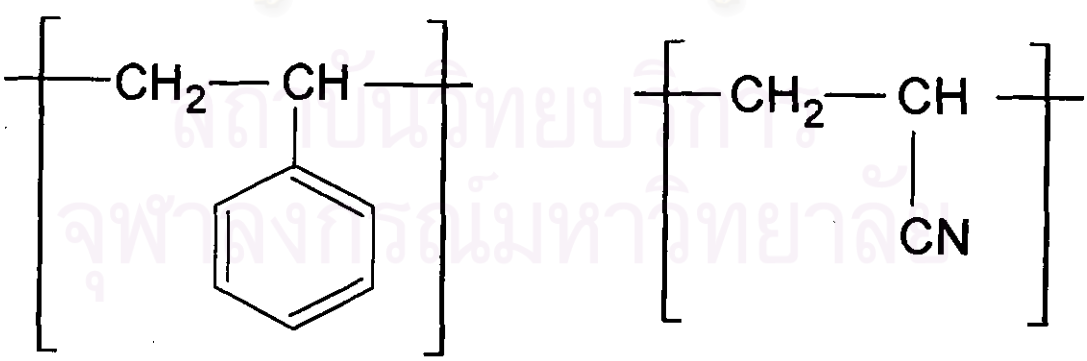
CHAPTER III

THEORY

3.1 Styrene-Acrylonitrile Copolymer (SAN)

Styrene-acrylonitrile copolymers (~ 20-30 wt% acrylonitrile content) have been commercially available for a number of years [Brydson, 1995] and are usually produced by suspension or emulsion polymerization. The repeating units of styrene and acrylonitrile in styrene-acrylonitrile copolymers are shown as in Figure 3.1.



Styrene **Acrylonitrile**

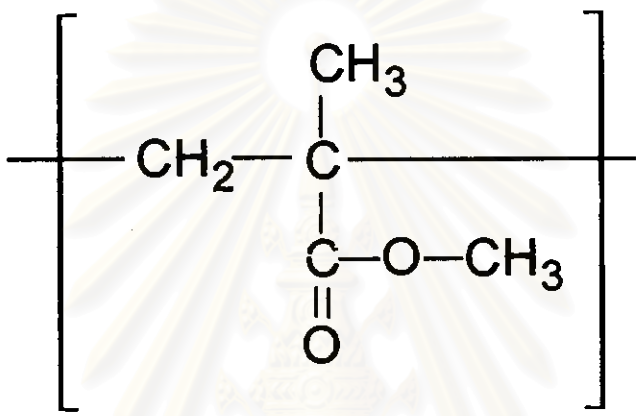
Figure 3.1 The repeating units of styrene and acrylonitrile.

Because of the polar nature of the acrylonitrile molecule, these copolymers have better resistance to hydrocarbons, oils and greases than polystyrene [Brydson, 1995]. They also have a higher softening point, a much better resistance to stress cracking and crazing and an enhanced impact strength and yet retain the transparency of the homopolymer [Brydson, 1995]. The higher the acrylonitrile content the greater the toughness and chemical resistance but the greater the difficulty in moulding and the greater the yellowness of the resin. So it is useful to add blue tint to counteract the yellowish tint.

The important features of rigidity and transparency make the material competitive with polystyrene and poly(methyl methacrylate) for a number of applications. However, it does not have such a high transparency or such good weathering properties as poly(methyl methacrylate). As a result of these considerations the styrene-acrylonitrile copolymers have found applications for dials, knobs and covers for domestic appliances, electrical equipment and car equipment, for picnicware and housewares, and for a number of other industrial and domestic applications. They are also widely used for transparent medical products and for meter or light lenses.

3.2 Poly(methyl methacrylate) (PMMA)

Poly(methyl methacrylate) is a clear, colorless and transparent thermoplastic. The general chemical structure of poly(methyl methacrylate) is shown in Figure 3.2.



Methyl Methacrylate

Figure 3.2 The chemical structure of poly(methyl methacrylate).

Poly(methyl methacrylate) is available as cast sheets, rods, and tubes, in extruded sheet and film form, and as compounds for the various fabricating processes. Poly(methyl methacrylate) compounds for molding or extrusion are made by bulk or suspension polymerization. The production of cast sheets, rods, and tubes is carried by bulk polymerization. The commercial poly (methyl methacrylate) is available in both atactic and syndiotactic structures. The glass transition temperatures (T_g) of the atactic and syndiotactic poly (methyl methacrylate) are approximately 104 °C and 115 °C, respectively. In

consequence of a T_g of 104 °C with its amorphous nature, commercial poly (methyl methacrylate) is thus a hard transparent plastic material in normal conditions of usage [Brydson, 1995].

Poly(methyl methacrylate) is resistant to many aqueous inorganic reagents, including dilute alkalis and acids [Charrier,1991]. The outstanding property of poly(methyl methacrylate) is its excellent transparency [Charrier,1991]. Coupled with its unusually good outdoor weathering behavior, its transparency makes it highly useful in all applications where light transmission is important.

The mechanical properties of the polymer are suitable for short-term loading, but for long-term service the tensile strength must be limited to 31,000 kPa (1,500 psi) to avoid crazing or surface cracking [Rosato, 1991]. Electrical properties are good but not outstanding. A limitation to the optical uses of the material is its poor abrasion resistance compared to glass.

Many applications of poly(methyl methacrylate) are found as hard contact lenses, automobile tail-light lenses, reflective devices, skylights, aircraft cabin windows, instrument and appliance covers, and home furnishing. It is also used as optical fibers [Charrier, 1991].

3.3 Solvents

3.3.1 Classification of Solvents

An analysis of solvent effects would be incomplete without a brief description of the properties of solvents. The obvious properties of solvents include dielectric constant, dipole moment, acidity and hydrogen-bonding ability. Of these, the dielectric constant (ϵ) emerges as the most-used guide to solvent solubility, since it often runs parallel to the dissolving power of solvents [Dack, 1976]. Polar compounds are often assumed to dissolve in solvent of high dielectric constant [Dack, 1976].

Solvents of similar dielectric constant usually have similar dipole moments (μ) which vary from zero to 4.5 Debye units. Values of dipole moments increase steadily from the hydrocarbon solvents (ϵ = 1 to 2, μ = 0 to 2 D) to solvents containing polar groups such as CN and NO_2 (ϵ > 20, μ = 2 to 4.5 D). The dipole moment largely determines the orientation of a solvent around an organic solute molecule in the absence of specific solute-solvent interaction.

As both ϵ and μ are important to organic systems, the common solvents have been classified according to their electrostatic factor "EF" defined as the product of ϵ and μ which takes into account the influence of both properties on the electrostatic solvation of solutes. A solvent's dissolving power depends on the effectiveness of this electrostatic solvation. Based on

the EF values and the structure of the solvents, they can be classified in three broad categories: weak hydrogen bonding solvent, moderated hydrogen bonding solvent and strong hydrogen bonding solvent [Wicks, 1992].

3.3.1.1 Weak Hydrogen Bonding Solvents

Hydrocarbon and chlorinated hydrocarbon solvents belong to this group. Due to their low electrostatic factors which lie between 0 and 2, electrostatic interactions between solute molecules and the solvents hardly occur at all. This is reflected by the weak dissolving abilities of the hydrocarbons [Dack, 1976]. Solute which does dissolve often exist as dimers or higher associates. Introduction of an electronegative atom (e.g., a halogen) into the hydrocarbon alters the situation considerably [Dack, 1976]. However, the use of chlorinated hydrocarbons, with higher dipole interactions than hydrocarbons, has been increasingly limited by toxic hazard concerns [Wicks, 1992].

3.3.1.2 Moderated Hydrogen Bonding Solvents

Esters, ketones and ethers belong to this category. Sometimes this group of solvents is called electron-donor solvent or hydrogen-bond acceptor solvent. The electrostatic factors of this group lie between 2 and 20. These electron-donor solvents are capable of interaction with the positive end of a solute dipole, causing an increase in the solvation and hence the solubility of that solute. In addition, preferential specific interactions

between solute and solvent molecules considerably reduce solute association. This group of solvents which are oxygen containing solvents is more effective in producing solute-solvent bonds than hydrocarbons and chlorinated hydrocarbons.

3.3.1.3 Strong Hydrogen Bonding Solvents

Alcohols, water and hydroxylic solvents are in this category. This group of solvents can perform as strong hydrogen-bond donor and acceptor solvents. According to their high electrostatic factors which lie between 15 and 50, the strong hydrogen bonding solvents can effectively dissolve the solute and prevent the association of the solute. These solvents are widely used for reactions because of the ability to dissolve organic solutes with ease, availability at low cost and their high rates of reactions.

3.3.2 Properties of Solvents

Five solvents which are methylene chloride, acetone, tetrahydrofuran, methyl ethyl ketone and 1,2-dichloroethane were used in this work. Methylene chloride and 1,2-dichloroethane are chlorinated hydrocarbons and are grouped as weak hydrogen bonding solvents. Acetone and methyl ethyl ketone are ketones while tetrahydrofuran is ether, they belong to moderated hydrogen bonding solvents. Brief properties of each solvent [Doolittle, 1954] are as follows.

3.3.2.1 Methylene Chloride [CH_2Cl_2]

Methylene chloride (or dichloromethane) is a volatile, practically nonflammable, colorless liquid of sweet, suffocating odor. It dissolves fats, oils, waxes, rubbers, alkaloids, bitumens, and cellulose triacetate. Methylene chloride is used as a paint remover, refrigerant, dewaxing agent for lubricating oils, and as an extractant for oils, fats, perfumes, flavors, and drugs. As a lacquer solvent methylene chloride is especially useful in dissolving those cellulose derivatives that are difficult to dissolve in the more conventional solvents. It is an intermediate in the manufacture of dyes, perfumes, hexamethylenetetramine, and other products.

3.3.2.2 Acetone [CH_3COCH_3]

Acetone (or 2-propanone or dimethyl ketone) is the first member of the homologous series of normal 2-ketones. It is a highly volatile, flammable liquid of pleasant odor. Acetone is a solvent for a great variety of resinous substances including cellulose acetate and vinyl chloride-acetate resins. The principal large volume application of acetone as a solvent is for dissolving cellulose acetate to produce the solution from which acetate rayon is spun and from which safety photographic film is cast. It is likewise used in volume in the manufacture of smokeless powder, and as a solvent in airplane dopes, artificial-leather dopes, cements, paint removers, and many other applications. Acetone is an absorbent for acetylene and permits relatively safe

shipment of this product as an acetone solution (under pressure) in steel cylinders.

3.3.2.3 Tetrahydrofuran [$O(CH_2)_3CH_2$]

Tetrahydrofuran is a volatile, colorless liquid of ethereal odor. This cyclic ether is an excellent solvent of a wide variety of resinous substances including the cellulose esters, ethylcellulose, polymethyl methacrylate, polystyrene, polyvinyl chloride, vinylidene chloride copolymers, and rubbers. The solvent power of tetrahydrofuran for cellulose acetate and alkaloids such as caffeine is improved by the presence of water. Tetrahydrofuran serves as a solvent in lacquers and adhesive formulations, for cementing plastic films, and as a chemical intermediate.

Tetrahydrofuran forms dangerous peroxides on exposure to oxygen. It should be destroyed or its absence established before distillation or evaporation of this solvent is attempted.

3.3.2.4 Methyl Ethyl Ketone [$CH_3COCH_2CH_3$]

Methyl ethyl ketone (or 2-butanone), the second member of the homologous series of normal 2-ketones, is a colorless, volatile, flammable liquid of rather pungent odor. It is an excellent solvent for most resinous substances, including the lacquer grade of cellulose acetate (acetyl content 55 to 56 percent). This solvent is employed widely for resins of vinyl chloride

type as well as for the more soluble vinyl chloride-acetate resins, polyvinyl acetate, and nitrocellulose. Another market for methyl ethyl ketone is in the dewaxing of lubricating oils, since a proper mixture of this solvent and benzene will precipitate the wax but retain the oil in solution.

The methyl ethyl ketone vapors are more irritating than those of acetone. Corneal injuries reported from vapors appear to have been caused by an unsaturated ketone present occasionally as an impurity in the commercial grade. Contact of methyl ethyl ketone vapors with eye membranes should be avoided.

3.3.2.5 1,2-Dichloroethane [$ClCH_2CH_2Cl$]

1,2-Dichloroethane (or ethylene chloride or ethylene dichloride) is a colorless, volatile, flammable liquid of sweet, pleasant odor. It dissolves fats, oils, waxes, many natural gums and resins, rubber, polyvinyl acetate, and vinyl chloride-acetate copolymers. With the addition of a small amount of ethyl alcohol, it is a solvent for nitrocellulose and cellulose acetate. Widely used as an extraction agent for many materials, ethylene chloride finds a market also as a metal-degreasing and textile-spotting solvent. It is useful in lacquers to dissolve those cellulose derivatives that are difficultly soluble in the conventional solvents. Additional outlets are as a fumigant and as an intermediate in the manufacture of other products.

Serious injury can result from brief inhalation of 1,2-dichloroethane at sufficiently high concentrations to produce near anesthesia.

3.4 Polymer Blends

A polymer blend is a mixture of at least two polymers or copolymers [Utracki, 1990]. The first polymer blend performed is not exactly known, but the first patent of polymer blend which was a blend between natural rubber and gutta percha was done in 1846 whereas the first patent on thermoplastic polymer blends, which was a blend of polyvinyl chloride (PVC) and acrylonitrile rubber (NBR), was performed in 1942 [Utracki, 1990].

The main purpose of blending polymers is to develop a new polymeric material which has specific properties different from those of the pure polymers at a lower cost instead of synthesizing a new polymer that requires more money, time and efforts. Many methods of preparation are used to form polymer blends.

3.4.1 The Preparation of the Blends

The preparation of polymer blends can be accomplished by several methods [Walsh, 1985].

3.4.1.1 Melt Mixing

Melt mixing is performed by mixing the polymers in the molten state under shear in the mixing equipment. It is the method of choice for the preparation of polymer blends in a commercial scale because of its simplicity, speed of mixing and the advantage of being free from foreign components (e.g. solvents) in the blends. A number of devices are available for laboratory-scale mixing such as brabender mixer, electrically heated two-roll mill, extruder, rotational rheometer.

The primary disadvantage of melt mixing is that both components must be in the molten state, which means that the temperature may be high enough to cause degradation. Besides, melt mixing is difficult to perform in some pairs of polymers due to a large difference in the melt viscosity of the components. The cost of the equipment is another disadvantage of melt mixing. Melt mixing only works well with large amounts of material, e.g. at least 50 grams is required for even laboratory-size mixing equipment. If mixing of quantities of less than 1 g is required, melt mixing is usually not feasible.

3.4.1.2 Solvent Casting

This method is done by dissolving polymers in a suitable solvent. Solution is then cast on a glass plate into thin films and the removal of solvent from the films is performed by evaporating at ambient or elevated

temperature. Solvent casting is the simplest mixing method available and is widely practised in academic studies. Very small quantities of experimental polymers can be handled easily.

The most severe problem with solvent casting is the influence of the solvent and the casting history on the resulting product. In spite of the fact that the most of the solvent can be removed from a cast film, the nature of the film depends strongly on the solvent and the conditions used during casting. Casting is best done in thin films, normally not exceeding 0.1 mm in thickness [Thongyai, 1990], with slow solvent removal to avoid concentration and temperature gradients during the removal of solvent

To remove traces of solvent from the casting, high temperature are invariably needed; protection of the polymer then becomes a consideration. Flowing inert gas or vacuums are typically used for this purpose and to reduce the partial pressure of the solvent over polymer films.

3.4.1.3 Freeze Drying

In the freeze drying process, a solution of the two polymers is quenched down to a very low temperature and the solvent is frozen. Solvent is then removed cleanly by sublimation. Dilute solutions must be used and the solution volume must be kept low for good heat transfer.

An advantage of this method is that the resulting blend will be independent of the solvent, if the solution is single phase before freezing and the freezing occurs rapidly. However, there are many limitations of this method. Freeze drying seems to work best with solvents having high symmetry, i.e. benzene, dioxane, naphthalene, etc. The powdery form of the blend after solvent removal is usually not very useful and further shaping must be performed. While not complex, freeze drying does require a good vacuum system for low-boiling solvents and it is not a fast blending method.

3.4.1.4 Emulsions

The handling of polymers as emulsion has as many advantages as the use of solvent casting. Films can be cast; mixing requires neither expensive equipment nor high temperature. However, emulsions of polymers are not always available or easy to make. While emulsion polymerization is highly advanced, it is not applicable to all monomers.

3.4.1.5 Mixing via Reaction

Co-crosslinking and interpenetrating polymer networks (IPN) formation are specialty methods for forming blends. The idea of these methods is to force a degree of miscibility by reactions between the polymers. Other methods involve the polymerization of a monomer in the presence of a polymer and the introduction of groups onto the polymer chain.

3.5 Miscibility Characteristics of the Blends

Mixing is the process that produces blends by putting several components together so that the blend become homogeneous or heterogeneous with small domain sizes. Miscibility of the blends can be classified into three categories [Thongyai, 1990] as follows:

1. Miscibility

Miscibility is the state of a single phase where the level of molecular mixing is adequate to yield macroscopic properties expected of single phase material [Olabishi, 1979].

2. Partial miscibility

Partially miscibility exhibits at least two miscible phases where each phase may comprise a high concentration of one component with a smaller dissolved portion of the other.

3. Immiscibility

Immiscibility is a state of two phases in which each phase comprises of the individual component and exhibits both macroscopic and/or microscopic properties of that component.

Miscibility characteristics of polymer blends depend on the conditions and methods of blend preparation such as compositions, temperature, pressure or

shear rate. The miscibility of polymer blends can be explained in terms of equilibrium thermodynamics.

3.5.1 Thermodynamics of Mixing

The miscibility of a mixture is determined by the Gibbs' free energy of mixing (ΔG_m), which is related to the entropic (ΔS_m) and enthalpic (ΔH_m) components through the simple relation in equation 3.1.

$$\Delta G_m = \Delta H_m - T\Delta S_m \qquad (3.1)$$

After blending, the value of free energy and other thermodynamics properties of the blend may be changed from the properties of the pure component. In general, the systems will change to an equilibrium condition of the lowest possible free energy. In other words, the system will be most likely to be more chaotic (more entropy) and has less internal energy (less enthalpy). Thus, the first criteria of miscibility is that the free energy of mixing must be less than zero. This criteria can be written as belows:

$$[\Delta G_m < 0]_{\text{Temperature, Pressure, Compositions}} \qquad (3.2)$$

The negative free energy change is a necessary but not a sufficient condition for homogeneity between two polymers. The additional criteria for miscibility, which is more important, is that the second derivative of ΔG_m with

the blend composition (volume fraction of either component, ϕ_i) must be greater than zero for the entire composition range. This criteria can be written as follows:

$$\left[\frac{\partial^2 \Delta G_m}{\partial \phi_i^2}\right]_{T,P} \geq 0 \qquad (3.3)$$

The concept behind the criteria for miscibility can be demonstrated by the approximate illustrations [Thongyai, 1990] as belows:

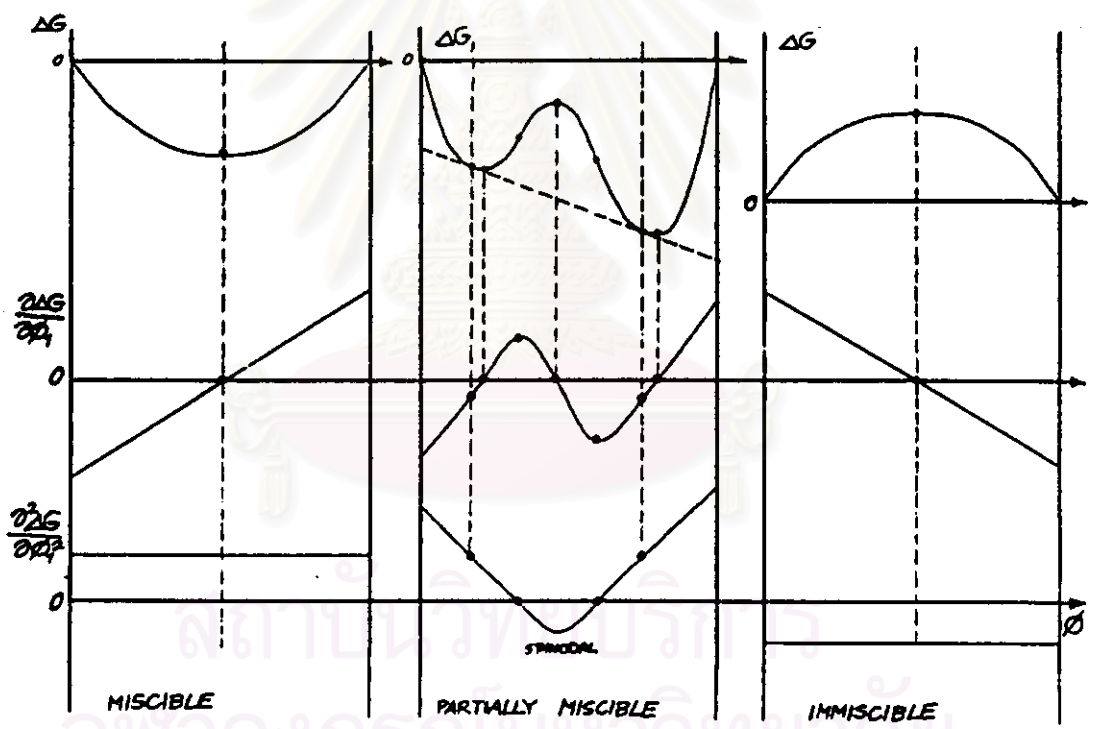


Figure 3.3 The illustrations of the criteria for miscibility [Thongyai, 1990].

3.5.2 The Phase Diagrams of Polymer Blends

A phase is a "uniform" piece of matter with "reproducible", "stable" properties depending only on thermodynamic variables. A certain amount of nonuniformity, such as small concentration and density fluctuations can change the behavior of phase [Olabishi, 1979]. For general usage, if the phase separation curves are available, the working conditions and the processing parameters of the blend can be properly determined. The phase separation curve can be obtained from the diagram called "Phase Diagram" which usually is a plot of temperature versus composition of the blend. Pressure and other process parameters also have some effects on phase separation, but these parameters hardly change in normal ambient conditions. In real polymer blend systems, many types of phase diagrams can be found as shown in Figure 3.4 [Kroschwitz, 1990]. The shade area in Figure 3.4 represents phase separation. The unshaded area in Figure 3.4 represents homogeneous region.

Figure 3.4a shows the upper critical solution temperature (UCST) behavior of a typical polymer blends in which an initially homogeneous mixture undergoes phase separation upon lowering of temperature. The UCST behavior is a characteristic of low molecular weight systems.

When the blend undergoes phase separation as the temperature is raised, the lower critical solution temperature (LCST) behavior is called. This behavior is in contrast to the UCST behavior and is shown in Figure 3.4b. The

main behavior observed in miscible polymer blends of high molecular weight belongs to this type of phase behavior.

Figure 3.4c illustrates the combination of both upper and lower critical solution phase boundaries, seen most commonly in nonpolar polymer solutions [Kroschwitz, 1990].

Figure 3.4d shows the convergence of upper and lower critical boundaries for an immiscible system to form an hourglass-shaped phase boundary. This type of phase diagram is the common phase diagram for the commercial polymer alloys [Thongyai, 1990].

Figure 3.4e illustrates the existence of upper, lower, and quasilower critical phase boundaries. This type of phase diagram can be observed in polar polymer solutions, e.g. poly(acrylic acid)-dioxane [Kroschwitz, 1990].

Figure 3.4f shows the immiscibility loop with upper and lower critical phase boundaries inverted. The examples of this type of system are nicotine-water and poly(vinyl alcohol)-water [Kroschwitz, 1990].

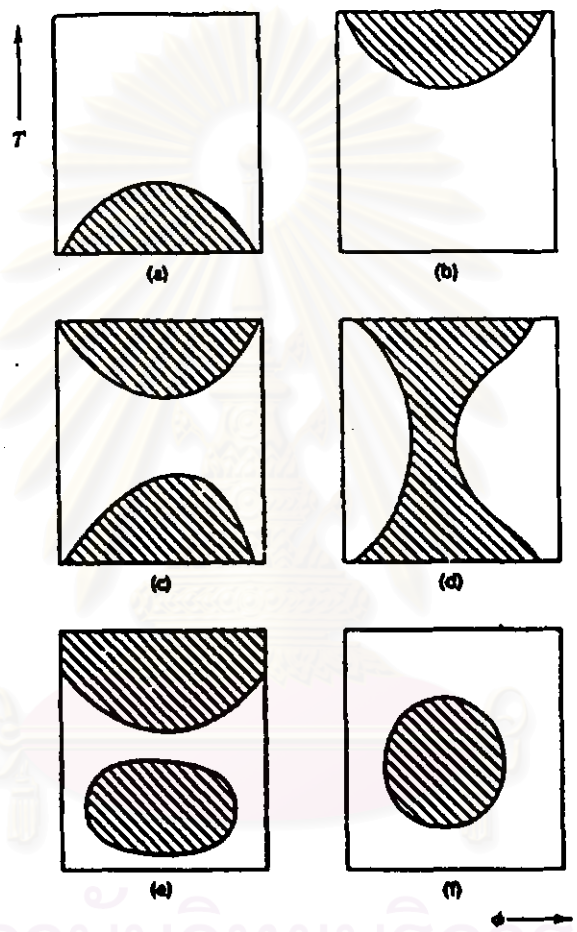


Figure 3.4 Schematic representation of six possible phase equilibria diagrams for binary mixtures in which the shaded areas represent phase separation [Kroschwitz, 1990].

3.6 Phase Separation Phenomena

The kinetic aspect of phase separation in binary mixture is considered to be important because mixtures of different morphologies can result from different decomposition mechanisms. This affords a possibility of enhancing the properties of compatible systems by phase separation [Paul and Newman, 1978]. Phase separation in miscible system is brought about by temperature, pressure and/or composition variations. To explain more about the phase separation phenomena in a polymer blend, the lower critical solution temperature (LCST) phase diagram which is a characteristic of most polymers system is considered. The LCST phase diagram as shown in Figure 3.4b is incomplete. In reality, there are two different phase boundaries in the diagram: the spinodal and the binodal. These phase boundaries are shown in Figure 3.5.

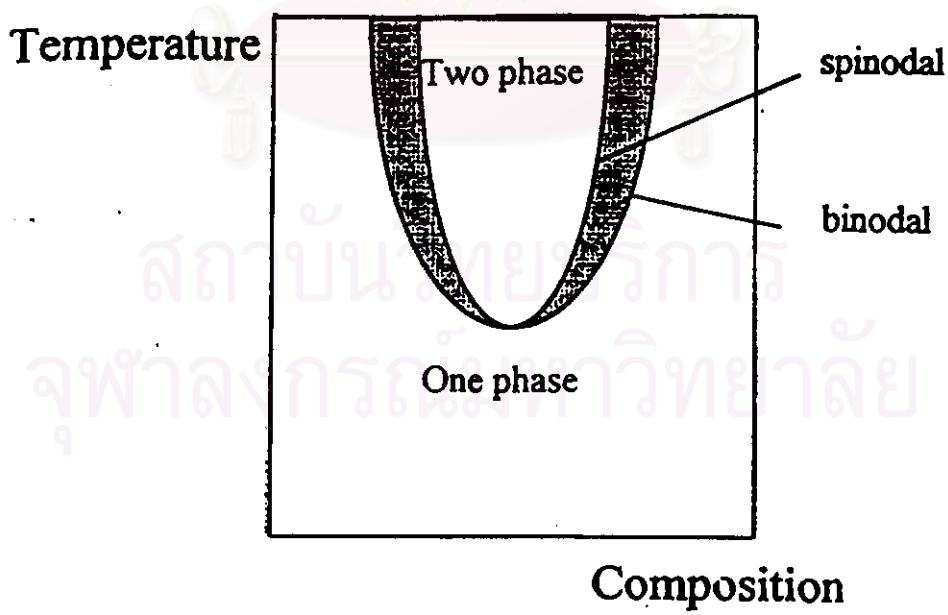


Figure 3.5 The LCST phase diagram of blend with the spinodal and the binodal phase boundaries [Oiarzabal, 1993].

These phase boundaries define three different zones in the phase diagram of a polymer mixture: stable or one-phase, metastable, and unstable or two-phase regions. The main difference between the spinodal and the binodal boundaries is the mechanism of phase separation. In the metastable region, between the spinodal and the binodal, phase separation occurs by nucleation and growth (NG) while in the two phase region, a spinodal decomposition (SD) mechanism is followed.

3.6.1 Mechanisms of Phase Separation

Two major mechanisms of phase separation which are responsible for phase separation in the metastable and unstable regions are as follows:

3.6.1.1 Nucleation and Growth (NG)

The process by which initial fragments of a new, more stable phase are generated from within a metastable mother phase is known as nucleation. The initial fragments are the nuclei and the formation requires an increase in free energy, this excess free energy can be referred to as the work of forming a fluid of a different phase within another homogeneous one. As the nuclei grow; this energy is lost and the single phase system deteriorates. The nuclei grow by diffusion of macromolecules into that domain. This is a downhill type diffusion as the nucleated area will be surrounded by a matrix poor in one of the polymers. A large number of nuclei will be growing at the same time and therefore a dispersed two phase system will appear. As the

droplets grow they will start to coarsen and, eventually, two individual phases will be reached. The composition of these two phases is defined by the binodal. The growth process as well as the corresponding phase structure is shown in Figure 3.6.

3.6.1.2 Spinodal Decomposition (SD)

The kinetic process of creating a continuous growth of a more stable phase from within an unstable mother phase is referred to as spinodal decomposition. Inside the spinodal boundary, phase separation occurs spontaneously. Concentration fluctuations are unstable and create a new phase by an uphill diffusion of like molecules against the direction of the concentration gradient. In the early stage, the size scale of the phase separation is constant and the concentration changes with time. In the intermediate stage, both the concentration and size of the phases change. Finally in the late stage the concentration is constant and the size of the phases increases because of the coalescence of smaller phases. The interconnected structure and the corresponding growth process are shown in Figure 3.7.

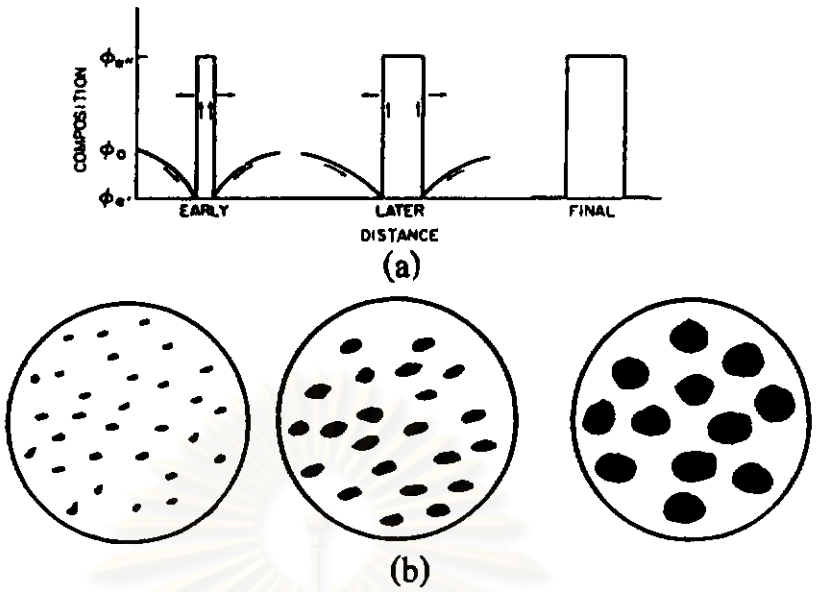


Figure 3.6 Schematic illustration of a phase separation by the nucleation and growth mechanism: (a) one-dimensional evolution of composition profiles; (b) two-dimensional picture of the resultant phase structure [Olabishi, 1979].

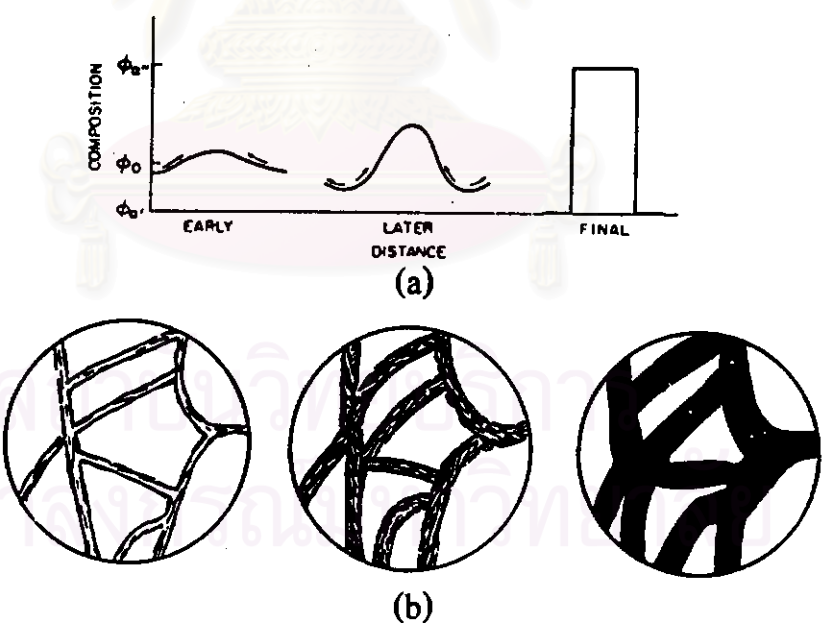


Figure 3.7 Schematic illustration of a phase separation by the spinodal decomposition mechanism: (a) one-dimensional evolution of composition profiles; (b) two-dimensional picture of the resultant phase structure [Olabishi, 1979].

3.7 Determination of Miscibility

In thermodynamical term, miscibility refers to a single-phase system at a molecular level. In practice, it simply means that the system appears to be homogeneous at a level assessed by the particular test performed [Gedde, 1995]. To determine the blend miscibility, the variety of experimental techniques are used. Some techniques, such as cloud point method, light scattering, X-ray and neutron scattering are based on turbidity measurement. Other techniques, such as calorimetric, dilatometric, dynamic mechanical, dielectric, are based on the determination of the number and the location of the glass transition temperature (T_g). Microscopy and volume of mixing are also used to determine the miscibility. Each technique has its own advantages, resolutions, difficulties, assumptions and availabilities. The summary of different techniques used for the assessment of miscibility of polymer blends is presented in Figure 3.8 [Gedde, 1995]. It also suggested the suitability of each technique in relation to the domain size of the blends.

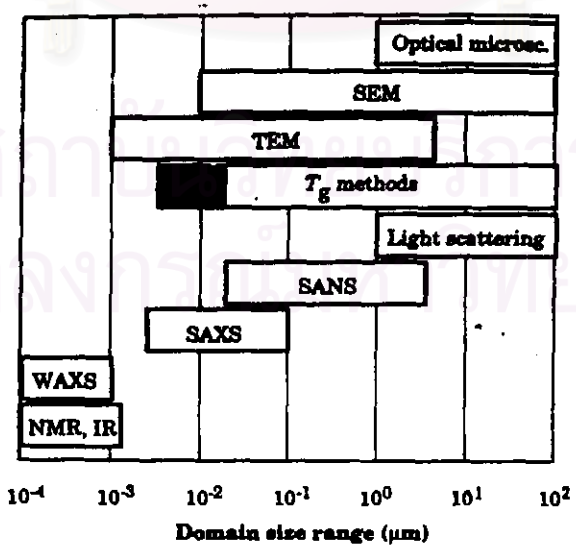


Figure 3.8 Size range covered by different techniques for the assessment of miscibility [Gedde, 1995].

3.7.1 Turbidity Measurement

By definition, a stable homogeneous mixture is transparent, whereas the unstable nonhomogeneous mixture is turbid unless the components of the mixture have identical refractive indexes [Olabishi, 1979]. Given a stable homogeneous mixture, the transition from the transparent to the turbid state can be brought about by variations of temperature, pressure, or composition of the mixture. The cloud point corresponds to the point of this transition.

The turbidity measurement is the oldest method for determination of phase relationship. It consists of preparation of a series of mixtures near the phase separation condition then causing the separation to occur. It is a quick and direct method to determine the blend miscibility.

However, this method may lead to erroneous conclusions if (a) the refractive indexes of polymer A and B are similar, (b) the domains are smaller than that of the wavelength of light, hence, the light is not scattered and a two phase blend can be transparent, (c) either component of an initially transparent miscible blend later crystallizes, the blend may become opaque.

3.7.1.1 Cloud-Point Method

For polymer mixture, the cloud-point curve is usually measured using a thin film made from a thoroughly mixed blend by melt mixing or solvent casting. The film is heated through the cloud point. The

first faint cloudiness appears, denoting the cloud point, and the temperature is recorded. This is repeated for a series of compositions and a temperature-composition plot is generated. The result is called the cloud-point curve (CPC). The cloud-point curve depends on many parameters, such as the heating rate, the film thickness [Utracki, 1990].

It is preferable to use a programmable hot stage with the slow heating rate not exceeding 0.1 °C/min. The sample can be illuminated with white light, laser beam or UV sources. The variation of turbidity is observed either directly, under microscope with a naked eye, or with a photoelectric detector, e.g. a light dependent resistor placed in the focal point of an optical microscope tube [Utracki, 1990].

3.7.1.2 Conventional Light Scattering Method

This turbidity method can be extended to rigorous study of the phase separation and it can provide both the binodal and spinodal regions of the phase diagram. The principle of this method involves a usage of light beam. If a light beam passes through a medium whose volume elements (containing the constituent particles) are small compared to the wavelength of the light, the light will scatter. The intensity of the scattered light as a function of temperature is recorded.

The cloud point is obtained from the temperature at which the shift of the intensity of light occurs in the plot of the intensity of the

scattered light versus temperature and shown in Figure 3.9 [Thongyai, 1994].

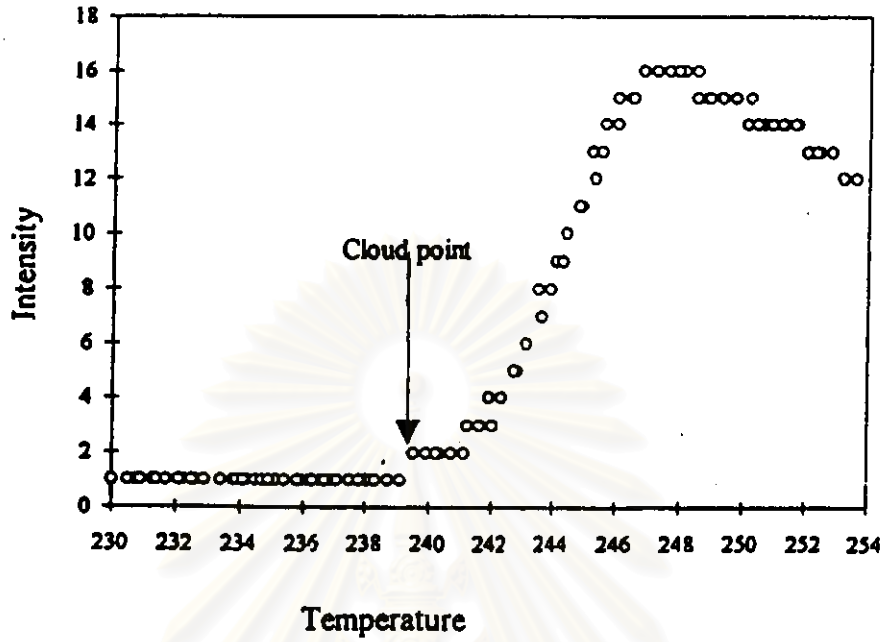


Figure 3.9 Schematic of the intensity of the scattered light as a function of the temperature [Thongyai, 1994].

The scattered intensity of light due to concentration fluctuation (R_θ^c) extrapolated to zero scattering angle may inversely be proportional to the second derivative of the free energy with respect to the concentration. That is, if one performs light scattering measurements at constant concentration but various temperature from homogeneous stable region to unstable region, a plot of $(1/R_\theta^c)_{\theta=0}$ versus temperature extrapolated to zero ordinate yields the spinodal temperature for the given concentration. The plot of $(1/R_\theta^c)_{\theta=0}$ versus temperature is shown in Figure 3.10. From the obtained cloud point and spinodal temperatures at a series of compositions, one can construct the phase diagram of the polymer blend.

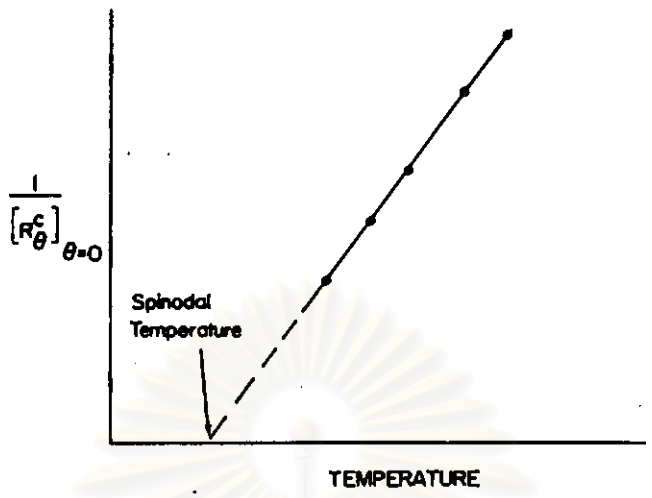


Figure 3.10 Schematic of scattered light intensity at zero scattering angle as a function of temperature [Olabishi, 1979].

3.7.1.3 Neutron Scattering and X-ray Scattering Methods

The principle of light scattering can be extended to other sources of radiation, in particular X-ray and neutron. While light scattering is sensitive to density and concentration fluctuations, X-ray scattering to density fluctuations, neutron scattering measures the differential neutron scattering cross section of small concentrations of protonated polymer dispersed in a matrix of deuterated polymer [Olabishi, 1979].

Scattering of radiation of short wavelengths (λ), X-ray and neutrons with $\lambda \approx 0.1$-0.3 nm, permits fine structures to be resolved. The small-angle techniques, small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS), can make assessment down to 5 nm (SAXS) and 50 nm (SANS). The requirement of the analyses is the electron densities

(SAXS) and the atomic numbers (SANS) differ between the different polymers. Wide-angle X-ray scattering (WAXS) can resolve even finer detail, in this case down to true molecular levels (0.1-1 nm) [Gedde, 1995].

3.7.2 Glass Transition Criteria for Miscibility

Glass transition temperature (T_g) is a characteristic of the amorphous part of a polymer. At T_g, a dramatic change occurs in the local movement of polymer chains which leads to large changes in a host of physical properties. These properties include density, specific heat, mechanical modulus and mechanical energy absorption, and their dielectric and acoustical equivalents, rate of gas or liquid diffusion through the polymer, as well as many other properties [Brandup and Immergut, 1989].

Measuring the T_g of a polymer blend is the most commonly used method for determination its miscibility. It is clear that a miscible system will show characteristic properties of a single phase. Hence, a single T_g, intermediate of the components' T_g can be expected for a miscible blend. In case of partial miscibility, two transitions that shift closer to each other occur. The immiscible system will show two separate transitions with little change from the transition temperatures of its pure components. Figure 3.11 shows schematically the recorded glass temperatures as a function of composition.

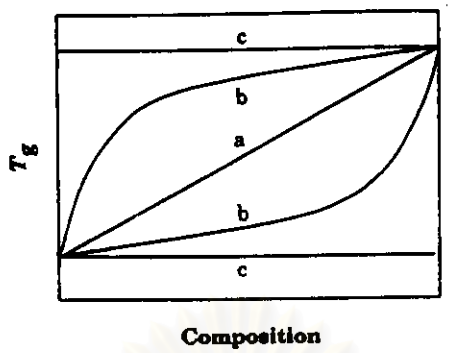


Figure 3.11 Glass transition temperatures as a function of composition in fully amorphous binary polymer-polymer blends: (a) a miscible blend, (b) a partial miscible blend, (c) an immiscible blend [Gedde, 1995].

However, this method has a limitation. It can be used to study polymer miscibility as long as the T_g's of the components are at least 20 °C different [Paul and Newman, 1978].

3.7.2.1 Glass Transition Determination

There are many methods by which T_g of polymer may be determined. Examples are differential thermal analysis (DTA), thermal optical analysis (TOA), differential scanning calorimetry (DSC), dynamical mechanical spectroscopy, dielectric measurement, and dilatometry. Some of the more widely used methods of T_g measurement in polymer blends are described belows [Walsh, 1985].

3.7.2.1.1 Differential Scanning Calorimetry (DSC)

The T_g is usually determined by a differential scanning calorimetry (DSC). DSC is the technique that monitors enthalpy changes (heat flow into or out) of a material (sample and reference) as a function of temperature or time. The sample and the reference are heated or cooled at a constant rate. The resulting temperature difference signal can then be recorded versus time or sample temperature [Fava, 1980]. An inflection in the plot is observed at the T_g because an increase in the specific heat of the polymer is accomplished by the increased molecular motion. This technique has the advantage of small sample requirements (typically 5-20 mg), rapid measurement and high sensitivity.

3.7.2.1.2 Dynamical Mechanical Spectroscopy

Dynamical mechanical measurements have been widely used in the study of polymer miscibility. With this technique, a dynamic modulus can be measured as a function of temperature over a range of frequencies. From traditional torsion pendulum measurements, the dynamic shear loss modulus (G'') and the dynamic shear storage modulus (G') may be obtained as a function of temperature at a nominal frequency in the vicinity of 1 Hz [Walsh, 1985].

The torsion pendulum consist of an inertial source (disk of rod) connected to a polymer specimen which is firmly fixed at the other

end. The inertial source is angularly displaced and released, allowed the specimen to vibrate freely. The resultant damped sinusoidal wave is then determined using a suitable recording device [Olabishi, 1979].

The T_g (or T_g's) of the blends is defined as the temperature corresponding to the maximum in G'' or tanδ (tan$\delta = G''/G'$) at the main relaxation, which marks the onset of main chain segmental mobility corresponding to the glass transition.

This technique has more stringent sample requirements than calorimetry, that only films or fibers (i.e. not powders) made from the blends can be studied. However, it is sometimes preferred because of a widely held belief that it is more sensitive than calorimetry.

3.7.2.1.3 Dielectric Relaxation

The electrical properties of polymers are analogous to mechanical properties in that the dielectric constant, ε', is similar to compliance, the dielectric lost factor, ε'', is similar to mechanical loss, and the dielectric strength is analogous to tensile strength. The dielectric loss factor and the dissipation factor, tanδ ($\varepsilon''/\varepsilon'$), are of primary interest as they are commonly used to ascertain polymeric transition such as the glass transition. The ε', ε'' can be measured by placing the sample between parallel plate capacitors and alternating the electric field [Sperling, 1992]. The experimental

advantage of obtaining transition data from electrical measurements over dynamic mechanical testing is in the ease of changing frequency.

The major disadvantage is the difficulty in determining the transition of nonpolar polymer. Generally, nonpolar polymer will require slight modification, such as oxidation, to provide sufficient polarity to resolve adequate secondary loss transition as well as glass transition in blends [Olabishi, 1979].

3.7.2.1.4 Dilatometry

The earliest used method for determination of T_g in polymers is dilatometry. It has been frequently employed in blend studies because of the greater speed and versatility of modern thermal analysis instrumentation.

A dilatometer consists of a glass bulb with an attached small capillary. The dilatometer is then placed in a temperature bath, and the temperature changed at a uniform rate so that a plot of volume as a function of temperature is obtained. An inflection point indicates the position of the glass transition.

In contrast to DSC, dilatometry requires larger samples and more time and care in sample preparation and measurement.

3.7.3 Microscopy

Microscopy is the name given to a group of experimental methods which permit magnification of morphological structures to make details visible. Microscopy provides detailed information about miscibility and phase morphology, i.e. the actual geometry of the phases [Gedde, 1995]. The microscopic methods can be divided into three categories as follows:

3.7.3.1 Optical Microscopy

The optical microscope is obtained by two-lens system, referred to as the objective and the eyepiece. The objective generates a magnified real image of the specimen. The real image is further magnified by the eyepiece and a magnified real image is formed at the retina of the eye [Gedde, 1995].

Optical microscopy resolves structures down to about 1 μm. The sample may need staining prior to examination. In other cases, where the refractive index mismatch is sufficiently large, direct examination can be made in the microscope using phase-contrast or interface-contrast optical microscopy.

3.7.3.2 Scanning Electron Microscopy (SEM)

Scanning electron microscope (SEM) uses the technique of a focus electron beam to scan the sample surface [Woodward, 1995]. The electron beam is controlled by lenses consisting of magnetic fields. Rotational symmetric electromagnets focus the electron beam in the same way as convex lenses do in optical microscopes [Gedde, 1995]. The polymer specimen to be examined by SEM was first coated with a thin layer of gold to provide a conductive layer.

Scanning electron microscope (SEM) provides more detailed information on the morphology; domains down to a size of 10 nm can be resolved. SEM is becoming the most popular method of observation of polymer blends. The great advantages of this technique are rapidity, great depth of focus, relatively simple image interpretation, and ease of sample preparation.

3.7.3.3 Transmission Electron Microscopy (TEM)

The transmission electron microscope is built according to the same principle as the optical microscope, with a condenser lens, and objective lens and a projector lens (the analogue of the eyepiece). A magnified image is obtained on a fluorescent screen or on a hairpin tungsten filament or a lanthanum boride (LaB_6) filament heated with a low-voltage

source. The potential of the filament is highly negative and the electrons are accelerated towards an anode held at a small positive potential [Gedde, 1995].

Transmission electron microscopy (TEM) involves complex and tedious preparation of the samples necessary to reveal the microphase. But the resolution of TEM is superior to optical microscopy and SEM.

3.7.4 Volume Change of Mixing

On mixing two polymers the total volume of the system will, in general, undergo some changes. If the miscibility of the components is very low, the volume change of mixing will be small. However, if the blend is miscible because of strong intercomponent interactions, a measurable negative volume change of mixing might be expected [Walsh, 1985].

The definition for volume change of mixing (ΔV^M) which will reflect only those changes due to interaction, is shown as belows:

$$\Delta V^M = V_B - \Sigma V_i \qquad (3.4)$$

where V_B is the total volume of the blend and V_i is the total volume of component i as it would be alone but in the same physical state as it exists in the blend.

3.8 Tensile Properties [Rosato, 1991]

The tensile test is the experimental stress-strain test method most widely employed to characterize the mechanical properties of materials like plastics, metals and woods. From any complete test record one can obtain important information concerning a material's elastic properties, the character and extent of its plastic deformation, and its yield and tensile strengths and toughness [Rosato, 1991].

The standard ASTM D638 explains the internationally accepted method of conducting tensile test and defines the terms generally used throughout the industry. The tensile test according to ASTM D638 is mostly performed on the dumb-bell specimen. ASTM D882 is also used as a standard procedure for tensile testing of materials in the film or sheet form.

A tensile test involves pulling or stretching a test specimen at a uniform rate of extension and measuring the corresponding load applied. The tensile force is recorded as function of the elongation. Figure 3.12(a) shows a typical plot of tensile force versus tensile elongation. Sometimes such plot is normalized with respect to specimen dimensions as in Figure 3.12(b) [Han, 1992]. Various tensile stress-strain curves are also shown in Figure 3.13. Explanation of the terminology [Rosato, 1991] used in tensile testing is as follows:

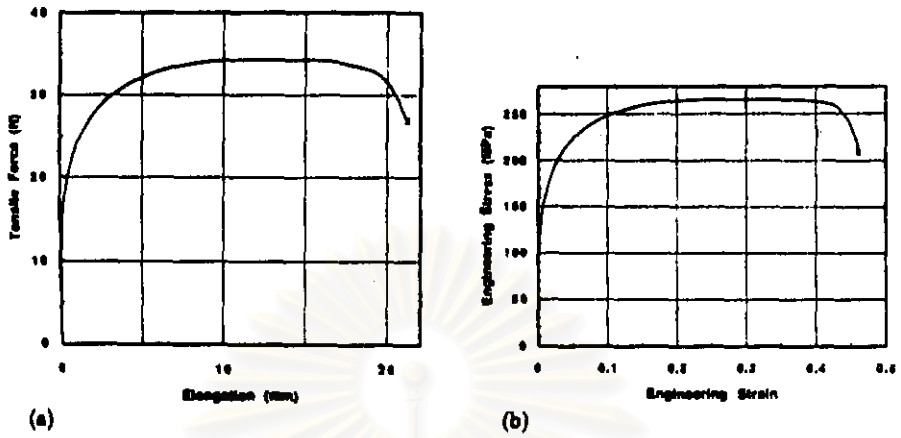


Figure 3.12 (a) Load-elongation curve from a tensile test and (b) corresponding engineering stress-strain curve [Han, 1992].

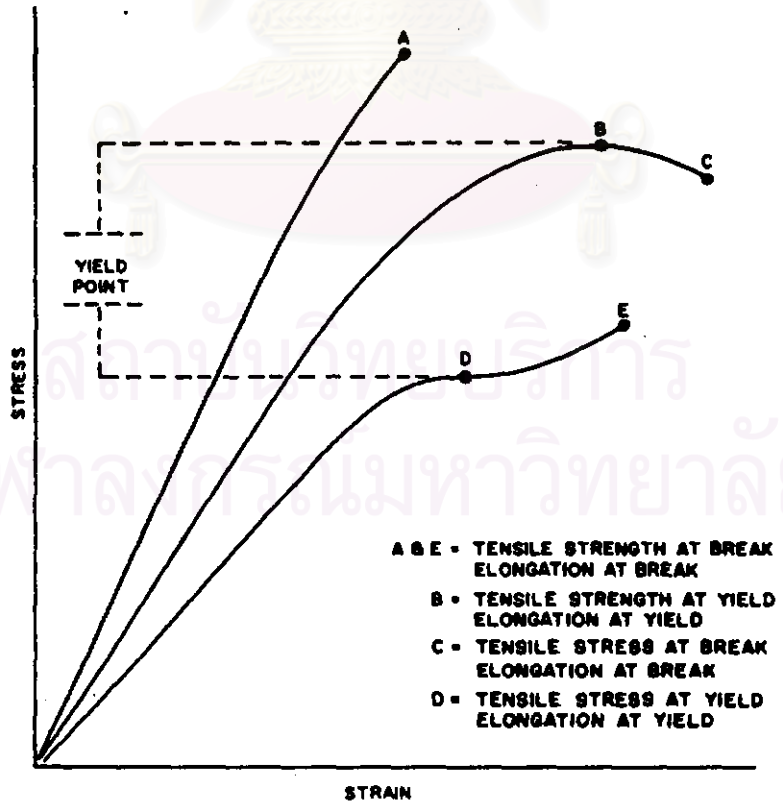


Figure 3.13 Tensile designations according to ASTM D638 [Rosato, 1991].

3.8.1 Stress

Stress is the tensile load applied per unit of the original cross-sectional area at a given moment of the specimen. The standard unit of measure in Pa (Pascal) or pound per square inch (psi).

3.8.2 Strain

Strain is the ratio of elongation or deformation to the gauge length of the test specimen, that is, the change in length per unit of original length. It is expressed as a dimensionless ratio; mm/mm (in/in). As the strain is increased beyond the material's proportional limit, the specimen's elastic limit is reached.

However, below the elastic limit the material's behavior is elastic; that is, once it is unloaded, its recovery from deformation is essentially complete and instantaneous. Stressing the specimen above its elastic limit results in a degree of permanent set. This nonrecoverable stressing is called plastic strain. This strain is usually associated with plastics, but it is also seen in metals and other materials.

3.8.3 Elongation

The increase in the length of a test specimen that is expressed as a percentage of its extensometer gauge length is called its percentage of elongation.

3.8.4 Yield

The first point on a stress-strain curve at which an increase in strain occurs without any increase in stress is its yield point of yield strength or tensile strength at yield. The yield strength is generally established by constructing a line to the curve where stress and strain is proportional at a specific offset strain, usually at 0.2 percent. The stress at the point of intersection of the line with the stress-strain curve is yield strength at 0.2 percent offset. The example of the yield strength at 0.2 percent offset is shown in Figure 3.14.

3.8.5 Proportional Limit

A material's proportional limit is the greatest stress at which it is capable of sustaining an applied load without deviating from the proportionality of stress to strain. The proportional limit is shown in Figure 3.14.

3.8.6 Elastic Limit

The elastic limit of a material is the greatest stress at which it is capable of sustaining an applied load without any permanent strain remaining, once stress is completely released.

3.8.7 Tensile Strength

The maximum tensile stress sustained by a specimen during a tension test is its tensile strength. Again it is expressed either in Pa (Pascal) or pound per square inch (psi). Tensile strength is shown in Figure 3.14.

When a material's maximum stress occurs at its yield point this is designated its tensile strength at yield. When the maximum stress occurs at a break, the designation is its tensile strength at break. In practice these differences are frequently ignored, often resulting in confusion in designs as to whether or not, for example, work hardening or cold drawing occurs before failure.

3.8.8 Modulus of Elasticity

Most materials, including plastics and metals, have deformation proportional to their loads below the proportional limit. Since stress is

proportional to load and strain to deformation, this implies that stress is proportional to strain. Hooke's law, developed in 1676, follows that this straight line (in Figure 3.14) of proportionally is calculated as

$$\frac{\text{Stress}}{\text{Strain}} = \text{Constant}$$

The constant is called the modulus of elasticity (E) or Young's modulus, the elastic modulus, or just the modulus. This modulus is the slope of the initial portion of the stress-strain curve, normally expressed in terms such as MPa or GPa (10^6 psi or Msi).

The modulus of elasticity is applied to describe the stiffness or rigidity of a plastic where its stress-strain characteristics depend on such factors as the stress or strain rate, the temperature, and its previous history as a specimen.

3.8.9 Area under the Curve

Generally, the area under the stress-strain curve is proportional to the energy required to break the plastic. It is thus sometimes referred to as the toughness of the plastic (Figure 3.15). However, there are types of behavior of plastics that are hard, strong, and tough.

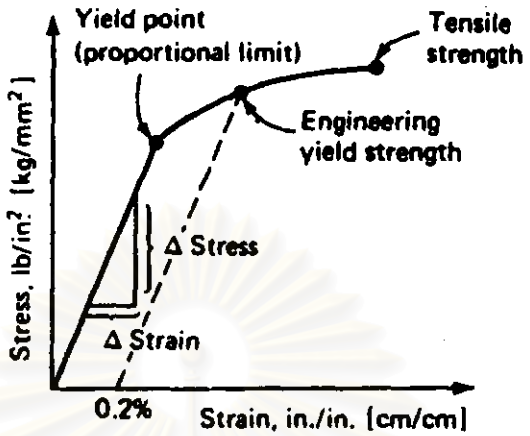


Figure 3.14 An example of the modulus of elasticity determined on the initial straight portion of the stress-strain diagram [Rosato, 1991].

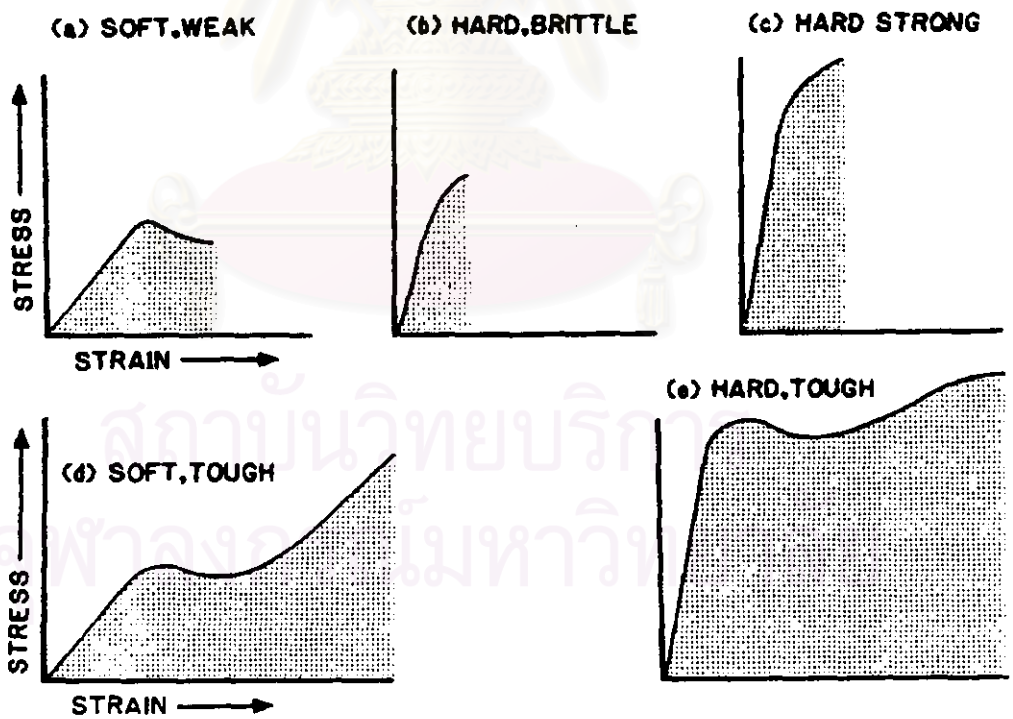


Figure 3.15 Tensile stress-strain curves for different plastics that relate the area under the curve to their toughness or physical properties [Rosato, 1991].

3.8.10 Test Rates

The test rate or cross-head rate is the speed at which the movable cross-member of a testing machine moves in relation to the fixed cross-member. The speed of such tests is typically reported in cm/min, mm/min or in/min.

An increase in strain rate typically results in an increasing yield point and ultimate strength as shown in Figure 3.16 (a) and (b). For most rigid plastics the modulus does not change significantly with the strain rate. For softer thermoplastics, the theoretical elastic or initial tangent modulus is usually independent of the strain rate.

The elastic modulus and strength of both the rigid and the softer plastics each decrease with an increase in temperature as shown in Figure 3.16 (c). While in many respects the effects of a change in temperature are similar to those resulting from a change in the strain rate, the effects of temperature are relatively much greater.

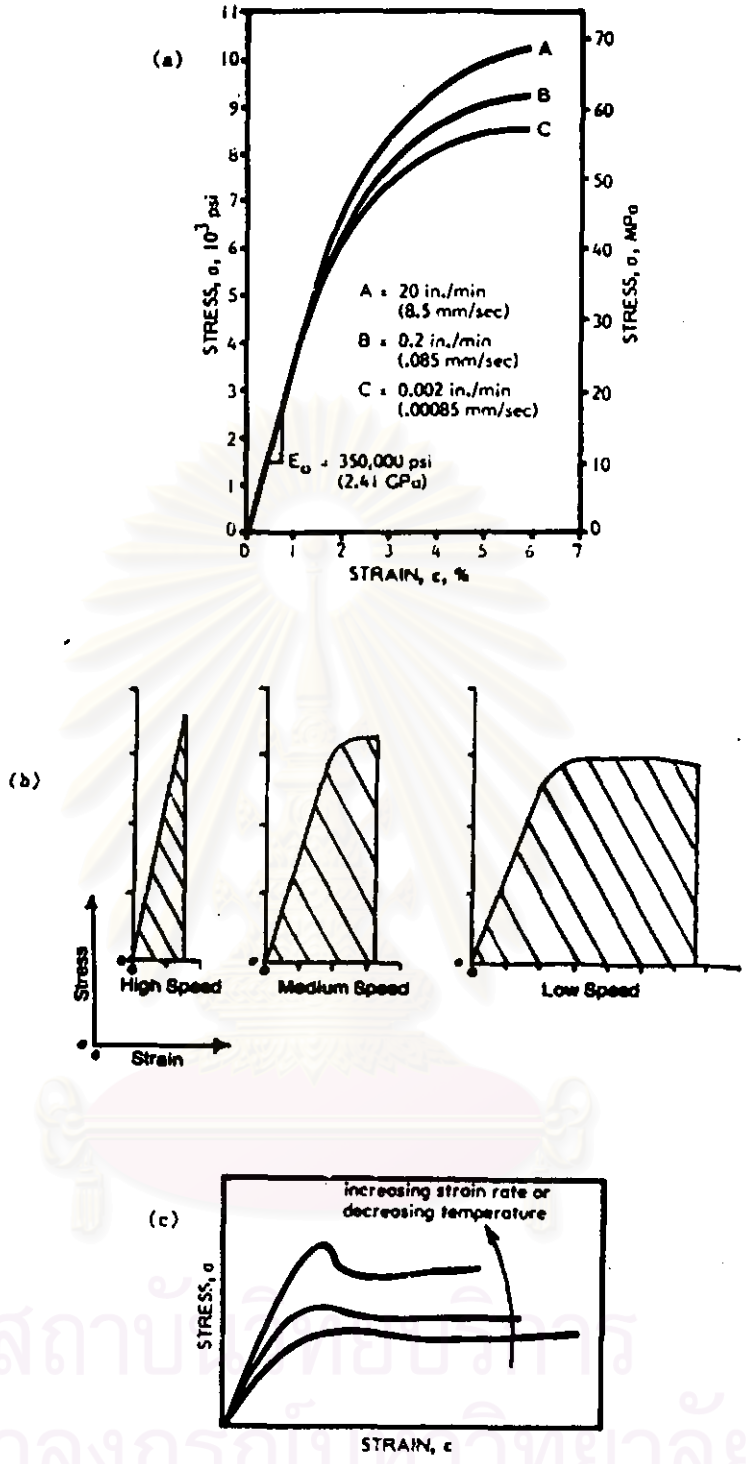


Figure 3.16 Examples of the influence of different test rates and temperatures on basic stress-strain behaviors of plastics: (a) different testing rates as shown for polycarbonate, (b) effects of tensile speeds on the shapes of stress-strain diagrams, (c) a simplified version of the effects on curves of changes in test rates and temperatures [Rosato, 1991].