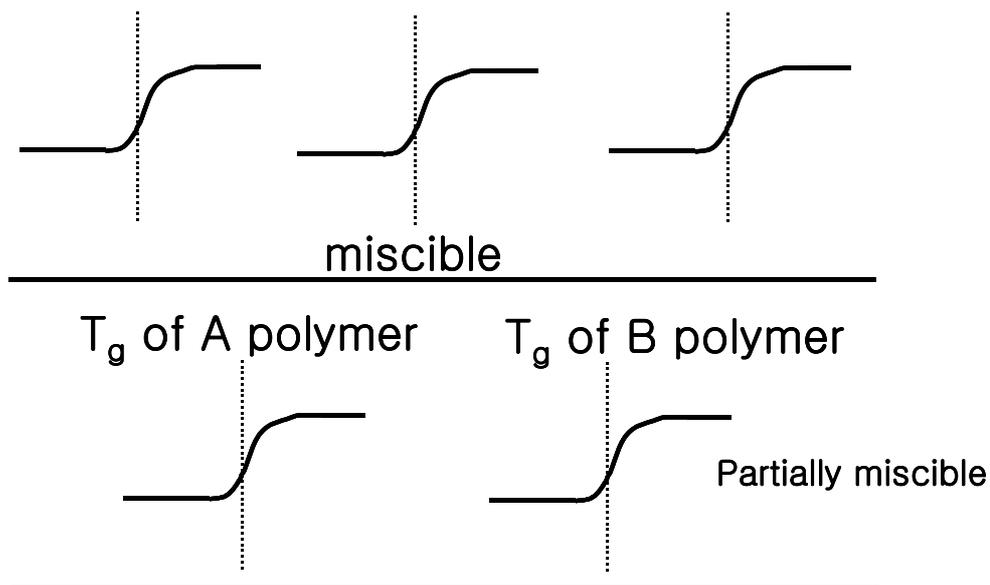


제 5 강의

Methods of Enhancing Miscibility

Chapter 5 Methods of Enhancing Miscibility

- Polymer Blend 시 두 고분자의 혼합후 상태를 나타내는 것으로 :
 - compatibility : engineering 측면에서 볼 때 partially miscible 한것도 compatible.
 - miscibility : thermodynamics 측면에서 볼 때 (expected of a single-phase system)
- Miscibility를 나타내는 혹은 측정기준.
 - ① film 의 투명성 (transparency) - amorphous 와 crystalline polymer를 잘 구별해야 함. 혹은 굴절률 (refractive index 도 check)
 - ② single glass transition을 나타내는지 확인.
 - a homogeneous blend exhibits one T_g .



shifted toward center by DSC (differential scanning calorimeter) measurement .

- Polymer Blends :

- ref)**
1. Polymer - Polymer Miscibility.
by Olabisi, Robeson, and Shaw, Academic (1979)
 2. Polymer Blends, by D. R. Paul. Ed., Academic (1978)
 3. Specific Interaction and the Miscibility of Polymer Blends.
by Coleman, Graf, Painter, (1991)
 4. Polymer Alloys and Blends, Thermodynamics and Rheology
by L. A. Utracki (1990)

- Blend preparation :

- i) Melt Blending
- ii) Solution blending

i) Melt Blends - Screw extruder 이용

ii) Solution Blends - solvent polymer
(solution)

iii) microscopy method (Scanning Electron microscopy).

iv) FT-IR (Fourier transform IR)

v) Ternary solution method

(polymer 1- polymer2 - solvent)

- Compatible components form a single, transparent phase in mutual solution, while incompatible polymers exhibit phase separation if the solution is not extremely dilute.

- Equilibrium is relatively easily achieved in dilute solution and

- Blend of immiscible (or partially miscible) materials can be useful so long as no significant desegregation occurs while the mixture is being mixed.

- Practical Aspects of Polymer Blending
 - Polymer blends have become a very important subject for scientific investigation in recent years.
 - Copolymerization and blending are alternative routes for modifications of properties of polymers.
 - Blending is less expensive.
 - The restriction of environment pollutions.
(solvent for polymerization)

- Objectives in Making Blends
 - components of the mixture adhesive to each other well enough to maintain an adequate mechanical integrity for the pair
 - load bearing capacity be maintained for the expected reasonable lifetime of the particular article.
 - miscible blends should give better mechanical properties.
(eq) poly(phenylene oxide) and polystyrene - trade name "Noryl" by General Electric.

- Procedures to Retard on Eliminate Demixing.
 1. Use of miscible component (i.e. $\Delta G_m = \Delta H_m - T\Delta S < 0$)
 - (a) Low-molecular-weight polymers
 - (b) Specific interaction to produce negative ΔH
 - (c) Generally match solubility parameter or Flory-Huggins interaction parameters.

 2. Rely on slow diffusion rates
 - (a) Mix high-molecular-weight polymers
 - (b) Cocrystallization

 3. Prevent segregation
 - (a) cross-linking
 - (b) Forming interpenetrating polymer network (IPN)

(c) Mechanical interlocking of components.

4. Use "Compatibilizing agents"

- (a) Statistical copolymers
- (b) Graft copolymers
- (c) Block copolymers

• Procedures to Retard or Eliminate Demixing of Polymer Mixture

1. Use of Miscible Components

- Thermodynamically stable mixtures will of course form stable blends.
This implies miscibility on a molecular level

(a) Use of low molecular-weight polymers

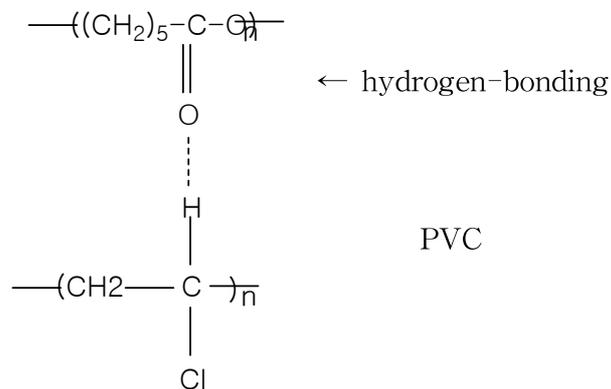
$$\Delta G_m = \Delta H_m - T\Delta S_m < 0$$

- increasing the entropy of mixing, ΔS_m will favor a more negative ΔG_m
(e.g.) low m.w. of polystyrene and poly(methyl methacrylate) are miscible,
but high m.w. > 100,000 are not.

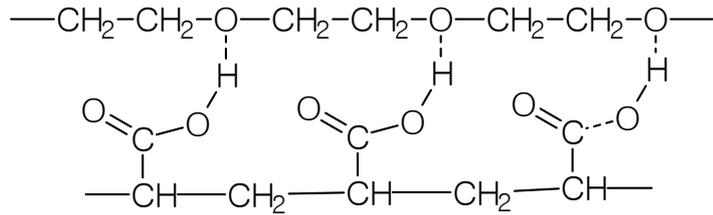
(b) Specific interactions to produce negative ΔH_m

- (e.g.) hydrogen-bonding, dipole-dipole interactions acid-base reactions.

poly(ϵ -caprolactone)



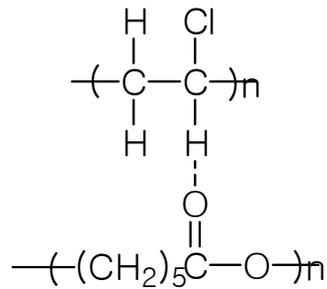
poly(ethylene oxide)



(e.g.) If specific interactions do occur between the components of a polymer blend, the mixing process will be exothermic ($\Delta H_{\text{mix}} < 0$) and miscibility can be realized.

(example)

1. The hydrogen bonding between the α -hydrogen of the PVC and the carbonyl oxygen of poly(ϵ -caprolactone)



2. The phenyl group coupling between the aromatic rings of poly(2,6-dimethyl-1,4-phenylene oxide) and polystyrene.
3. Dipole interactions in the blends of poly(vinylidene fluoride) and poly(methyl methacrylate)

(e.g.)

- Acid-base interactions



(c) Solubility parameter or Flory-Huggins interaction parameters.

- The most widely used method for predicting miscibility \rightarrow matching solubility parameters and hydrogen-bonding tendency
- A small or negative Flory-Huggins parameter value is also characteristics of a stable mixture

(e.g.) $\chi_{12} = V_1^\circ (\delta_1 - \delta_2)^2 / RT$

assume : ΔH_m is derived only for the van der Waals interactions. Specific interactions like ionic, or hydrogen bonds are implicitly eliminated from the model

- Solubility parameters can be assigned a priori to the components of a mixture, while χ value must be determined by experiments with the actual mixture.
- The χ parameter refers to a pair of components and can include specific interactions even if they are not mentioned in the basic Flory-Huggins theory

2. Reliance on Slow Diffusion Rates

(a) High-Molecular-weight Polymers

- since demixing is a diffusional process, it can be reduced to an acceptable level by using higher-molecular-weight, more viscous polymers
- the rate of segregation will be retarded

(b) cocrystallization

- portions of each are anchored in the ordered regions in which they both participate

(e.g.) polyethylene + polypropylene + ethylene/propylene copolymer
(compatibilizing agent)

(3) Prevention of Segregation

(a) Cross-Linking

- a thermoset system - cross-linked
- a thermoplastic system

(e.g.) conductive carbon black is mixed with a peroxide, polyethylene, rubber - yield semiconductive polymers when peroxide decomposes it produces radicals, and the parent polymers are linked by primary valence forces(bonds)

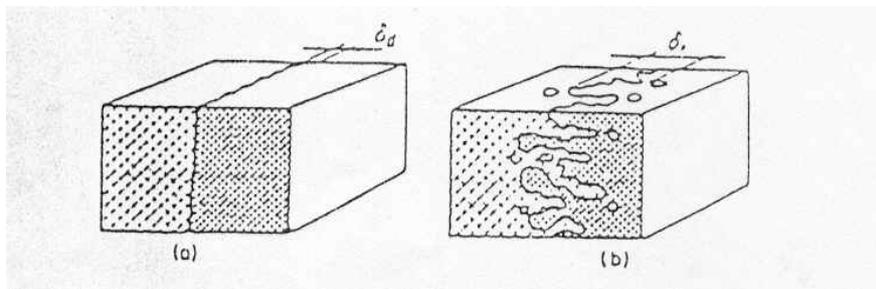


Fig.34 Model of the interphase layer in a polyolefin blend (a) after dispersive mixing: (b) after laminar mixing and/or heat treatment (Courtesy Yu. S. Liparov

Lipatov et al., Kolloid Zh, 481 (1975) in 'Polymer Blends' D.R. Paul and S. Newman eds., Chapter 21. Part II (1978)

(b) Interpenetrating Polymer Networks (IPN)

- IPN is formed by swelling a cross-linked polymer with a monomer and polymerizing and cross-linking the latter to produce interlocked networks
- In semi IPN systems, only the first polymer is cross linked.
- Most of these materials reveal phase separation but the phases vary in size, shape and sharpness of boundaries depending on the basic miscibility of the component polymers, the cross-link density in the two polymers, and the polymerization method.

- A certain degree of inherent affinity of the components is needed for ordinary IPN because they must form solutions or swollen networks during synthesis.
- This may not be required (inherent affinity) for IPNs based on latex polymer, where a solvent can be added to the first, cross-linked latex polymer to open it up to penetration by the second monomer and cross-linker

(c) Mechanical Interlocking of Components

- a blend may be prevented from demixing because of numerous mutual entanglements produced by mechanical processing.

(e.g) If the melt viscosity of polypropylene and poly(ethylene terephthalate) polymers are reasonably matched under extrusion condition a finely dispersed blend may be produced in fiber form

- oriented of such fibers yield strong filaments in which microfibrils of the two partially crystallized polymers are intertwined and unable to separate.

(4) Use of "Compatibilizing Agent"

- mixtures of immiscible polymers can be made more stable by addition of another material that adheres strongly to the original components of the blends.

(e.g) poly(vinyl chloride) (PVC)/poly(methyl methacrylate) (PMMA) --- dioctyl phthalate, phthalate ester.

(a) statistically copolymer 사용

(e.g) PVC/(ethylene-ethyl acrylate-carbon monoxide copolymer)

(b) Graft copolymer

(e.g.) high impact polystyrene (HIPS)

poly(acrylonitrile-butadiene-styrene)

rubber-toughened glassy polymers → polystyrene and poly(styrene-co-acrylonitrile)

- grafting procedures are needed for effective rubber toughening of relatively brittle glassy polymers like polystyrene and SAN.

(c) Block copolymers

- Block and graft copolymers have generally similar effects of collecting at interfaces and stabilizing dispersions of one homopolymer in another
- graft copolymers - made by free radical process
- block copolymers - made by ionic or step growth process

(e.g) ABA type (styrene/butadiene/styrene) block copolymer

● Several types of phase behavior in liquid.

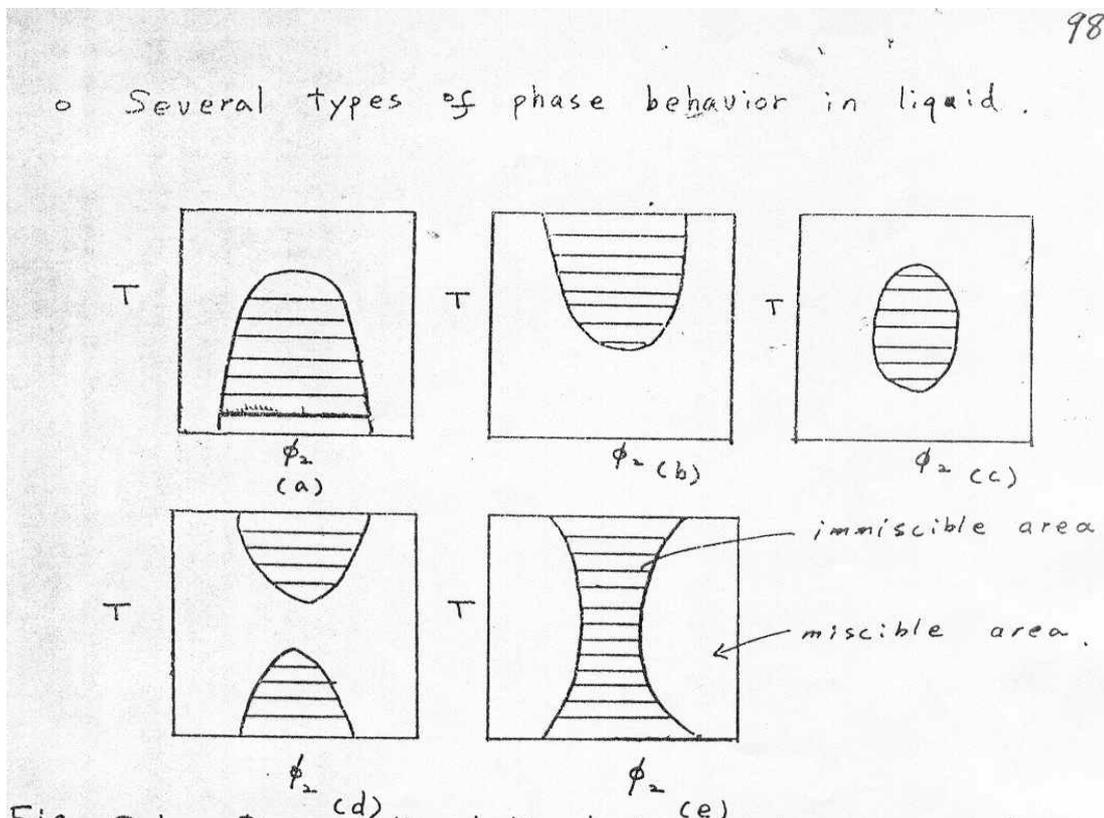


Fig. Schematic of liquid - liquid temperature - composition phase diagrams.

Example : (a) A common one (b) water + n-hexane (c) water + triethylamine (d) water + nicotine (e) partially miscible polymer mixtures (e.g.) polycarbonate + PET or polystyrene in cyclohexane depending m.w. of polystyrene

We call :

- (a) upper critical solution temperature (UCST)
- (b) lower critical solution temperature (LCST)
- (d) UCST and LCST 공존

- Method for Determining Polymer - Polymer Miscibility.

① glass transition temperatures (T_g) :

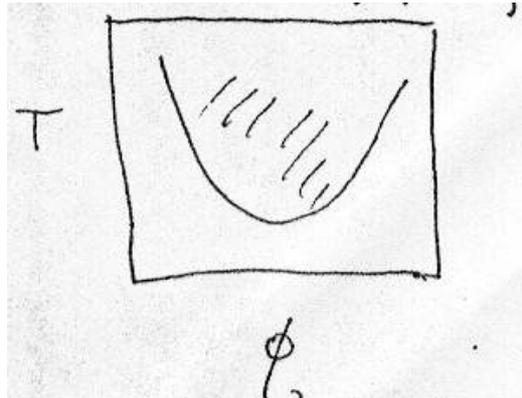
- the most commonly used method for establishing miscibility in polymer - polymer blends or partial phase mixing.
- a miscible polymer blends will exhibit a single glass transition between the T_g's of the components while for partially miscible systems the T_g's approach each other but do not become identical.
- differential scanning calorimetry (DSC) can be used.
- mechanical method using dynamic mechanical thermal analysis. (DMTA)
 - the elastic and viscoelastic properties of polymers derived by subjecting polymer to small - amplitude cyclic deformation can yield important information concerning transitions occurring. (tan δ vs temperature)

② Microscopy

- direct visual confirmation of presence of two phases.
- Heterogeneities exist even in miscible polymer systems by electron microscopy.
- phase contrast microscop : require as a minimum a difference in refractive index between the phases for contrast
- Electron Microscope : transmission electron microscopy(TEM) has been widely used in polymer-polymer studies.
the necessary step of microtoming (500 \AA) can be facilitated by cryogenic.

(e.g) SBR-PB(Styrene-butadiene rubber) and (polybutadiene) are immiscible
scanning electron microscopy(SEM) is very useful in surface (cross-section) studies of polymer blends. (need gold coatings for about 400 \AA)

③ Scattering Methods.



- cloud-point curve(CPC) : the CPC's found on heating and on cooling.

LCST found

: polystyrene-poly(vinyl methyl ether)

poly(ϵ -caprolactone)-SAN

poly(ϵ -caprolactone)-polycarbonate

poly(vinylidene fluoride)-PMMA

light scattering : sensitive to density and concentration fluctuations

X-ray scattering : sensitive to density fluctuation

Neutron scattering : measures the differential neutron scattering cross section of small concentrations of protonated polymer dispersed in matrix of deuterated polymer.

④ Ternary-solution Methods

- by allowing the polymer-polymer-solvent mixture to stand, usually for a few days, if phase separation does occur the two polymers are said to be immiscible.

(a) when two high polymers are incompatible in one solvent, they are generally also incompatible in all other solvents, but it is not always fulfilled.

(b) the limit of phase separation depends on the nature of the solvent.

(c) the molecular weight of the polymers is of great importance.

(d) there is no obvious relationship between the compatibility of the two polymers and the chemical nature of their monomers.

⑤ melting point(T_m) depression method :

$$\frac{1}{T_{m(blend)}^{\circ}} - \frac{1}{T_m^{\circ}} = -\frac{RV_2}{\Delta H_f^{\circ} V_1} \left[\frac{\ln \phi_2}{M_2} + \left(\frac{1}{M_2} - \frac{1}{M_1} \right) \phi_1 \right] + \frac{-RV_2}{\Delta H_f^{\circ} V_1} (x_{12} \phi_1)^2$$

where V : molar volume

ΔH_f° : perfect crystal heat of fusion

T_m° : equilibrium melting point

$T_{m(blend)}^{\circ}$: equilibrium melting point in the blend

Ref.) 1. Nishi & Wang, *Macromolecules* 8, 909 (1975)

2. Rostan:, *Polymer*, 31 , 899(1990)

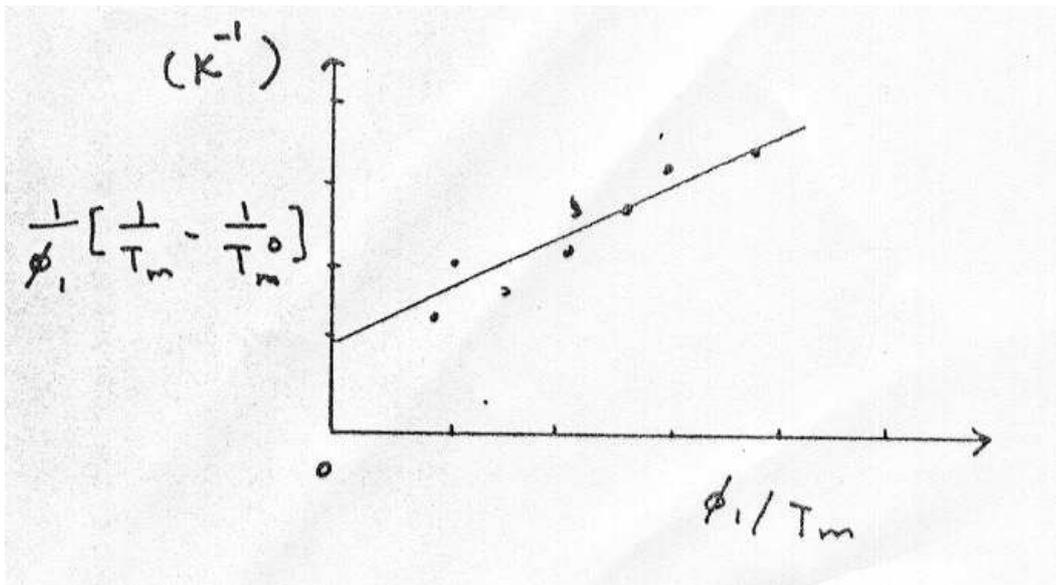
Subscript 1 for amorphous polymer, 2 for crystalline polymer

If M_1 and M_2 (molecular weight or degree of polymerization) are very large, then

$$\frac{1}{T_{m(blend)}^{\circ}} - \frac{1}{T_m^{\circ}} = \frac{-RV_2}{\Delta H_f^{\circ} V_1} (x_{12} \phi_1)^2$$

Let $BV_1/RT = \chi_{12}$ (Flory-Huggins interaction parameter)

$$\left(\frac{1}{M_2} - \frac{1}{M_1} \right) \phi_1 = \frac{-\beta V_2 \phi_1}{\Delta H_f^{\circ} T_m}$$



e.g) PVF2-PMMA blend $\chi_{12} = -0.295$ at $160\text{ }^{\circ}\text{C}$
 ref.) Olabisi et. al. , Polymer- Polymer Miscibility

⑥ Inverse Gas Chromatography Method (IGC)

- traditional gas chromatography determine the property of an unknown sample in the moving phase with a known stationary phase, while the inverse method determine the property of the stationary phase with the aid of a known vaporizable solute in the moving phase.
- in operation, the polymer material is placed in the column maintained at a temperature which is at least $50\text{ }^{\circ}\text{C}$ above the system T_g for glassy material and T_m for a crystallizable system.

(e.g.) ① poly(vinyl chloride) - Dioctyl phthalate by IGC, Su, Patterson, and schreiber

(ref.) J. Appl. Polym. Sci. , 20, 1025 (1976)

② PVC - poly(ϵ -caprolactone)(PCL), O.Olabisi, Macromolecules, 8, 316 (1975)

Polymer mixing 방법 :

- i) screw extrusion
- ii) solution casting / precipitation
- iii) freeze drying etc.

- screw extruder 사용시 측정할 수 있는 polymer melt properties.

melt density of mixture :

$$\frac{1}{\rho_m} = \frac{w_1}{\rho_1} + \frac{w_2}{\rho_2}$$

apparent shear rate ($\dot{\gamma}$) 측정:

$$\dot{\gamma} = \frac{4Q}{\pi R^3}$$

where Q is the volumetric flow rate,
R the radius of the die.

apparent shear stress (τ)

$$\tau = \frac{PR}{2L}$$

where P is the measured pressure
L the die length

Extrudate swell ratio = diameter of the extrudate / diameter of the capillary