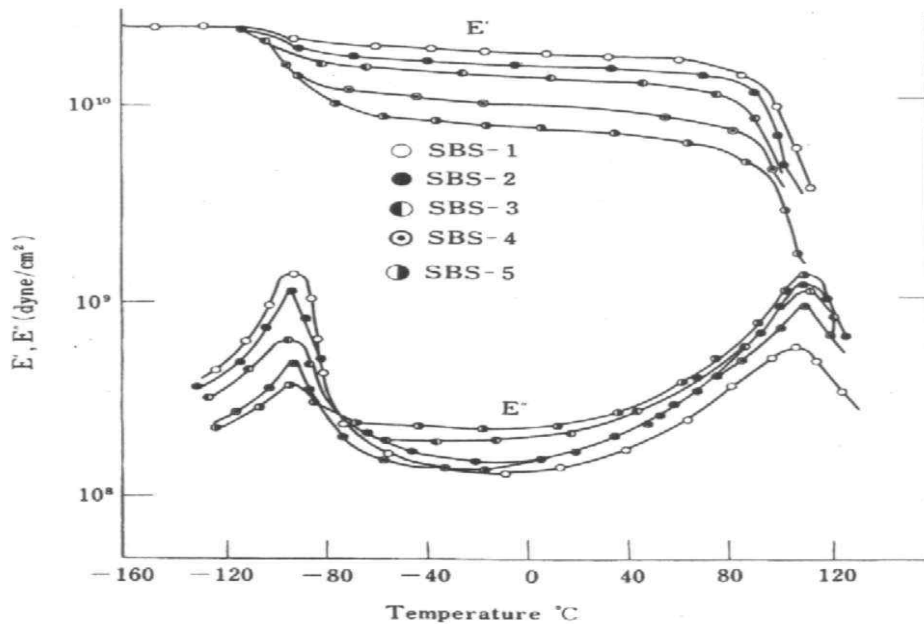


Figure 17, Dynamic mechanical behavior of polystyrene-*block*-polybutadiene-*block*-polystyrene, as a function of the styrene-butadiene mole ratio(M.Matuo)

(9) Blends

- ① Polymers exhibit their characteristic properties depending on their chemical structure, physical structure (branching, side chain, liquid crystalline segment, etc).
- ② To design better property and improved characteristics, mixing technique of two pure polymers is used.
- ③ © Compatible polymer blend: rheological properties of the blends followed by the rule of the mixture. Similar to the random copolymer which is homogeneous

$$Y = x_1y_1 + x_2y_2$$

© Incompatible mixture: Two different characteristics, no time-temperature superposition principle applied. By adding compatibilizer into the system or different processing conditions, better properties can be obtained .

- ④ Dynamic experiment at low frequency range is suggested.
- ⑤ Rheological properties of blend ; influenced by the morphology of the system.
- ⑥ Interfacial characteristics between the domain and matrix influence the rheological properties.

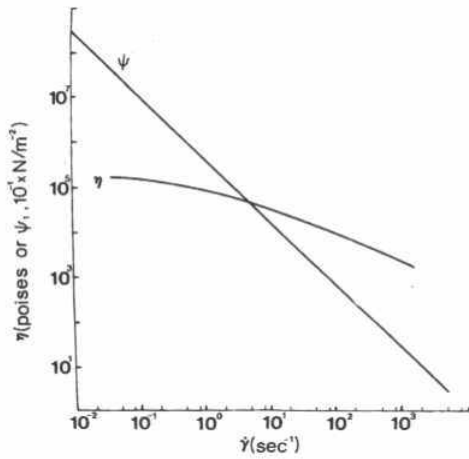


Figure 18. Shear rate dependence of melt viscosity  $\eta$  and elasticity,  $\psi = N(dt/d\dot{\gamma})^2$ , observed for Malen.

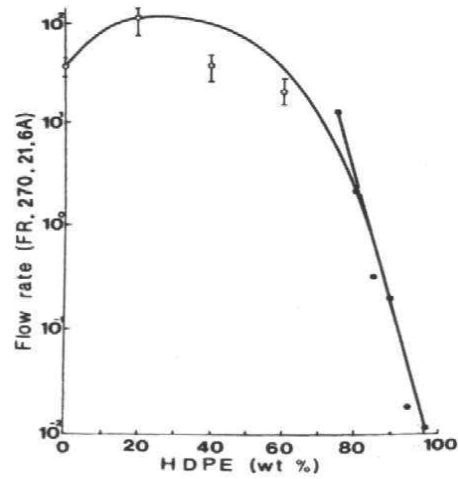


Figure 19. Composition dependence of melt fluidity for PP-HDPE blends measured at 543K.

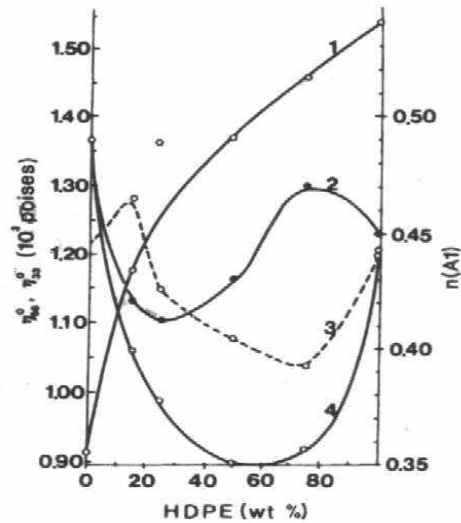


Figure 20. Composition dependence of various melt viscosity parameters at 463K. PP-HDPE blends

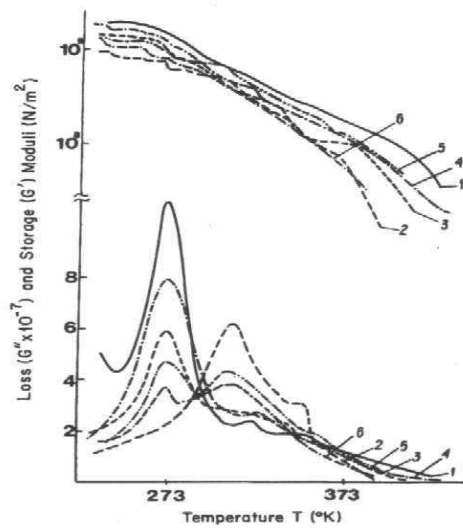


Figure 21. Temperature and composition dependence of the complex shear modulus  $G^*$ ,  $G'$ , and  $G''$ .

## (11) Solvent and Concentration

- ① Interaction between polymer and solvent exists(solubility parameter( $\delta$ ), cohesive energy density( $\delta^2$ ), like dissolves like).
- good solvent: PS in toluene,
  - theta( $\Theta$ ) solvent: PS in
  - poor solvent: PS in water

## ★ Solubility parameters of solvents and polymers

Polymer	$\delta(\text{cal}/\text{cm}^3)^{1/2}$	Solvent	$\delta(\text{cal}/\text{cm}^3)^{1/2}$
polyethylene	8.00	n-C <sub>6</sub> H <sub>14</sub>	7.24
polystyrene	8.60	CCl <sub>4</sub>	8.58
poly(methymethacrylate)	9.10	C <sub>6</sub> H <sub>6</sub>	9.15
poly(vinyl chloride)	9.50	CHCl <sub>3</sub>	9.24
Nylon 66	13.60	(CH <sub>3</sub> )C=O	9.71
polyacrylonitrile	15.39	CH <sub>3</sub> OH	14.50

★ Group molar attraction constants: calculating the solubility parameter for polymers. According to Small

Group	G	Group	G	Group	G
-CH <sub>3</sub>	214	Ring 5-membered	105-115	Br single	340
-CH <sub>2</sub> - single-bonded	133	Ring 6-membered	95-105	I single	425
-CH <	28	Conjugation	20- 30	CF <sub>2</sub> } <i>n</i> -fluorocarbons only	150
> C <	-93	H (variable)	80-100		
CH <sub>2</sub> =	190	O ethers	70	S sulfides	225
-CH= double-bonded	111	CO ketones	275	SH thiols	315
> C=	19	COO esters	310	ONO nitrates	~440
CH=C-	285	CN	410	NO <sub>2</sub> (aliphatic nitro-compounds)	~ 440
-C=C-	222	Cl (mean)	260	PO <sub>4</sub> (organic phosphates)	~ 500
Phenyl	735	Cl single	270	Si (in silicones)	-38
Phenylene (o,m,p)	658	Cl twinned as in > CCl <sub>2</sub>	260		
Naphthyl	1146	Cl triple as in -CCl <sub>3</sub>	250		

(12) Fillers

- ① Fillers; glass fiber,  $\text{TiO}_2$ ,  $\text{CaCO}_3$ (calcite), carbon black.
- ② Improvements; mechanical properties, color control, dielectric property control, cost down.
- ③ Inorganic fillers; - viscosity increases(reinforcing effect).
  - yield stress observed because of high viscosity at low shear rate.
  - $T_g$  and modulus increase.
- ④ organic fillers; polymer particles( $\eta$ varies depending on the role of particles)
- ⑤ fiber fillers; need carefulness because of orientation of the fiber.

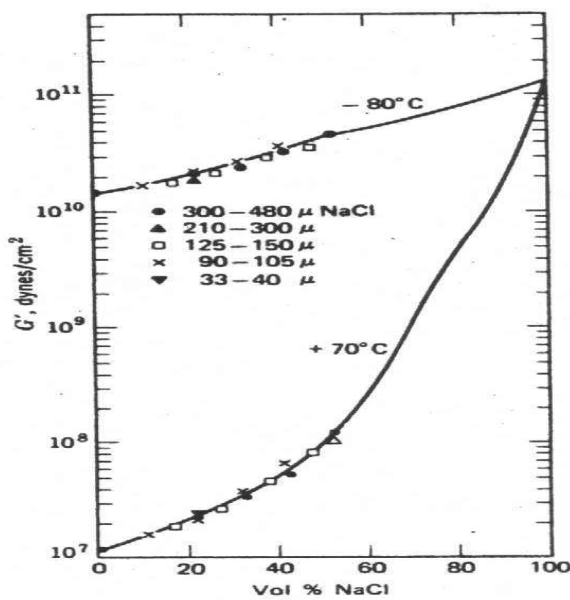


Figure 22. Shear storage modulus  $G'$  at 1 Hz for a cross-linked polypropylene ether containing sodium chloride particles with sharp size distributions.

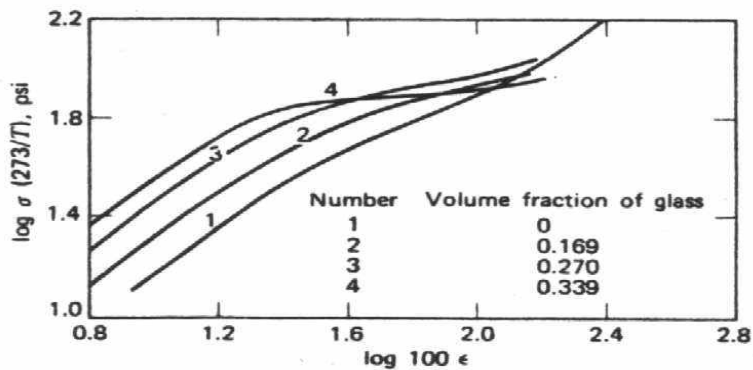


Figure 23. Stress-strain curves at 60 °C for styrene-butadiene rubber containing small glass beads at several fractions(Fedors and Landel)

## 8. Conclusions

By measuring rheological properties, we understand or investigate the structure/property, process/fabrication relationships. For better understanding, thermal, mechanical, and morphological properties are needed.

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