Chapter 8. Interfacial Energy Properties

- surface energy is a direct manifestation of intermolecular forces.
- the specific free surface energy of a material is the excess energy per unit area due to the existence of the free surface.
- The interfacial tension is the excess energy per unit area due to the formation of an interface.

여기서 γ_l : surface tension of liquid (mN/m, erg/cm^2, dyne/cm)
γ_s: surface tension of solid
γ_{sl}: interfacial tension between liquid and solid

- In liquids, the surface energy manifests itself as an internal force which tends to reduce the surface area to a minimum.

A. Surface Energy of Liquid and Melts

· Methods for determining the surface tension of liquids
  (a) direct method : a metal disk out of a liquid
  (b) quasi-static methods : capillary rise, 등
  (c) dynamic methods : measuring the period of oscillation of vibrating drops.

· Estimation of surface tension of liquids
· Calulation of surface tension from an additive function : the Parachor

$$\gamma = \left(\frac{P_s}{V}\right)^4 \qquad (8.5)$$

여기서 P_s : Parachor, (cm^3/mol)×(erg/cm^2)

$$P_s = \gamma^{\frac{1}{4}}\left(\frac{M}{P}\right) = \gamma^{\frac{1}{4}} \cdot V \qquad (8.4)$$

· Interfacial Tension between a solid and a liquid,

$$\gamma \cos\Theta \approx \gamma_s - \gamma_{sl} \qquad (8.6)$$

여기서 $\cos\Theta$ = contact angle,
complete wetting 인 경우 $\Theta = 0^\circ$

식 (8.6),(8.7),(8.8),(8.9)로 부터

$$\cos\Theta \approx 2\Phi\left(\frac{\gamma_s}{\gamma_l}\right)^{1/2} - 1 \qquad (8.10)$$

여기서 θ를 알면 γ_s를 구할 수 있음.

또한 식(8.10)으로부터 contact angle, θ도 predict 할 수 있음.

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· Methods to determine surface tension of solids : 3 가지 방법

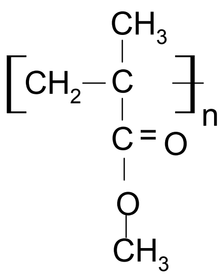
(a) measuring the θ between the solid and different liquids and applying Eq.(8.9)

(b) determination of

(c) extrapolation of surface tension data of polymer melts to room temp.

· Estimation of surface tension of solid polymer from the Parachor.

(Ex8.1) Estimate the surface tension of solid PMMA and its contact angle with methylene iodide, (γ =50.8)



M=100.1 (g/mol)

ρ_g= 1.17

V_g= 86.5 (cm^3/mol)

From Table 8.1 (p.229)

$$P_s = \gamma^{1/4}\frac{M}{\rho} = \gamma^{1/4}\cdot V \qquad (8.4)$$

$$\gamma = \left(\frac{P_s}{V}\right)^4$$

	Psi
1×(-CH_2-)	39.0
1×(-C-)	4.8
2×(-CH_3-)	112.2
1×(-COOH-)	64.8
	220.8

$$\gamma = \left(\frac{220.8}{86.5}\right)^4 = 42.5\,(mN/m)$$

식(8.10)과 (8.8) 로부터

$$\cos\Theta \approx 2\Phi\left(\frac{\gamma_s}{\gamma_l}\right)^{1/2} - 1 = 2\left(\frac{42.5}{50.8}\right)^{1/2} - 1 = 0.8$$

θ=34º (실험치 θ=41º)

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· Temperature dependence of γ

- since the Parachor, Ps is independent of the temp.

$$\gamma(T) = \gamma(298)\left(\frac{\rho(T)}{\rho(298)}\right)^4 \qquad (8.12)$$

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C. General Expression for the interfacial tension

- By Owen and Wendt;

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^{\,d}\cdot\gamma_2^{\,d})^{1/2} - 2(\gamma_1^{\,a}\cdot\gamma_2^{\,a})^{1/2} \qquad (8.21)$$

여기서 d= dispersion forces

a= the combined polar interactions,

- dipole, induction, and hydrogen bonding

-by Wu ; polymer Interface and Adhesion

$$\gamma_{12} = \gamma_1 + \gamma_2 - \frac{4\gamma_1^{\,d}\cdot\gamma_2^{\,d}}{\gamma_1^{\,d}+\gamma_2^{\,d}} - \frac{4\gamma_1^{\,p}\cdot\gamma_2^{\,p}}{\gamma_1^{\,p}+\gamma_2^{\,p}}$$

(Data) $\begin{cases} \gamma_1 \text{(vectra)} = 43.8 \text{ (mN/m)} \quad \text{at } 310^\circ C \\ \gamma_1^d = 27.7 \qquad \gamma_1^p = 16.1 \text{ (mN/m)} \end{cases}$

$\begin{cases} \gamma_2\text{(PET)} = 26.5 \text{ (mN/m) at } 310 \\ \gamma_2^d = 24.2 \quad \gamma_2^p = 2.3 \quad \text{(mN/m)} \end{cases}$

여기서 $\gamma = \gamma^d + \gamma_1^p$

$\begin{cases} \text{p=polar interaction} \\ \text{d=dispersion interaction} \end{cases}$

따라서 $\gamma_{12} = 10.6$ (mN/m)

(Ex) Estimate the surface tension of polypropylene at 200ºC

(Ex) Estimate the interfacial tension of polyethylene(linear) and polypropylene(isotatic) at 200ºC.
(i) Wu method, (ii)Owen and Wendt

(Ex) Estimate the surface tension of polypropylene (isotactic) at 200ºC
sol)

$$\gamma(T) = \gamma(298)\left(\frac{\rho(T)}{\rho(298)}\right)^4 \qquad (8.12)$$

i) $V_c(298) = 44.4$ (cm^3/mol) (Table 4.7) p.84

$V_c(473) = Vc(298)+E_c(T_m-298)+\Delta V_m+E_l(T-T_m)$
여기서 $V_c(298) = 44.4$ (cm^3/mol)
$E_c=138\times10^{-4}$ (cm^3/mol·K)
$\Delta V_m = 0.55\times10^{-3}\times V_w\times T_m$
$= 0.55\times10^{-3}\times30.7\times4.45$(K)
$= 7.5$ (cm^3/mol), (Table 4.12 참조)
$E_l = 307\times10^{-4}$
$T_m= 44.5$ (K) (from table 6.11) p.164

$\therefore V_c= 44.5+138\times10^{-4}(445-298)+7.5+307\times10^{-4}(473-445)$
$= 54.89$ (cm^3/mol)

. 200ºC 에서 PP 의 density 는

$\rho(200^{\circ}C) = M/V_c = 42.1(g/mol) / 54.89(cm^3/mol)=0.77(g/cm^3)$

. $\gamma(473) = \gamma\ (298)\ (0.77/0.95)^4$

$= 32.5\ (0.432) = 14.03\ (mN/m)$

ii) $V_l(473) = V_l(298) + E_l(T-298)$

여기서 $V_l(298) = 49.5$

$E_l = 307\times10^{-4}$

$T_m=445(K)$

.$V_l(473) = 49.5+307\times10^{-4}\ (4.73)$ p.298

$= 54.87\ (cm^3/mol)$

$\rho(200)=42.1/54.87=0.77$

$\gamma(473)=32.5(0.454)=14.03\ (mN/m)$