(b) the temperature at which the modulus for a measuring time of 10^{-6}h is the same as that at -80℃ for a measuring time of 1h

(sol) -80℃, measuring time 1h에서 polyisobutylene의 stress relaxation modulus는 $10^9 N/m^2$이다. 여기서 shift factor 10^6에 해당하는 temp 변화는?

식(13.70)에서

loga(273-80) = loga(193) = 1.5

$$\log\frac{a(193)}{a(T)} = 6 = 1.5 + 4.5$$

$$\log a(T) = -4.5 = \frac{-17.44\Delta T}{51.6+\Delta T}$$

여기서 $\Delta T = 18$

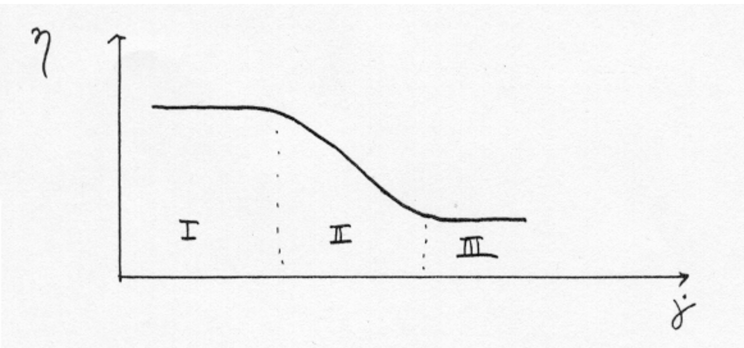
∴ $T = T_g + 18 = 197 + 18 = 215K = -58$℃

Chapter 15. Rheological Properties of Polymer Melts

(i) Shear viscosity (η)

$$\eta = \frac{shear\_stress}{shear\_rate} = \frac{\tau}{\frac{dv}{dx}} = \frac{\tau}{\dot{\gamma}}$$

- At the very low rates of deformation, polymeric melt also show Newtonian behavior. In this case the shear viscosity will be characterized by the symbol η_0



Region I : Lower Newtonian region
Region II : Non-Newtonian region (pseudo plastics region)
Region III : upper Newtonian region

- shear viscosity depends on

  $\bar{M}_w$, MWD, Temp, $\dot{\gamma}$, τ, P

(ii) Extensional viscosity (λ)

$$\lambda = \frac{tensile\_stress}{rate\_of\_extension} = \frac{stress\_component\_in\_the\_direction\_of\_tensile\_deformation}{rate\_of\_relative\_increase\_of\_length}$$

$$= \frac{\sigma}{\frac{1}{L}\frac{dL}{dt}} = \frac{\sigma}{\dot{\varepsilon}}$$

여기서 the extension, $\varepsilon = \ln\left(\frac{L}{L_0}\right)$

rate of extension, $\dot{\varepsilon} = \frac{d\varepsilon}{dt} = \frac{1}{L}\frac{dL}{dt}$

also, $\lambda_0 = \underset{\longrightarrow}{Lim}\,\lambda(\dot{\varepsilon})$

- under Newtonian condisions a simple relationship exists between η_0 and λ_0

$$\lambda_0 = 3\eta_0$$

* Mode of deformation

- simple extension – a cylindrical rod of polymer is subjected to extension in axial direction under the influence of a tensile stress which is constant over the cross section
- simple shear − the polymer melt subjected to simple shear is contained between two (infinitely extending parallel walls)
- extensional viscosity depends on : M_w, temp, rate of extension, tensile strain (degree of extension)
- 매우 높은 shear rate에서는 “melt fracture”가 생길 가능성이 있음.

* complicated modes of deformation

(a) convergent flow – an extensional deformation and a shear deformation are superposed, as encountered in the extry and exit effects of capillary flow

(b) biaxial flow – shear process in different directions are superposed, as encountered in the barrel of a screw extruder.

B. Newtonian shear viscosity of polymer melt

- Newtonial viscosity or zero-shear viscosity

  $\eta_0 = \lim(\dot{\gamma} \rightarrow 0)\eta(\dot{\gamma})$

  this is the case under steady state conditions at low rates of shear

- Effect of molecular weight on η_0

  $\log\eta_0 = 3.4\log M_w + A$

  for molecular weight higher than a certain critical value, M_{cr}(see table 15.3)

- Effect of molecular temperature on η_0

- melting point보다 높은 온도에서는
  $\eta = B \exp(E_\eta/RT)$
  where E_η is an activation energy
  B = const. By Anderson and Eyring

- temp가 T_m과 T_g 사이에서는 (by WLF equation)
  $$\log \eta(T) = \log \eta(T_s) - \frac{C_1(T - T_s)}{C_2 + (T - T_s)}$$
  여기서 standard temp = T_g 이면, C_1=17.44, C_2=51.6
  if T_s is chosen arbitrary, then C_1=8.86, C_2=101.6

◦ M_w와 M_{cr}과의 관계
  $\log\eta_0 = \log\eta_{cr} + 3.4\log(M_w/M_{cr})$ if $M_w > M_{cr}$
  $\log\eta_0 = \log\eta_{cr} - \log(M_{cr}/M_w)$ if $M_w < M_{cr}$

◦ A new viscosity-temp relationship(by van Krevelen and Hoftyzer)
  $$\log\eta_{cr}(1.2T_g) = E_\eta(\infty)\left(\frac{0.052 - 8.5*10^{-5}T_g}{T_g}\right) - 1.4$$
  Fig15.4에는 $\frac{\eta_{cr}(T)}{\eta_{cr}(1.2T_g)}$ 와 A, 그리고 Tg/T의 관계를 나타내었음
  여기서 A = $\frac{1}{2.3}\frac{E_\eta(\infty)}{RT_g}$

(Ex 15.1) Estimate the Newtonian viscosity of PET with a molecular weight $M_w = 4.7*10^4$ at 280℃

C. Non-Newtonian shear viscosity of polymer melt
◦ viscosity as a function of shear rate
  $\tau = K \cdot \dot{\gamma}^n$ (n, see Table 15.8)
◦ Rheological quantities and their interrelations
◦ Experimental methods
  - the Cox and Merz equations : found empirically that the steady-state shear viscosity at a given shear rate is practically equal to the absolute

value of the complex viscosity $|\eta^*|$ at a frequency numerically equal to this shear rate :

$$\eta(\dot{\gamma}) \approx |\eta^*|(\omega)$$

여기서 $|\eta^*| = \dfrac{|G^*|}{\omega} = \dfrac{\sqrt{(G')^2 + (G'')^2}}{\omega}$

◦ An approximate method has been proposed by Adamse et al (1968)

$P_{11} - P_{22} = \tau_{11} - \tau_{22} = \gamma_1$ (first normal stress difference)

$\approx$ 2G’ (storage modulus)

◦ Correlation of non-Newtonian shear data

Fig. 15.6, 15.7, 15.8, 15.9 설명

여기서 $Q = M_w/M_n$ (distribution factor)

Prediction of viscosity as a function of shear rate

i) For monodisperse polymer : Q=1.0 일 때

- characteristic time const : θ_0

$$\theta_0 = \frac{\eta_0}{G_0} = \frac{6}{\pi^2}\frac{\eta_0 M}{\rho RT}$$

여기서 $G_0 = \dfrac{\pi^2}{6}\dfrac{\rho RT}{M}$

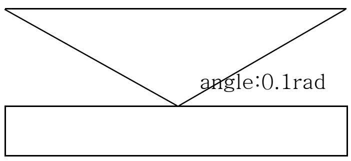
그림 15.6에는 η/η_0 vs $\dot{\gamma}\theta_0$의 관계를 나타내므로 η_0 should be known, $\dot{\gamma}$를 알고 있으므로 θ_0를 알면 된다. η_0는 estimate 할 수 있음

- By using RMS(Rheometrics Mechanical Spectrometer)

We can measure dynamic properties:

◦ G’ = dynamic storage modulus (Real M/Θ)

(component of torque in phase with the strain) (dyne/cm^2)



(회전하면 strain $\Rightarrow$ $\dfrac{2\pi}{\theta} = \dfrac{2\times 3.14 rad}{0.1 rad} = 62.8$)

◦ G” = dynamic loss modulus

(component of torque 90° out of phase with strain ; in phase with strain rate)

$|G^*|$ (complex modulus)

$= \sqrt{(G')^2 + (G'')^2}$ (dynes/cm^2)

η’ = (dynamic in-phase viscosity)

$= \dfrac{G''}{\omega}$ (poise) (dyne·sec/cm^2, g/cm·sec)

η” = (dynamic out of phase viscosity)

$= \dfrac{G'}{\omega}$ (poise)

$|\eta^*| = \sqrt{(\eta')^2 + (\eta'')^2} = \dfrac{|G^*|}{\omega}$ (poise)

tanδ= G”/G’

Cox-Merz rule :

$\eta(\dot{\gamma}) \cong |\eta^*|(\omega)$ (15.46)

: 일반적인 relation은 아님

ii) For polydisperse polymer :

$$\theta_0 \cong \frac{6}{\pi^2}\frac{\eta_0 \overline{M}_w Q}{\rho RT} \qquad (15.56)$$

이식과 η_0로부터 Fig(15.6)으로부터 η를 estimate 할 수 있음

$$\theta_M = \frac{6}{\pi^2}\frac{\eta_0 \overline{M}_w}{\rho RT} \qquad (15.57)$$

이식과 그림15.11로부터 η를 estimate할 수 있음

(Ex. 15.2) Estimate the decrease in the viscosity of a PET melt at a shear rate of 5000s^{-1}. M_w=3.72*10^4, Q=3.5, T=553K, η_0=156 N·S/m^2

(sol) According to eq(15.57)

$$\theta_M = \frac{6}{\pi^2}\frac{\eta_0 \overline{M}_w}{\rho RT} = \frac{6}{\pi^2}\frac{156 \cdot 3.72\times10^4}{1160\times8310\times553} = 6.6\times10^{-4}$$

∴ $\dot{\gamma}\theta_M$ = 5000*6.6*10^{-4} = 3.3

From Fig15.11로부터 $\dot{\gamma}\theta_M$=3.3 and Q=3.5, η/η0≈0.50

$\eta_{esti} \approx 80 N \cdot S/m^2$, $\eta_{exp} = 81.5 N \cdot S/m^2$

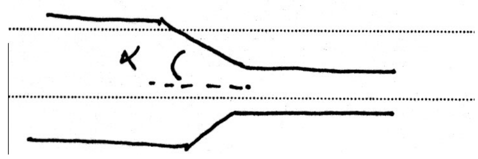
D. Extensional Viscosity of Polymer Melts

- measurement of rheological quantities on the tensile deformation of polymer melts is extremely difficult and requires the development of special techniques
- $$\lambda = \frac{\sigma}{\frac{1}{L}\frac{dL}{dt}} = \frac{\sigma}{\dot{\varepsilon}} = \frac{tensile\_stress}{rate\_of\_extension}$$
  - ◦ the tensile force is measured as a function of time, so that at a constant rate of deformation $\dot{\varepsilon}$ it is possible to calculate the true tensile stress and the extensional viscosity $\lambda = \sigma/\dot{\varepsilon}$ at an arbitrary time t
- extensional viscosity of polymer melts increase with increasing rate of deformation
- Fig15.12 has no universal validity, but depends on the nature of the polymer
- It is not possible to predict the extensional viscosity behavior of an arbitrary polymer

E. Elastic Effects in Polymer Melts

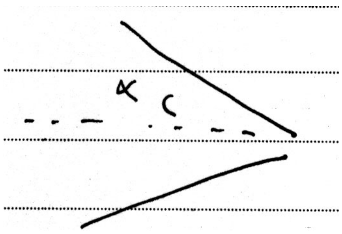
◦ Converging flow phenomena

i) for coni-cylindrical flow :



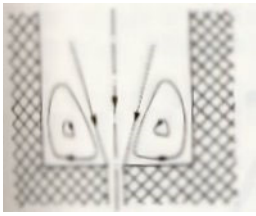
$$\tan\alpha = \left(\frac{2\eta}{\lambda}\right)^{\frac{1}{2}}$$

ii) for wedge-flow :



$$\tan\alpha = \frac{3}{2}\left(\frac{\eta}{\lambda}\right)^{\frac{1}{2}}$$

- the most extreme case of converging flow arises when a melt is forced from a large reservoir into a narrow tube



the large ring vortex

- this phenomenon is a direct consequence of a high extensional viscosity linked with a relatively low shear viscosity

◦ Die swell

F. Rheological Properties of LCP melts

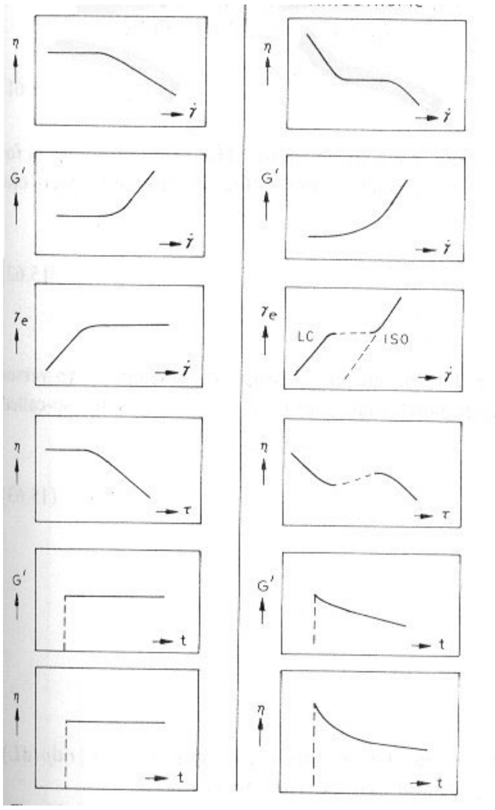
- LCP melts show a number of characteristic deviations:

1) a high elastic response to small amplitude oscillations, but absence of gross elastic effects, such as post-extrusion swelling

2) a flow curve (viscosity vs flow rate) which clearly shows several (usually three regions

3) a strong dependence on the thermo-mechanical history of the melts

4) a low even very low thermal expansion



$$|G^*| = complex\ \ viscosity = \sqrt{(G')^2 + (G'')^2}$$

G' = Storage modulus

G" = Loss modulus

η*= complex viscosity

$$|\eta^*| = \sqrt{(\eta')^2 + (\eta'')^2} = \frac{|G^*|}{\omega}, \qquad \tan\delta = \frac{G''}{G'}$$

$\eta' = \dfrac{G''}{\omega}$, $\eta'' = \dfrac{G'}{\omega}$, Cox-Merz rule : $\eta(\dot{\gamma}) \approx |\eta^*|(\omega)$