

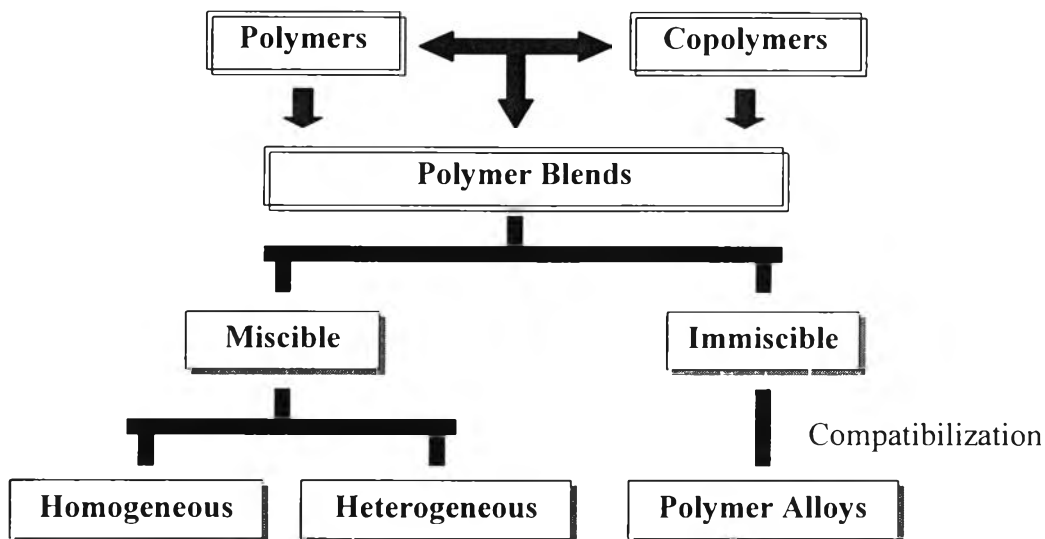
# **CHAPTER I**

## **INTRODUCTION**

For many decades ago, scientific and commercial progresses in the area of polymer blend have been very substantial because blending of materials can be implemented rapidly and economically than the development of a new material. The great majority of useful blends are immiscible. The mechanical properties can be optimized by controlling the blend morphology (Sundararaj and Macosko, 1995): the size, the shape and the size distribution of the constituting domains. Generally, a blend of immiscible polymers gives a material with poor dispersion, low interfacial adhesion and, consequently, poor mechanical properties (Taha and Frerejean, 1996). Compatibility problems are often overcome by using a suitable compatibilizing agent, normally a graft or block copolymer, to alter the enthalpy and entropy between unlike polymer segments providing to control the miscibility and blend's properties (Adedeji, Hudson and Jamieson, 1997).

### **1.1 Polymer Blends**

Polymer blend is a mixture of at least two polymers or copolymers (Utracki, 1993). It can be divided into 2 major categories based on their thermodynamic phase behavior as shown in figure 1.1.



**Figure 1.1** Interrelations in polymer blend nomenclature.

Thermodynamics is the key to understanding the behavior and properties of polymer blends and is a factor to classify the miscibility of polymer blend. It was explained in the term of Gibb's free energy ( $\Delta G_m$ ) and chi parameter ( $\chi_{12}$ ) of mixing as shown in equation 1.1.

$$\Delta G_m = RT(\chi n_1 \phi_2 + n_1 \ln \phi_1 + n_2 \ln \phi_2) \quad (1.1)$$

where  $\phi$  is volume fraction,  $\chi$  is polymer-polymer interaction parameter,  $T$  is temperature and  $n_i$  is the number of moles of  $i^{\text{th}}$  polymer. If  $\Delta G_m$  is less than zero, the blend system is an miscible blend. An example of this is the blends of polystyrene with poly(2,6-dimethyl-1,4-phenylene oxide). An immiscible blend will occur if  $\Delta G_m$  is more than zero such as PS/PP blend. PP/PE blend and PS/PI blend.

In the case of immiscible blends, the overall physicomechanical behavior depends critically on two demanding structural parameters: a proper interfacial tension leading to a small enough phase size to allow the material to be considered as macroscopically "homogeneous". The second parameter

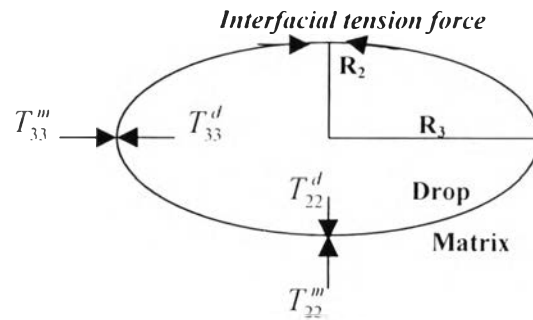
is the strong enough interphase adhesion to assimilate stresses and strains without disruption of the established morphology (Anastasiadis, Gancarz and Koberstein, 1989).

## **1.2 The Morphology of Immiscible Blends**

The morphology of immiscible blend associating with the size, shape and size distribution of the minor phase depends strongly on various parameters: the thermodynamic properties (interfacial tension), the rheological properties of each component (viscosity, the first normal stress difference), the processing conditions (flow field applied during blending), the blend's composition and so on (Arashiro and Demarquatte, 1999). The size of the dispersed phase during processing is determined by two interesting behaviors consisting of the droplet breakup and droplet coalescence whereas the shape of the drop is determined not only by the dissipative force but also by the pressure distribution around the droplet arising from elasticity.

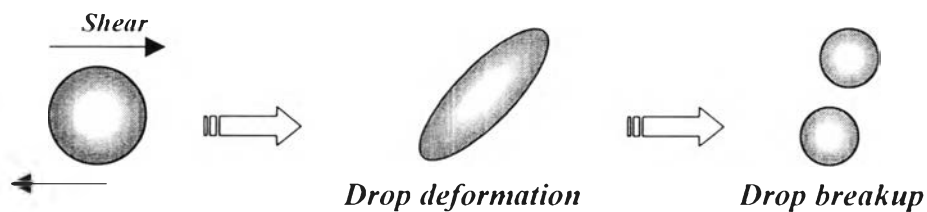
### ***1.2.1 Droplet Breakup***

Droplet breakup depends on the balancing of two forces, viscous force and interfacial tension as a restoring force, after shearing. The interfacial tension force tends to keep the spherical shape of drops whereas the viscous force tends to elongate the drops as shown in figure 1.2 (Levitt and Macosko, 1996).



**Figure 1.2** Force balance, squeezing from the matrix  $N_2^m = (T_{22}^m - T_{33}^m)$ , and interfacial tension ( $\Gamma / R_2$ ), is balanced by interfacial tension force and the second normal stress difference of the drop,  $N_2^d = (T_{22}^d - T_{33}^d)$ .

When the interfacial tension force can no longer balance the viscous force, the deformation becomes unstable and then the drop will burst into smaller size as illustrated in figure 1.3.



**Figure 1.3** Mechanism of drop breakup behavior after applying the shear.

Moreover, drop breakup also depends on many parameters such as viscosity, the blend's composition, processing conditions, etc. Taylor (1932) studied the drop breakup of a single Newtonian drop in a simple shear field and suggested that at low stress in steady uniform shearing flow the deformation degree and drop breakup can be expressed by means of two dimensionless parameters: the capillary number:

$$Ca = \frac{\dot{\gamma}\eta_m D}{2\Gamma} \quad (1.2)$$

and the viscosity ratio:

$$\eta_r = \frac{\eta_d}{\eta_m} \quad (1.3)$$

where  $\dot{\gamma}$  is the shear rate,  $\eta_d$  and  $\eta_m$  are the dispersed phase and matrix phase viscosity, respectively,  $D$  is the droplet diameter and  $\Gamma$  is the interfacial tension. Taylor predicted that no drop breakup occurred when  $\eta_r > 2.5$  and the critical capillary number of simple shear would predict the upper limit of drop size for the breakup in a Newtonian system. He balanced the interfacial forces and the shear forces and obtained a relation for the maximum drop size that would be stable:

$$D = \frac{4\Gamma(\eta_r + 1)}{\dot{\gamma}\eta_m \left(\frac{19}{4}\eta_r + 4\right)}, \quad \eta_r \geq 2.5 \quad (1.4)$$

The effect of viscosity ratio ( $\eta_r$ ) was later extended by Grace (1982) to consider the breakup of Newtonian drops in both simple shear and extensional flows. He found that breakup for simple shear occurred easily for  $0.1 < \eta_r < 1$  but it was impossible when  $\eta_r$  was greater than 4. Wu (1987) followed up the Taylor's theory to study the dependence of drop size on  $\eta_r$  for viscoelastic system and obtained the correlation relating capillary number to  $\eta_r$ . He gave a relation for the final droplet size of minor phase as in equation 1.5.

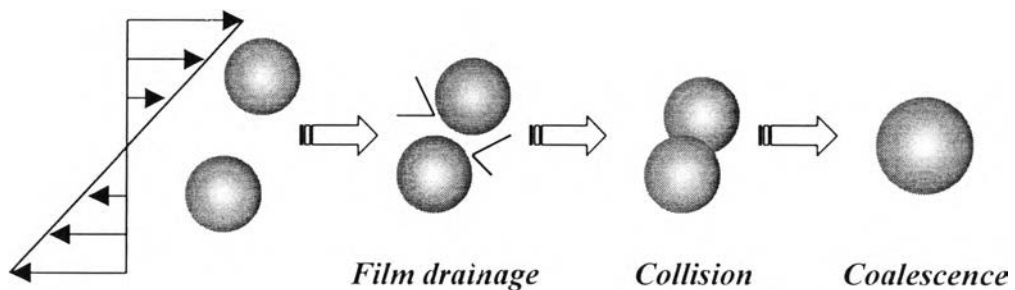
$$D = \frac{4\Gamma \eta_r^{\pm 0.84}}{\dot{\gamma}\eta_m} \quad (1.5)$$

where the plus (+) sign in the exponent applied for  $\eta_r > 1$  and the minus (-) sign in the exponent applied for  $\eta_r < 1$ . In all blends used for the correlation,

the dispersed phase concentration was 15 wt.% and the effective shear rate was arbitrarily chosen as  $100 \text{ s}^{-1}$ .

### *1.2.2 Droplet Coalescence*

During mixing, the dispersed phase progressively breaks down until a minimum drop diameter is reached. As  $D$  decreases, the drop breakup becomes more and more difficult. For Newtonian systems the size of the smallest drop that can be broken can be calculated from Taylor's theory. However, many experimental studies have shown that the final particle size is usually larger than predicted for polymer systems (Sundararaj and Macosko, 1995 and Elmendorp and van der Vegt, 1986). This was because of the coalescence. An important factor for coalescence process is the composition of minor phase. At high concentration of minor phase, the probability of particle collision is high which favors coalescence. The mechanism for the coalescence in polymer blend has been studied and confirmed by several researchers (Elmendorp, 1986 and Jang, Uhhmann and Vander Sande, 1984) that was illustrated in figure 1.4.



**Figure 1.4** Collision of two deformable drops in simple shear flow with drainage of the film in between.

Firstly, the particles approach each other until only a thin film of matrix polymer remains at their interface. Coalescence of the two drops can only take place when the matrix between them is removed. The rate of drainage of the thin polymer film depends on its mobility. Then, if the film thickness becomes smaller than the critical distance for film rupture, instabilities in the film lead to its rupture and one single particle is formed. Coalescence may be regarded as being completed at this stage or when the newly formed particle has reached a spherical shape (Ica and Tadmor, 1994).

Another factor influencing the magnification of coalescence probability is the interfacial mobility which is related to  $\eta_r$  (Chester, 1991). The high polymer matrix viscosity (=low  $\eta_r$ ) gave rise to a relatively immobile interface which resulted in a long drainage time for the intervening film. Then the coalescence was inhibited. Another method to immobilize the interface is adding a compatibilizer. This method can prevent a close approach during collision of drops and stabilize the morphology against coalescence.

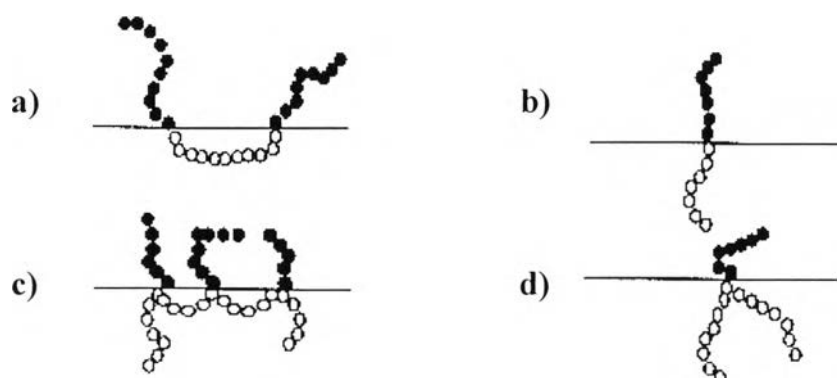
### **1.3 Compatibilization**

Controlling the morphology can be achieved by many methods. Compatibilization is often chosen for improving the dispersion, interfacial adhesion and coalescence. Compatibilization is a process of converting an otherwise useless polymer blend into a commercially useful product.

In most cases, melt mixing two polymers results in blends that are weak and brittle. This is because the incorporation of a dispersed phase in a matrix leads to the presence of stress concentrations and weak interfaces. This is most common for compatibilization to be achieved by addition of a third component called "compatibilizer". One effect of compatibilizer is to reduce the interfacial tension in the melt, causing an emulsifying effect and leading

to an extremely fine dispersion of one phase in another. Another major effect is to increase the adhesion at phase boundaries, giving improved stress transfer. A third effect is to stabilize the dispersed phase against growth during annealing, again by modifying the phase boundary interface (Folkes and Hope, 1993).

Types of compatibilizers may be non-reactive, reactive, or both. The most obvious type of non-reactive compatibilizer is a block copolymer of A and B for a mixture of polyA and polyB, as illustrated in figure 1.5. However, other copolymers may be effective if they have specific interactions, i.e., miscibility, with one or both of the blend components. Graft copolymer is also a non-reactive compatibilizer.



**Figure 1.5** Schematic diagram showing the conformations of non-reactive compatibilizers at the interface: a) triblock copolymer; b) diblock copolymer; c) graft copolymer; d) star-branched copolymer.

Reactive compatibilizer is a new method for producing compatible blend that relies on the *in situ* formation of copolymers or interacting polymers (Folkes and Hope, 1993). This differs from other compatibilization routes in that the blend components themselves are either chosen or modified so that reaction occurs during melts blending, with no need for addition of a

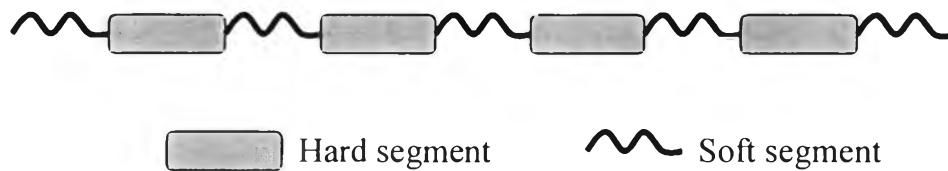


separate compatibilizer. It can provide the strength and stability of the blend morphology throughout the processing and service life of the final products.

## 1.4 Block Copolymer

### 1.4.1 Morphology of Block Copolymer

Block copolymers consist of chain molecules, each of which consists of sequences of “soft” and “hard” segments as illustrated in figure 1.6.

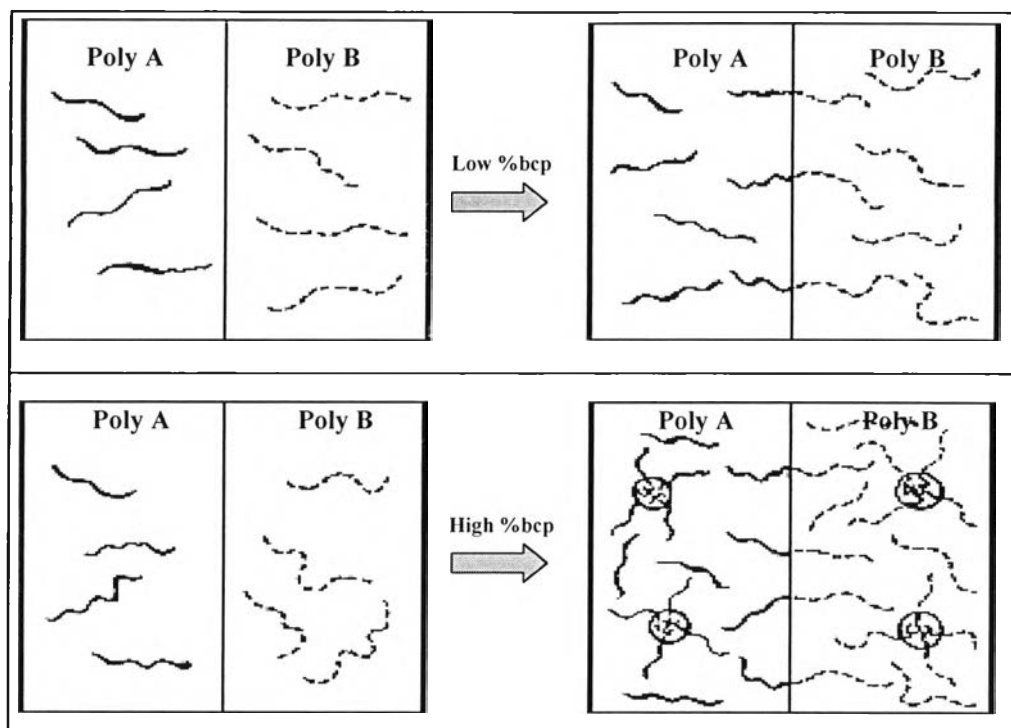


**Figure 1.6** A chain molecule of block copolymer.

### 1.4.2 Interfacial Properties of Block Copolymer and Immiscible Polymer Blends

When two homopolymers A and B are immiscible, they exhibit a high interfacial tension that leads to a low interfacial adhesion, and to stable dispersed phase particles of large sizes and wide size distribution (Adedeji, Hudson and Jamieson, 1996). Addition of a block copolymer as a compatibilizer is one way to modify the interfacial properties. This copolymer will diffuse and migrate to the interface and compatibilize the phase-separated blends. There are a number of factors that determine the state of the block copolymer in a phase-separated homopolymer system. First, the entropy of mixing of the block copolymer with the homopolymer favors a random distribution of the copolymers. On the other hand, localization of the

block copolymers at the interface displaces the homopolymers away from each other that provides a lower enthalpy of polymer mixing. In the addition, each segment of block copolymer will prefer to extend into its compatible homopolymer to lower the enthalpy of the block copolymer-homopolymer mixing. This situation is illustrated schematically in figure 1.7.



**Figure 1.7** Schematic diagram of interfacial behavior between the immiscible homopolymers containing corresponding block copolymer. Some of block copolymers settle in the interface, while those in the bulk are either randomly distributed (upper panel) or aggregate to form micelles (lower panel), depending on the block copolymer concentration.

### **1.5 The objective of this work**

To study the effect of triblock copolymer on blend morphology in the term of the swelling between matrix and PS segment of block copolymer.

#### **Scope of this works:**

1. Study the effect of mixing time on blend morphology.
2. Study the effect of shear rate on blend morphology.
3. Study the effect of triblock copolymer concentration on blend morphology in both solvent casting and melt mixing process.
4. Study the effect of triblock copolymer as a function of shear rate on blend morphology of the three blends.