

## CHAPTER II

### LITERATURE SURVEY

Controlling the morphology of the polymer blends generally depends strongly on many parameters: interfacial tension, processing condition, rheological properties of each polymer, blend's composition and so on. Understanding all of these parameters is important to develop and improve the blend's properties.

#### 2.1 Uncompatibilized Polymer Blends

##### 2.1.1 Effect of Rheological Properties on Blend Morphology

Rheological properties is the particularly properties of each polymer. Taylor (1932) was the first one to carry out the experiment to study the dispersion phenomena of immiscible in Newtonian-Newtonian system. He found that drop deformation was mainly governed by two dimensionless parameters: the capillary number (Ca):

$$Ca = \frac{\dot{\gamma}\eta_m R}{\Gamma} \quad (2.1)$$

and the viscosity ratio ( $\eta_r$ ):

$$\eta_r = \frac{\eta_d}{\eta_m} \quad (2.2)$$

where  $\dot{\gamma}$  is shear rate, R is radius of the drop,  $\Gamma$  is the interfacial tension between major and minor phase,  $\eta_d$  is dispersed phase's viscosity and  $\eta_m$  is viscosity of matrix. Drop breakup can occur at  $Ca \geq Ca_{crit}$ . Moreover, Grace (1971) also showed the same results with Taylor that  $Ca_{crit}$  depended on both the viscosity ratio and the flow type: extensional flow and simple shear flow

type. He noted that the deformation and breakup of both extensional and simple shear flow occurred easily in  $0.1 < \eta_r < 1$  especially at  $\eta_r$  around unity. Furthermore, extensional flow was more effective than the simple shear flow. If  $\eta_r > 4$ , it was impossible to break drops in simple shear due to the rotational character of the flow.

In 1987, three researchers, Wu and Chalivoux and Favis, studied to extend the Taylor's theory criterion to the case of viscoelastic drop dispersed inside the viscoelastic medium by using different polymer pairs. Wu reported that drops could be broken up during extrusion even when  $\eta_r$  was greater than 4. He suggested that the dispersed particles became larger at  $0.1 > \eta_r > 1$ . He also provided a correlation relating capillary number to  $\eta_r$  of polyamide/rubber system as followed this:

$$Ca = 4\eta_r^{\pm 0.84} \quad (2.3)$$

or gave the final particle diameter:

$$D = \frac{4\Gamma \eta_r^{\pm 0.84}}{\gamma \eta_m} \quad (2.4)$$

The plus (+) sign in the exponent applies for  $\eta_r > 1$  and the minus (-) sign in the exponent applied for  $\eta_r < 1$ . Chalivoux and Favis also studied the effect of viscosity ratio on morphology of PP/PC blends during processing. The results showed that the viscosity ratio had an effect of the particle size with the phase size increasing from the viscosity ratio of 4.5 to 17.3. Reduction of the droplet size was occurred at  $\eta_r$  less than unity and a minimum size was achieved at  $\eta_r = 0.15$ . By the way, the plot of critical capillary number versus  $\eta_r$  for Newtonian - Newtonian system gave a U-shaped master curve whereas the master curve became more V-shaped, as the elasticity of the system was increased.

Han, Feng and Li (1995) studied the effect of flow geometry on the rheological properties of PS/PMMA blends. PS and PMMA was mixed in a twin-screw extruder by varying the blend's composition of PMMA/PS as 90/10, 70/30, 50/50, 30/70 and 10/90. In this study, they measured the steady shear viscosity as a function of shear rate and oscillatory shear flow properties as a function of angular frequency ( $\omega$ ) by a cone and plate rheometer and a capillary rheometer. They found that the steady shear viscosity from both rheometers did not overlap with each other in blending whereas it was in good agreement between the two homopolymers. For oscillatory shear flow properties, graph between  $G'$  and  $G''$  gave rise to curvature for blends but a straight line for the constituent components, leading to conclude that such plots were very sensitive to variation in the morphological state of the blends.

The shear history and hysteresis behaviors were the parameters to control the morphology associating with drop breakup and coalescence and related to the rheological properties. Mario, Paul and Jan (1997) studied the effect of shear history on blend morphology of PIB/PDMS by using a cone and plate rheometer. By means of rheological experiments it was shown that multiple steady states could be obtained below a critical shear rate whereas above the critical shear rate the morphology is determined by equilibrium between breakup and coalescence. By changing the viscosity ratio, they could be summarized the applicability of three different coalescence theories. The accuracy of the fully mobile interface theory increased with decreasing the viscosity ratio whereas the opposite held for the immobile interface theory. The partially mobile interface theory described the various results equally well.

Manale, Mewis and Moldenaers (1998) studied the morphological hysteresis in immiscible polymer blends. The steady state morphology of blends is a single-valued function of the shear rate whenever a critical shear

rate is exceeded whereas it became very difficult to reach equilibrium between breakup and coalescence below this critical value because of hysteresis. The critical shear rate decreased with increasing concentration of minor phase.

## **2.2 Compatibilized Polymer Blends**

As you know that most polymer blends are thermodynamically immiscible in the molten state. Hence, the blending process yields a heterogeneous and the properties are largely influenced by its morphology. For improving the blend's properties, it is essential to model the development of the morphology during compounding. Addition of compatibilizers is a method to prevent coalescence and stabilize the morphology.

### **2.2.1 Effect of Block Copolymer Concentration on Blend Morphology**

This effect was studied by Sundararaj and Macosko in 1995. The morphology of blends with and without block copolymer was compared to each other by using SEM. They obtained the results that larger droplet sizes occurred at higher concentration of minor phase that is because of coalescence behavior. Addition of block copolymers suppressed coalescence at higher concentration because it stabilized the interface and increased the interfacial adhesion.

Jerome *et al.* (1996) studied the effect of block copolymer composition of PS/EPR blend and poly(styrene-hydrogenated butadiene) was used as compatibilizer. The result exhibited that no coalescence occurred at low % minor phase (~1-5%). So compatibilizers did not have any effects on the reduction of the particle sizes in this range. At higher concentrations of minor phase, the drops started to coalesce with each other. The effect of compatibilizer became more significant.

Xu and Lin (1996) examined this effect for blending of isotactic polystyrene and isotactic polypropylene. Addition of *iPS-*b*-iPP* diblock copolymer less than 10% to the system had a large compatibilizing effect on its morphology and properties, showing the importance of the adhesion between the components of a non-compatible blend.

### **2.2.2 Effect of Molecular Structure of Block Copolymer on Blend Morphology**

Cho, Jo and Nam (1996) reported the effect of molecular structure of styrene-isoprene diblock copolymer on the interfacial tension, morphology and interfacial adhesion of PS/PI blends by using 3 different types of diblock copolymer: SI-8/2, SI-5/5 and SI-2/8. PI acted as the minor phase dispersed inside the PS matrix. The reduction in interfacial tension of asymmetric diblock copolymer having longer isoprene block is more significant than the symmetric or the styrene-rich diblock copolymer. The particle size is significantly reduced and its size distribution became narrower when a small amount of block copolymer was added.

Dadmun (1996) examined the effect of copolymer architecture on the interfacial structure and miscibility of blending by using 3 types of copolymer structure: block, random and alternating structure. From this experiment, the phase transition from miscible to immiscible did not change with addition of 1% copolymer because the copolymer present was not sufficient to cover the biphasic interface. Besides, the configuration of the copolymer at the interface was a function of sequence distribution within the copolymer: both alternating and block copolymers showed promise as interfacial modifiers whereas the purely random copolymer had the weakest effect on the interfacial strengthening.

Jerome *et al.* (1996) studied the influence of molecular weight, architecture of diblock copolymer on blend morphology. The system chosen was a blend containing 80% polystyrene and 20% ethylene-propylene rubber (EPR), compatibilized by diblock copolymers of poly(styrene-hydrogenated butadiene). The results were shown that the droplet size decreased rapidly at low concentration of interfacial agent followed by a leveling off to a plateau value at a certain critical concentration which was around 20%. Moreover, no significant difference was observed between the emulsifying capability of tapered and pure diblocks of similar composition and molecular weight. For the effect of molecular weight, increasing MW of block copolymer led to decreasing the droplet size because of the swelling effect.

### **2.2.3 Effect of Interfacial Activity of Block Copolymer on Blend Morphology**

Several theoretical and experimental studies on the interfacial activity of a block copolymer in immiscible polymer blends have been reported. It has been found experimentally that the interfacial tension decreased with increasing concentration of block copolymer. The block copolymer micelles are formed when the copolymer concentration in the homopolymer phase exceeds the critical micelle concentration (CMC).

Patterson *et al.* (1971) used a rotating drop apparatus to study the effect of addition of poly(dimethylsiloxane-*block*-oxymethylene) copolymers on the interfacial tension between methyl terminated poly(dimethylsiloxane) and a poly(oxyethylene-*block*-oxypropylene) copolymer. They found that the interfacial tension was reduced by 72% with the addition of 2% of a 60/40 poly(dimethylsiloxane-*block*-oxyethylene).

Noolandi and Hong (1982) studied theoretically the interfacial properties of block copolymers in immiscible homopolymer blends by using a general formalism for inhomogeneous multicomponent polymer systems.

The same result with Patterson was observed. They found that the interfacial tension was reduced with increasing block copolymer concentrations for a range of copolymer and homopolymer molecular weights. They pointed out that not only copolymer concentration but also its molecular weight were equally important in reducing the interfacial tension. For the concentrations below the CMC, the interfacial tension was expected to decrease linearly with copolymer concentration and followed by a levelling off to a plateau value at above CMC.

Hu, Koberstein, Liniger and Gallot (1995) examined the interfacial tension reduction in polystyrene/poly(dimethylsiloxane) blends by addition of poly(styrene-*b*-dimethylsiloxane). The interfacial tension was measured by using an automated pendent drop tensiometer. They found that the interfacial tension of the blend initially decreased upon an increase in the copolymer concentration and then attained a constant value above a certain critical copolymer concentration (0.002%).

#### **2.2.4 Effect of Exothermic Interaction of Block Copolymer on Blend Morphology**

One purpose to add block copolymer is for developing the thermodynamic properties relating to entropy and enthalpy in the system. They were reported in many research works.

Tucker, Barlow and Paul (1988) studied the effect of molecular weight on phase behavior of poly(phenylene oxide) (PPO) with styrenic triblock copolymers. They found that the exothermic heat of mixing for PPO and PS units caused a dramatic increase in the extent of homopolymer solubilization. This solubilization was measured by using DSC. The result also showed that the molecular weight of the PS block was a major factor determining the extent of PPO and PS segments. While the molecular weight

of the PPO has only a little or no effect over the range investigated ( MW = 23,900 to 39,000 g/mole).

Akiyama and Jamieson (1992) studied the enthalpic interaction in the copolymer / homopolymer blend systems. They measured the morphology of solvent casting films containing a polystyrene/poly(methyl methacrylate) (PS/PMMA) with polystyrene, random styrene acrylonitrile copolymer (SAN) and PMMA. They found that the morphology of the blends changed systematically from dispersed spheres to cylinder, vesicles and lamellae, depending on the strength of the enthalpic interaction between the matrix and the copolymer segments.

Adedeji, Hudson and Jamieson (1996) studied the effect of exothermic interfacial mixing on interfacial activity of a block copolymer. They measured the variation in the exothermic interaction of PMMA-*b*-PS in solvent casting blends of SAN and PS matrix. The exothermic mixing between SAN and PMMA and the repulsion between SAN and PS were systematically varied by changing the AN content of the SAN between 15 to 33%. The degree of incompatibility,  $N\chi_{SAN-PS}$ , the molecular weight ratio,  $M_h/M_b$ , of homopolymer to the segment of block copolymer, and the degree of exothermic mixing between SAN and PMMA were all important in determining the morphology of the dispersed phase.

Adedeji, Jamieson and Hudson (1996) studied the morphology of solvent cast ternary isochemical (A/A-*b*-B/B) and heterochemical (A/X-*b*-B/B) blends by using transmission electron microscope (TEM). They found that the morphology of such blends is controlled by the delicate balance in the swelling of each block copolymer segment by the corresponding compatible homopolymers. The morphologies of A/A-*b*-B/B and A/X-*b*-B/B type were also related to the phase behavior. For the best solubilization, the molecular weight of homopolymer (P) was required to be less than or equal to that of the block copolymer segment (N).



Adedeji, Hudson and Jamieson (1997) studied the enthalpic interaction in the heterochemical system of PVC/PMMA blend and PMMA-*b*-PS was used as the compatibilizer. In general, the microphase formation will occur only if  $N/P \leq 1$  (Adedeji *et al.*, 1996). In this work, they found that the microphase formation can enable even  $N/P > 1$ . That was because of the exothermic interaction between PVC and PS segment providing to the enthalpy swelling.

Kim, Jamieson *et al.* (1998) studied the influence of exothermic interaction on the morphology and droplet coalescence of SAN and Poly (cyclohexyl methacrylate) (PCHMA) blend containing a poly(styrene-*b*-methyl methacrylate) block copolymer. The parallel plate rheometer with simple shear deformation was chosen for blending in this work. They found in the same result in 1996 that the degree of exothermic interaction between SAN and PMMA segment of block copolymer can be varied by changing the AN content of SAN from 15 to 35%. The maximum exothermic reaction was performed at 26% AN content in SAN whereas the minimum one was occurred at 33% AN.