액정고분자.

Skin

Oriented fiber

5 μm   Macrofibril

0.5 μm   Fibril
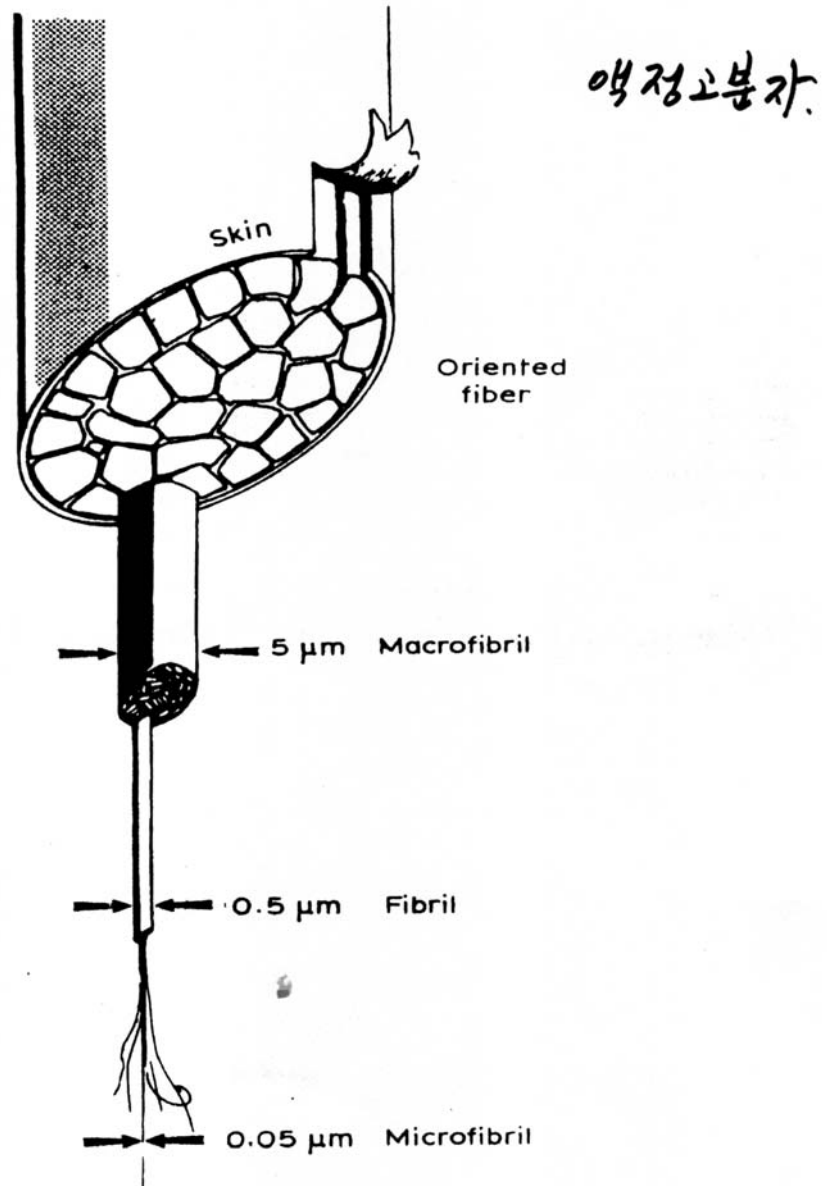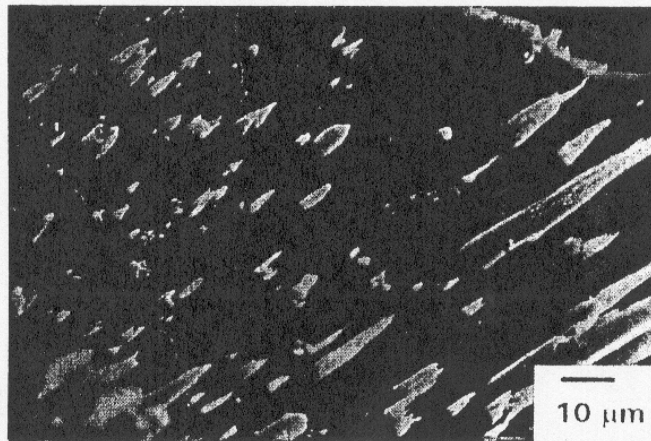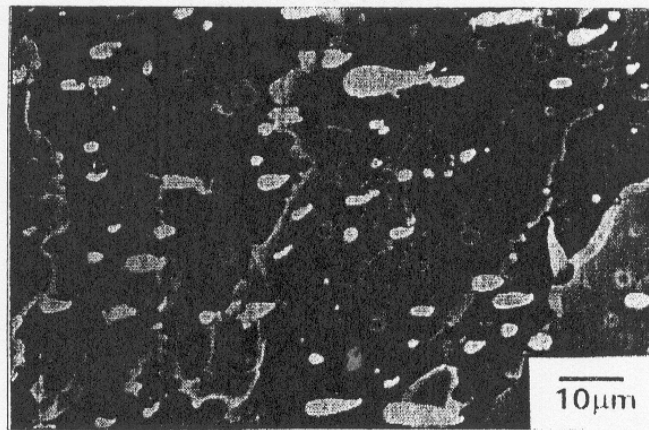
0.05 μm   Microfibril

Figure . The structures observed in uniaxially oriented LCP fibers, ribbons and films can be summarized by this structural model. The model defines the nature of the fibrillar textures into three categories based upon size: macrofibrils, fibrils and microfibrils.
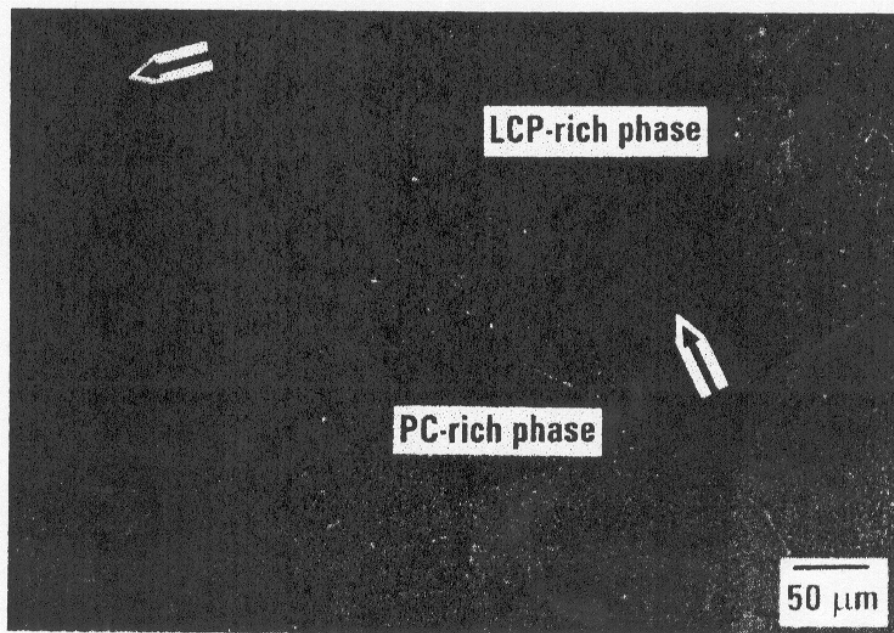
(a) LCP-PC 3/7 blend
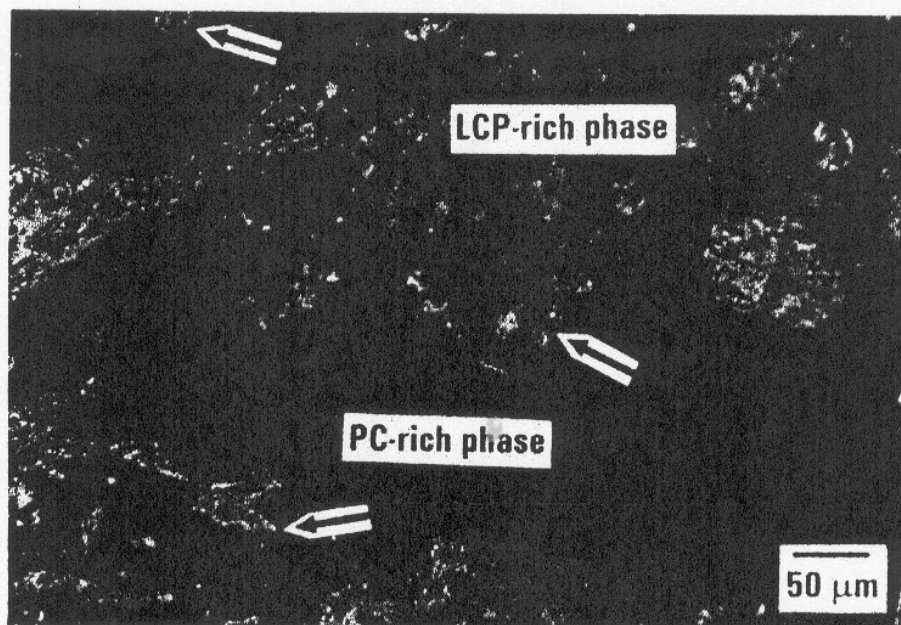

(b) LCP-PAS 1/9 blend

Fig.   Scanning electron micrograph cyrogenically fractured cross-sectional surfaces of the:
(a) LCP-PC 3/7 blend; (b) LCP-PAS 1/9 blend.

LCP-rich phase

PC-rich phase

50 μm

(b)

LCP-rich phase

PC-rich phase

50 μm

(c)

Fig. Polarized light micrographs of the PC-LCP blends
at 523 K: (b) not porlarized, PC-LCP (6/4)
(250°C) (c) polarized, PC-LCP (6/4)

● Polymer Blends

(reference)

    1. Polymer- polymer Miscibility

    By Olabisi, Robeson, and Shaw

    Academic Press(1979)

    2. Poplymer Blends, by D.R Paul, Ed,

    Academic Press (1978).

    3. specific Interactions and the Miscibility of Polymer Blends,

       by Coleman, Graf, and Painter(1990)

    4. Polymer   Alloys and Blends, Thermodynamics and

       Rheology, by L.A. Utracki,(1990).

● Blend Preparation   :

     (a) Melt blending- screw extruder   blend

                      extrusion   mixing .

     (b) Solution blending- mixing   cosolvent

           solution   cast   (film)

       blend   .

     (ex) polymer membrane(   )   .
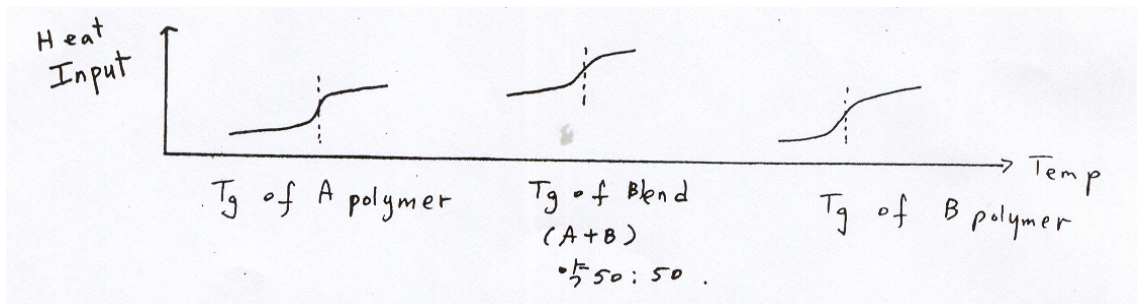
      , amorphous polymer   crystalline polymer   blend

    film   .

(2)DSC(differential scanning calorimetry):

                  T_g(   )

           -           .

(i) a single phase exhibits one Tg.

(ex) A polymer : Polycarbonate, Tg=150°C (423 K)

    B polymer : Polycaprolactane, Tg=- 52°C (221 K)

Blend (A+ B)/50:50

$$\frac{1}{Tg_{Blend}} = \frac{w_A}{Tg_A} + \frac{w_B}{Tg_B}$$

$$\frac{1}{Tg_{Blend}} = \frac{0.5}{423} + \frac{0.5}{221}$$ (Tg$_{Blend}$=17.3°C (290.3 K)

(2)   microscopy method (Scanning Electron microscopy).

(3)   FT- IR (Fourier Transform IR)

(4)   Ternary solution method (polymer 1- polymer 2 - solvent)

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

- Equilibrium is relatively easily achived in dilutions and

- Blends of immiscible (or partially miscible) materials can be useful so long as no significant desegration 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 Marking Blends

- components of the mixture adhere 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.

(e.g) poly (phenylene oxide) and polystyrene-trade name "Noryl" by General Electric.

● Procedure to Retard on Eliminate Demixing.

1. Use of miscible component (i,e, $\triangle G_m = \triangle H_m - T \triangle S < 0$).

    (a) Low-molecular-weight polymers

    (b) Specific interactions to produce negative $\triangle H_m$

    (c) Generally match solubility parameter of 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) Statical copolymers

(b) Graft copolymers

(c) Block copolymers

● Procedures to Retared or Eliminate Demixing of Polymer Mixtures.

1.Use of Miscible Components

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

(a) Use of low molecular- weight polymers

$$\triangle G_m = \triangle H_m - T \triangle S_m \quad < 0$$

Increasing the entropy of mixing, $\triangle S_m$ will favor a more negative $\triangle G_m$.

(e.g.) low m.w. of polystyrene and poly(methyl methacrylate) are miscible, but high m.w > 100,000 are not.
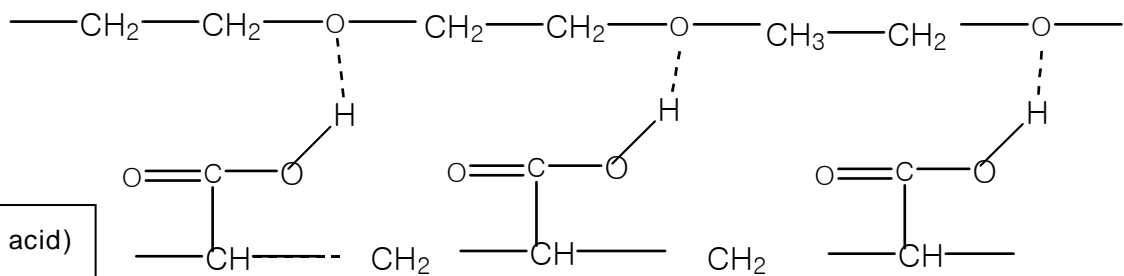
(b) Specific interactions to produce negative $\triangle H_m$.

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

(b) specific interactions to produce negative $\triangle H_m$

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

$$-\left(\!(CH_2)_5\!-\!\overset{\displaystyle O}{\underset{\displaystyle \|}{C}}\!-\!O\right)_{\!n}$$

hydrogen bonding

$$-\left(\!CH_2\!-\!\underset{\displaystyle Cl}{\overset{\displaystyle |}{\underset{\displaystyle |}{C}}}\!-\!\right)_{\!n}$$ PVC

poly(ethylene oxide)

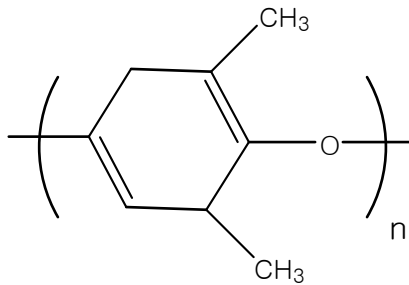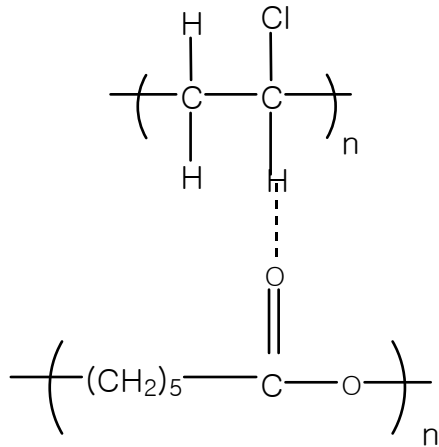$$-CH_2\!-\!CH_2\!-\!O\!-\!CH_2\!-\!CH_2\!-\!O\!-\!CH_3\!-\!CH_2\!-\!O-$$
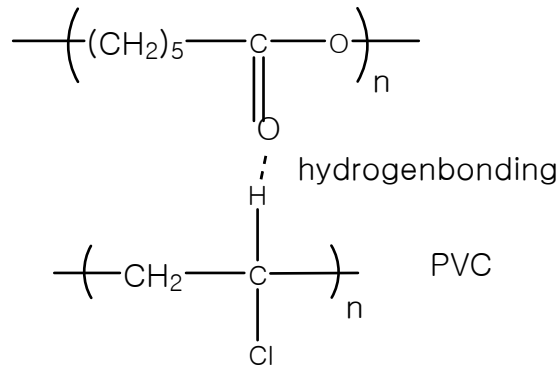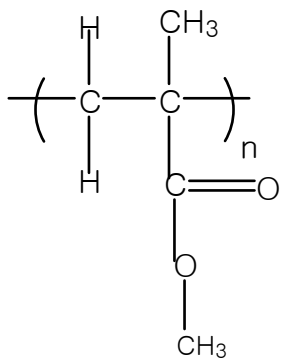
poly(acrylic acid)

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

(examples)

1. The hydrogen bonding between the -hydrogen of the carbonyl oxygen of poly(-caprolactone).

$$-\left(\!\begin{matrix}H\\ |\\ C\\ |\\ H\end{matrix}\ -\ \begin{matrix}Cl\\ |\\ C\\ |\\ H\end{matrix}\!\right)_n$$

$$-\left(\!(CH_2)_5 - \overset{\overset{O}{\|}}{C} - O\!\right)_n$$

$$-\left(\!\begin{matrix}CH_3\\ | \\ \end{matrix}\ O\!\right)_n$$
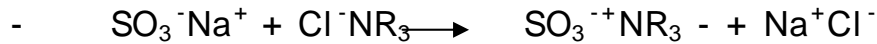
2. The phenyl group coupling between the aromatic rings of poly(2,6- dimethyl- 1,4- phenylene oxide)and polystyrene.

$$-\left(\!\begin{matrix}H\\ |\\ C\\ |\\ H\end{matrix}\ -\ \begin{matrix}CH_3\\ |\\ C\\ |\\ C=O\\ |\\ O\\ |\\ CH_3\end{matrix}\!\right)_n$$

3. Dipole interactions in the blends of poly(vinylidene fluoride)and poly(methyl methacrylate).

(e.g)

Acid - Base interactions

- $\quad$ $SO_3^- Na^+ + Cl^- NR_3 \longrightarrow \quad SO_3^{-\,+} NR_3^- + Na^+ Cl^-$

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

• The most widely used method for predicting ~~mis~~cibility mayching solubility parameters and hydrogen- bonding tendency.
• A small or negative Flory- Huggins parameter value is also characteristics of a stable mixture.

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

assume: $\triangle H_m$ is derived only for the Van der Waals interactions.
$\quad$ Specific interactions like ionic, or htdrogen bonds are implicitly eliminated from the model.

• Solubility parameters can be assigned a priori to the components of a mixture, while χ values must be determined by experiments with the actual mixture.
$\quad$ 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 resions in which they both participate.

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

(3) Prevention of Segregation

(a) Cross-Lingking

•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 decompses it produces radicals, and the parent polymers are linked by primary balance forces(bonds) .
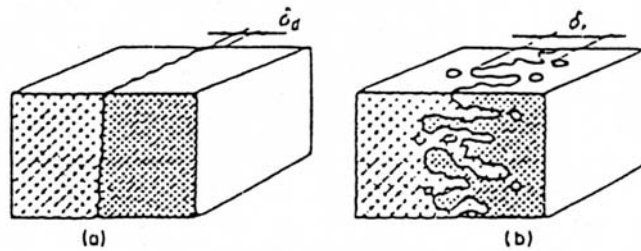
Fig. 34 Model of the interphase layer in a polyolefin blend: (a) after dispersive mixing; (b) after laminar mixing and/or heat treatment. (Courtesy Yu. S. Lipatov [141].)

- 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-lingking the latter to produce interlocked networks.

- In semi IPN systems, only the first polymer is cross linked.

- Most of these materials reveal phase seperation 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 conditions, a finely dispersed blend may be produced in fiber form.

- orientation 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 Agents"

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

(e.g.) poly(vinyl chloride)/poly(methyl methacrylate)

              PVC   PMMA

       plus   dioctyl phthalate, phthalate ester.

(a) statistically copolymer   .

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

(b) Graft copolymer

  (e.g.)   high impact polystyrene(HIPS)-polystyrene with polybutadiene

poly(acrylonitrile- butadiene- styrene) (ABS)

rubber- toughened glassy polymers $\longrightarrow$ polystyrene and poly(styrene- co- acrylonitrile) (SAN)

- 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.) ABS type(styrene/butadiene/styrene) block copolymer.

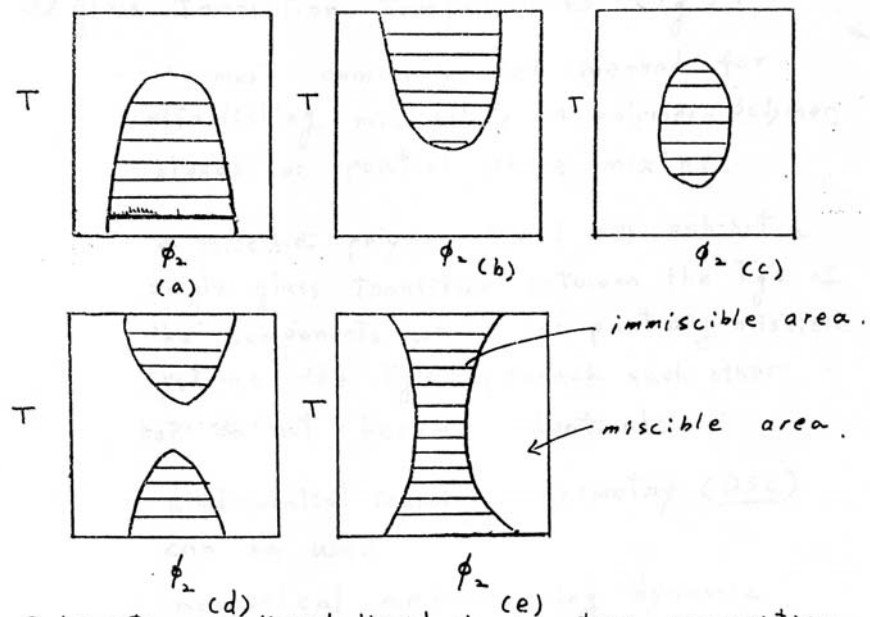• Several types of phase behavior in liquid.

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 on m.w. of polystyrene.

we call:

(a) upper critical solution temperature (UCST)

(b) lower critical solution temperature (LCST)

(c) UCST and LCST   .

• Method for Determining polymer- polymer Miscibility.

  glass transition temperatures (Tg):

- the most commonly used method for establishing miscibility in

  polymer- polymer blends or partial phase mixing.

- a miscible polymer blend will exhibit a single glass transition

  between the Tg's of the components while for partially miscible

  systems the Tg's approach each other but do not become

  identical.

  - differential scanning calorimetry (DSC)

  - mechanical method using dynamic mechanical thermal

    analysis

  (DMTA).

  : the slastic and viscoelastic properties of polymers derived by

  subjecting polymers to small- amplitude cyclic deformation can

  yield important information concerning transitions occurring

  (tanδ vs temp.)

  Microscopy

- Direct visual confirmation of the presence of two phases.

- Heterogeneities exist in miscible polymer systems by electron

  microscopy.

- Phase contract microscopy: 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 ($500\overset{o}{\text{A}}$) can be facilitated by

cryogenic.

(e.g.) SBR- PB (Styrene- Butadiene rubber)and (Polybutadiene)

are

immiscible.
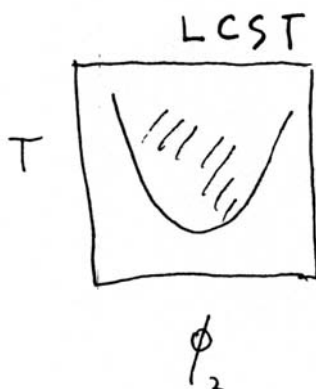
• scanning electron microscopy(SEM) is very useful in surface

(cross- section) studies of polymer blends.(need gold coatings

for

about $400\overset{o}{\text{A}}$)

Scattering Methods.

- cloud- point curve (CPC) : the CPCs found on heating and on

cooling.

LCST found— polystyrene- poly(vinyl methyl ether).

poly (- carolactone)- SAN

poly(- carolactone)- polycarbonate

‑ poly(vinylidene fluoride)‑ PMMA

• light scattering : sensitive to density and concentration
  fluctuations.

• X‑ ray scattering: sensitive to density fluctuations.

• Neutron scattering : measures the differential Neutron
                                                    scattering
cross section of small concentrations of protonated polymer
  dispersed in a matrix of deutrerated polymer.

  Ternary‑ Solution Method
‑ by allowing the polymer‑ polymer‑ solvent mixture to stand,
                                                    usually
for a few days, if phase seperation 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 seperation depends on the nature of the
  solvent.

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

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

melting point (T_m) depression method :

$$\frac{1}{T_{m\,blend}} - \frac{1}{T_m^0} = -\frac{R\bar{V}_2}{\Delta H_f^0 \bar{V}_1}\left[\frac{\ln \Phi_2}{M_2} + \left(\frac{1}{M_2} - \frac{1}{M_1}\right)\Phi_1\right] + \frac{R\bar{V}_2}{\Delta H_f^0 \bar{V}_1}(\chi_{12}\Phi_1)^2$$

where

$\bar{V}$: molar volume.

ΔH_f^0 : perfect crystal heat of fusion.

T_m^0 : equilibrium melting point

$T_{m\,blend}$: equilibrium melting point in the blend.

Subscript 1 for amorphous polymer, 2 for crystalline polymer.

Ref.)
1. Nish & Wang, Macromolecules 8,909 (1975).
2. Rostami, Polymer, 31, 899(1990).

Inverse Gas Chromatography Method (IGC).
- traditional gas chromatography determines the property of an unknown sample in the moving phase with a known stationary phase, while the inverse method determines the property of the stationary phase with the aid of a known vaporizing solute in the moving phase.

- in operation, the polymer material is placed in the column

maintained at a temperature which is at least 50°C above the system Tg for glassy material and Tm for a crystallizable system.

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

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

   PVC- poly(- carolactone)(PCL),

O.Olabisi, Macromolecules,8,316 (1975)

• Polymer mixing   :

i) screw extrusion

ii) solution casting / precipitation

iii) freeze drying etc.

- screw extruder   polymer melt properties.

• melt density of mixture:

$$\frac{1}{\sigma_m} = \frac{\omega_1}{\sigma_1} + \frac{\omega_2}{\sigma_2}$$

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

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

where Q is the volumetric flow.

      R is the radius of the die.

- apparent shear stress ( )

$$\tau = \frac{P\ R}{2L}$$

P is the measured pressure.

R is the die length.

- Extrudate swell ratio.

= (diameter of the extrudate)/(diameter of the capillary)