CHAPTER I

INTRODUCTION

Polymer blending has provided an efficiency way to fulfill the new requirement for material properties. For example, PS blended with PP will improve the thermal stability of PP during processing (Henri, 1993). Most polymer blends are thermodynamically immiscible, but some of polymer blends are compatible and exhibit excellent physical properties that offer advantage over either of the individual polymers. The great majority of useful blends are immiscible blends such as PS/PP blend, PP/PE blend, and Nylon/EPR blend. The miscibility of a polymer pair depends on thermodynamic interaction at interface, which can be explained in terms of Gibb's free energy of mixing (ΔG_m) and chi-parameter (χ_{12}). If ΔG_m is more than zero, the polymer blend is an immiscible blend. The immiscible blend shows a limited solubility and a finite interfacial tension, therefore a mixture of two immiscible polymers is expected to result in a two-phase structure. The mechanical properties of these blends are also strongly depended on their microstructure or morphology.

1.1 Physical Properties of Polymer Blends

Some polymer blends are fabricated to improve the melt flow and mechanical properties and/or to reduce shrinkage. High impact strength may be obtained by blending polystyrene either with polybutadiene or with styrene which has been rafted, or with a block copolymer of butadiene and styrene (Henri, 1993). For example, impact polystyrene is blended with PPO to improve melt flow properties, while polyblends of PVC with ABS or acrylate graft copolymer have impact strength higher than either of the components.

Binary blends of PP with LLDPE are commercially attractive for their strength, modulus, and low-temperature impact performance (Utracki, 1991). Addition of a rigid polymer to a soft matrix, SBR/PS blending, results in an increase in modulus, tensile and tear strengths. The mechanical properties of the blends depend on the state of dispersion: shape, size, and orientation of the dispersed phase (Gonialez, 1996). For example, at 15% by weight of rubber/polyamide blend, a fourfold drop in the Notched Izod Impact Strength was observed in increasing the number average minor size from 0.7 μm to 0.8 μm (Wu, 1985). It has been found that the addition of interfacial agents can improve the properties of immiscible blends.

1.2 Controlling the Morphology of Immiscible Blends

Controlling the morphology of immiscible blends is very important. The relations among the original morphology (size, shape), the process variables (flow field applied during blending), and material parameter (rheological properties and miscibility), are of concern. The composition of blend can also affect morphology. At low concentration of minor phase, the droplet formation occurs. While at high concentration of minor phase, the co-continuous structure is expected. For example, for ABS/PET blend with 50/50 composition, ABS and PET morphologies were continuous throughout the structure (Cook, 1996). The 50/50 NR-LLDPE blend was a honeycomb structure (Abdullah, 1995).

Controlling the morphology can be achieved by two methods. The first method is by adding a compatibilizer into the blend to reduce the interfacial tension or inhibit coalescence. The second method is by controlling the viscoelastic properties and processing conditions such as shear rate, temperature, and shearing time. The rheological properties of blend, viscosity ratio and elastic ratio were found to have a strong influence on the shape and

the size of minor phase due to mechanical mixing (Wu, 1987 and Macosko, 1995). Thus the finest minor drop size can be obtained by choosing the system that provides one of viscosity ratio (Wu, 1987). Increasing the viscosity ratio has a drastic effect on the morphology of dispersed phase while the phase size can increase by factor of 3 to 4 times as the viscosity ratio is varied from 4.5 to 17.3 (Favis, 1987).

During processing, the material is usually sheared in the gap of extruder or chamber. For immiscible blends having two phases, droplet deformation, droplet break-up and coalescence always occur during flow. For simple flow fields of discrete liquid drops, stress arising in continuous phase tends to deform and orient a droplet. Moreover, within the range of compounding and processing conditions, the shape of droplets is determined not only by dissipative (viscous) force, but also by pressure distribution around the droplet arising from elasticity. The droplet elasticity is expected to reduce the deformation and increase the critical shear rate of droplet breakup, while matrix elasticity should increase the deformation. The controlling of morphology process consists of drop breakup and coalescence depending on characteristics of the polymer. Some researchers have been trying to investigate these processes, but they are still far from completed.

1.2.1 Drop Breakup

Drop breakup depends on shear force and interfacial tension as a restoring force. At low shear stress, the sub-critical deformation of a droplet results from balancing the interfacial tension force (tending to keep the droplet spherical) against the viscous force (tending to elongate the droplets).

Apply shear stress

(original droplet)   (drop-deformation)   (drop-breakup)
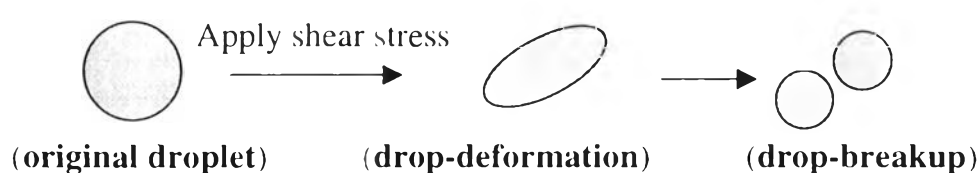
When the interfacial tension force can no longer balance the viscous force, the deformation becomes unstable and then the droplet will burst into smaller size. The bursting of the droplet depends on viscoelastic properties of system blend at that shear stress. At high viscosity ratio, the droplets undergo only limited deformations without bursting (Utracki, 1991). Grace (1982) noted that burst occurred easily for 0.1 < viscosity ratio < 1.0. Wu (1987) reported that the droplets can breakup during extrusion even when viscosity ratio is more that 4. Thus the deformation of droplet also depends on its elasticity of the blend. At a higher elasticity of dispersed phase than the continuous phase results in more stable droplets. The bursting of the droplets also occurs after cessation of flow and the time requires for complete bursting depends on viscosity ratio (Stone *et al.*, 1986). Actually, the breakup process is gradual and that it leads to a distribution of particle size (Stone *et al.*, 1986). Therefore viscosity and elastic properties of minor and matrix phases play an important role for drop break up process. Finally, the droplets of the dispersed phase progressively break down until a minimum droplet diameter is reached. A further decrease the droplet size becomes more and more difficult.

To explain the drop breakup process, the combination of many factors, which influenced the morphology of the blend via dimensionless parameters, were analyzed. Staring by G. I. Taylor in 1932, He studied the breakup of a single Newtonian drop in a simple shear field. He modeled drop size using viscosity ratio, η_r, and capillary number, Ca:

$$Ca \cong \dot{\gamma}\eta_m D/(2\Gamma) \qquad (1.1)$$

where $\dot{\gamma}$ is the shear rate, η_m is the matrix viscosity, η_d is the dispersed phase viscosity, $\eta_r = \eta_d/\eta_m$, D is the drop diameter, and Γ is the interfacial tension. He balanced the interfacial force and the shear forces and obtained a relation for the maximum drop size that would be stable:

$$D = \frac{4\Gamma(\eta_r + 1)}{\dot{\gamma}\eta_m (\frac{19}{4}\eta_r + 4)} \qquad (1.2)$$

This relation is valid for small deformations in Newtonian fluids. Wu (1987) followed up Taylor's theory and found the correlation relating capillary number to viscosity ratio. He gave a relation for final particle diameter of polymer blends:

$$D = \frac{4\Gamma\eta_r^{\pm 0.84}}{\dot{\gamma}\eta_m} \qquad (1.3)$$

where the plus (+) sign in the exponent applies for viscosity ratio > 1.0 and the minus (-) sign in the exponent applies for viscosity ratio < 1.0. In all blends used for this correlation, the weight percentage of minor phase was 15 %wt and the effective shear rate was arbitrarily chosen as 100 s^{-1}.

1.2.2 Coalescence

For the coalescence process, the composition of minor phase is an important factor. At high concentration of minor phase, the probability of particle collision is high. When two drops come close to each other and the pair rotates in the shear field. The film of the matrix phase between two drops drains until the critical thickness value reaches, the two drops will form into the bigger one, coalescence. However, the coalescence can be accelerated by shear flow. The number of collisions per unit time can be determined from (by Smoluchwski, 1916):

$$N_T = (4/\pi)\, n\, \phi_d\, \dot{\gamma} \qquad (1.4)$$

where n is the number of particles, ϕ_d is minor phase concentration, and $\dot{\gamma}$ is shear rate. Applied shear stress induces the minor drop size to increase; the

process is called *shear-induce coalescence*. At high shear rate or high shear stress, the drops are not only broken up, but they can also collide. So the final drop size is usually larger than the predicted value.

Another important factor influencing the magnitude of coalescence probability is the mobility of interface. High mobility of interface, high rate of drainage results in a fast rate of coalescence. The mobility of the interface is considered to be related to the viscosity ratio (Chesters, 1991). A model by Chesters describes the partially mobile situation. This model leads to the following equation for drainage rate:

$$-\frac{dh}{dt} = \frac{2(2\pi\sigma/R)^{3/2}h^2}{\pi\eta_d F^2} \qquad (1.5)$$

where h is the film thickness between two drops, R is the droplet radius, Γ is interfacial tension, F is the coalescent force, and η_d is the dispersed phase viscosity. However the temperature is one important factor because of the temperature dependence of polymer. Coalescence can occur after cessation of flow due to annealing (Fortenly and Kovar, 1988). The shearing at a low shear rate after mixing can promote coalescence (Jamieson, 1998). Moreover, the annealing at $T > T_g$ of phases influence the droplet motion, and coalescence will increase, causing both the growth of average dispersed size and its size distribution (Kumin and Han, 1996).

1.3 Literature Survey

Roland and Bohm (1984) studied the shear-induced coalescence in two-phase polymeric fluid by small angle neutron scattering. The rheological properties of two phases and the flow field used in the blending were reported to greatly influence the process. They found that coalescence could be accelerated by the same factors that favor the drop breakup (e.g., higher shear

rates, reduced dispersed phase viscosity). The drop collisions, which could lead to coalescence, occurred not only in flow but also in quiescent systems; they were caused by Brownian motion, dynamics of concentration fluctuation, etc.

Wu (1987) extended the Taylor's theory criterion to the case of viscoelastic drop dispersed inside the viscoelastic medium. He reported that drops could be broken up during extrusion even when viscosity ratio, η_d/η_m, was greater than 4. He suggested that as the viscosity ratio increased above unity or decreased below unity the dispersed particles became larger. He also provided the correlation between Capillary Number (Ca), $\dot{\gamma}\eta_m/(\Gamma/R)$, and viscosity ratio. Ca $= 4\eta_r^{\pm 0.84}$, where $\dot{\gamma}$ is the shear rate, R is the particle radius, Γ is the interfacial tension, η_m is the matrix viscosity, η_d is the dispersed phase viscosity, and $\eta_r = \eta_d/\eta_m$. Moreover, he found that the dispersed drops were the smaller, when the viscosity ratio was closer to unity.

Favis and Chalifoux (1987) studied the effect of viscosity ratio on the morphology of polypropylene(PP)/polycarbonate(PC) blends. The size of dispersed phase PC was examimed as a function of viscosity ratio (η_r). The η_r had a marked effect on the size of dispersed phase with the phase size increasing by a factor of 3 to 4 from $\eta_r = 4.5$ to $\eta_r = 17.3$. Reduction in the size of dispersed phase was achieved below $\eta_r = 1$ with the minimum particle size occurred at $\eta_r \approx 0.15$. Below this value at low concentration of minor phase, 7%, the particle size remained constant within the experimental range of 0.058-0.142. They also found that at high concentration of minor phase, the size distribution widened and the deformation of dispersed phase became more difficult.

Prabodh and Stroeve (1991) observed that during shearing, some drops were greatly extended and would break only when the flow was stopped. They investigated the effect of elasticity of dispersed phase on the drop breakup process. They concluded that at $\eta_r < 0.5$ the droplet elasticity had a stabilizing effect, but for $\eta_t > 0.5$ the elasticity was more important. They also found that the critical Capillary Number (Ca) for viscoelastic droplets was higher than for Newtonian system, because the elasticity stabilized the drop.

Palierne (1991) provided the correlation between linear viscoelastic behavior and morphology parameters, such as inclusion size, interfacial tension and concentration, of incompatible polymer blend in the melt. He worked out a linear viscoelastic constitutive equation for the emulsion as a function of complex modulus of two phases, interfacial tension, and inclusion size. The experiment was carried out in the oscillatory shear mode at small strain amplitudes to prevent the morphology from being affected by the rheological testing. He showed that the relaxation times of phase corresponded to the time required for the deformation of morphology to recover its original morphology. The longest relaxation time of emulsion corresponded to the relaxation time of the shape of droplets. It was found that the relaxation times of the phases increased with increasing viscosity ratio. The increasing of volume fraction of minor phase increased the complex modulus of emulsion, but slightly increased the relaxation time of droplets.

Macosko and Sandararaj (1995) showed that a limiting dispersed phase particle size existed at very low concentrations for polymer blends. The final particle size increased with the minor phase concentration due to increased coalescence. The particle size distribution broadened at higher

concentrations. They also studied the effect of compatibilization using in-situ reaction during blending. Adding diblock copolymers suppressed coalescence at high concentration of minor phase resulting in smaller particle size and narrower particle size distribution. They founded that upon increasing shear rate was more than 130 s^{-1}, the particle size actually increased. Because at higher shear rates, the matrix viscosity decreased and droplet elasticity increased, so that drop resisted the deformation to a greater extent. However, at higher shear rates, the droplets had higher approach velocities and thus the coalescence probability increased.

Levitt and Macosko (1996) found the influence of normal stress difference on drop deformation, PS/PP blends. They in-situ observed the drop deformation during applied shear field. They carried out on dynamic measurement testing at the fixed the frequency of 1 s^{-1} but at varied the %strain.   At η_r = 4.4 and elastic ratio of G'$_r$ = 14, the droplet formed a torpedo-like shape at low %strain and stretched into a fiber and folding at high %strain. At η_r = 2.4 and elastic ratio of G'$_r$ = 7, the droplet formed an ellipse shape at low %strain and no folding of drop at high %strain. They concluded that the widening of drops was indeed inversely proportional to the ratio of drop/matrix elasticity, G'$_r$ = G'$_d$/G'$_m$ where the G'$_d$ and G'$_m$ were the storage modulus of dispersed phase and matrix phase respectively.

Kumin and Change (1996) studied the effect of shear flow and annealing on morphology of rapidly precipitated immiscible blends of PS/PI. They varied the composition of PS from 70% to 30% by weight, and found that the co-continuous structure formed when $(\dfrac{\eta_1}{\eta_2})(\dfrac{\phi_2}{\phi_1})$ = 1 as dispersed-continuous phase formed when $1 < (\dfrac{\eta_1}{\eta_2})(\dfrac{\phi_2}{\phi_1}) < 1$.   The component with higher viscosity and lower volume fraction would form the dispersed phase. After blending by precipitated method, they found that dispersed phase

droplets coalesced during annealing at 110 °C. The effect of viscosity ratio on morphology development was also investigated by applying shear flow using capillary die. The blends were extruded at 160 °C and 180 °C. They found the extruded morphology parallel to the extrusion direction was highly dependent on the viscosity ratio and the applied shear rate. When the dispersed phase viscosity was less than that of the matrix, the elongation of the dispersed phase along the extrusion direction was observed.

Wensheng and Jiasong (1996) investigated the effect of mixing time on the morphology of immiscible blends. They studied two immiscible blends, polyamide/polyethersulfone and poly (butylene terephthalate)/polystyrene. At short mixing time, the morphology of each phase depended not only on the composition, but also on the viscosity difference of the two phases. The lower viscous phase (PA) formed particles, fibrils, and layers progressively with its increasing content and became a continuous one at low concentration as the minor phase, while the high viscous phase (PES) appeared mainly in the form of particles and directly became a continuous one at high concentration. With increasing mixing time, the effect of viscosity ratio became less and the morphology was determined mainly by the volume fraction of each phase.

Nakatani (1996) studied the relationship between polymer blend morphology and shear behavior and adapted the results for utilization in industrial processing equipment. Shear effects on the phase behavior of polymer blends, semi-dilute polymer solution, and block copolymers were examined. His work covered the shear behavior of the materials as a function of temperature and shear rate, and the phase separation kinetics in homogenized systems following cessation of shear. The shear rate and temperature dependence of droplet break-up in solution of polymer blend (PS/PB in dioctyl phthalate) and a low molecular weight polymer blend were

examined by phase contrast optical microscopy and light scattering. They found regimes of droplet deformation at 2.0 s^{-1} and break-up before homogenization at 20 s^{-1}. At the high shear rate of 200 s^{-1}, and temperatures just within the two phase region, a string-like phase was observed. Finally, at low shear rates, droplets of the labeled polystyrene were observed under the fluorescence microscope. With increasing shear rate, the labeled polymer became uniformly distributed throughout the sample, indicating that along with droplet break-up, the concentration difference between the two phases decreased.

Minale, Moldenaers, and Mawis (1997) found the morphology of immiscible blends depending on shear history. They showed that the initial conditions of blending greatly affected the morphology of immiscible blends. There was a critical shear rate, above which a unique morphology was attained regardless of the initial conditions. The morphology resulted from equilibrium between breakup and coalescence processes. Below this critical shear rate, the multiple steady states, or pseudo steady states, were possible and therefore the final morphology did not only depend on the characteristics of the applied flow but also on the initial conditions of blends.

Schoolenberg et al. (1998) developed the novel technique to measure the coalescence phenomena in a polymer blend, PS/LDPE, using a spinning drop apparatus. They found that the time of coalescence increased with dispersed phase viscosity. They varied the speed of rotation of spinning drop apparatus, and found that the coalescence results were unaffected by speed of rotation. This method is more rapid and more versatile in its control of the contact radius and coalescent force. They assessed the governing parameters of the coalescence process, interfacial mobility and matrix film rupture thickness, by testing a range of droplets of various sizes. They suggested that

in the final stages of film drainage and rupture, entropic effects of the macromolecules play only a minor part. They compared the coalescence between the commercial polymers and purified system, and found that commercial polymers were shown to coalesce considerably faster than a purified system. Because impurities may lead to premature coalescence though lubrication of the interface.

1.4 Objectives

In this work, we will investigate the effects of shear, rheological and thermodynamic properties on drop breakup and coalescence of various immiscible blends subjected to shearing as occurred in polymer process. The scope of this work is divided into 3 parts:

(1) To study the effects of
- shearing time on morphology
- shear strain rate on equilibrium morphology
- mixing conditions on initial morphology

(2) To find the relationship between viscoelastic properties and morphology.

(3) To study the Palierne's theory for prediction the morphology of immiscible blends.