

CHAPTER II

LITERATURE SURVEY

2.1 Immiscible Polymer Blends in Newtonian System

The interesting experiment pertaining to the Taylor's theory was done by Grace (1982). He carried out the experiment to study the dispersion phenomena of high viscosity immiscible Newtonian fluid systems in both rotational shear flow and extensional shear flow. He noted that burst occurred easily for $0.1 \leq \eta_r \leq 1.0$, and the smallest droplet size was obtained at η_r around unity for both flow fields. In addition, it was impossible to break drops when η_r exceeded 3.5 in rotational shear flow whereas extensional shear flow could break drops even at η_r greater than that. It was also evident that extensional flow was more efficient than shear for breaking the drops.

The shear-induced coalescence in two-phase polymeric fluid using small angle neutron scattering method was studied by Roland and Bohm (1984). They found that droplet coalescence could be accelerated by the same factors that favor the droplet breakup (e.g., higher shear rate, 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.

Based on the Grace's experimental result, De Bruijn (1989) proposed a semiempirical equation for the dependence of the critical capillary number on viscosity ratio:

$$\log (Ca_c) = c_1 + c_2 \log \eta_r + c_3 (\log \eta_r)^2 + \frac{c_4}{(\log \eta_r + c_5)} \quad (2.1)$$

where $c_1 = -0.5060$, $c_2 = -0.0994$, $c_3 = 0.1240$, $c_4 = -0.1150$, and $c_5 = -0.6110$

for simple shear flow and $c_1 = -0.64853$, $c_2 = -0.02442$, $c_3 = 0.02221$, $c_4 = -0.00056$, and $c_5 = -0.00645$ for elongational flow.

2.2 Immiscible Polymer Blend in Non-Newtonian System

Experimental results on the breakup of Newtonian drops in simple shear fields of viscoelastic fluids were reported by Flumerfelt (1972). The interesting point was the relationship between the drop size, critical shear rate for breakup, and the material properties of the fluids. The results indicated the existence of a minimum drop size (D_{\min}) which varies with each fluid system, below which breakup could not be achieved. An increase in the elasticity of the matrix phase tended to increase D_{\min} as well as the critical shear rate (γ_c) required for breakup when $D > D_{\min}$. An increase in the viscosity of the matrix phase should cause the opposite effect. Breakup resulting from steady shear conditions (a step change application of shear) showed significantly decreased values of D_{\min} and γ_c from those associated with “steady” shear conditions.

For polymer blends, the effect of viscosity ratio on drop size in melt blends has been investigated. A correlation relating capillary number to viscosity ratio in extruded polymer blends had been given by Wu (1987). He showed for polyamide/rubber systems that viscoelastic drops can breakup during extrusion even when the viscosity ratio was greater than 4. Then he gave a relation for the final particle diameter:

$$D = \frac{4\Gamma\eta_r^{\pm 0.84}}{\gamma\eta_m} \quad (2.2)$$

where the plus (+) sign in the exponent applies for $\eta_r > 1$ and the minus (-) sign in the exponent applies for $\eta_r < 1$. He also suggested that as the viscosity ratio increased above unity or decreased below unity the dispersed particles became larger.

Favis and Chalifoux (1987) set up an experiment to study the effect of viscosity ratio on the morphology of PP/PC blends in a Brabender Mixer. The sizes of the minor phase in PP/PC blends were examined by light and scanning electron microscope after melt processing as the function of both viscosity ratio (η_r) in the regions of $\eta_r > 1$ and $\eta_r < 1$. Using the Rheometrics Mechanical Spectrometer to measure the dynamic viscosity for the varied MFI of both PP and PC at 250 ° C, they found that PC exhibited higher viscosity than PP. When $\eta_r > 1$ (PC dispersed in PP) both the number average and volume average diameter of the dispersed phase were highly dependent on viscosity ratio; at 7 vol% PC the volume average diameter varied from 1.3 μm at $\eta_r = 4.5$ to 7.7 μm at $\eta_r = 17.3$ and the number average diameter varied from 1 μm to 3 μm . When $\eta_r < 1$ (PP dispersed in PC) a minimum particle size was achieved at $\eta_r \cong 0.15$. It was interesting to note that the position of the minimum particle size appeared to correspond at both low and high concentration (7 vol% and 23 vol% PP in PC). Their experiment results were in conflicted with the Wu's correlation that the minimum particle size occurred at approximately $\eta_r = 1$.

A computer-controlled four-roll mill developed by Bently and Leal (1986) was used by Milliken and Leal (1991) to investigate the deformation and breakup of polymeric drops (polyacrylamide, carboxymethyl cellulose, and polyacrylic acid) suspended in Newtonian liquid (Pale 4 oil and Pale 1000 oil). It was found that, generally, drops with zero-shear-rate viscosity ratios of order 1 and higher exhibited steady drop shapes that were similar to Newtonian drops. However, drops with viscosity ratios less than order 1 showed markedly smaller critical deformations and the critical capillary number was found to be substantially smaller.

The development of morphology from pellet-sized particles to submicrometre droplets during the polymer blending process was investigated for several polymer blends by Scott *et al.* (1995). The dispersed phase for the

model experiments was an amorphous nylon. The matrix phases investigated included polystyrene, an oxazoline functional polystyrene, a styrene-maleic anhydride copolymer, an amorphous polyester and a polycarbonate. The major reduction in phase domain size occurred in conjunction with the melting or softening of the components. The initial mechanism of morphology development involved the formation of sheets or ribbons of the dispersed phase. These sheets or ribbons became unstable due to the effects of flow and interfacial tension. Holes developed in ribbons, which grew in size and concentration until a fragile lace structure was formed. This mechanism resulted in very fast formation of small dispersed-phase particles, which were nearly the same size as those observed at long mixing times. Continuous mixing action primarily reduced the size of the largest particles in the size distribution.

Han *et al.* (1995) studied the effect of flow geometry on the rheology of polystyrene (PS)/poly (methyl methacrylate) (PMMA) blends by comparison between cone-and-plate and capillary rheometer. They observed that the plots of steady shear viscosity versus shear rate obtained by cone-and-plate rheometer for blends did not overlap those obtained by capillary rheometer, whereas for pure polymers, PS and PMMA, showed the opposite results. The reason they gave was the differences in the morphological states of the blends between the uniform shear flow in cone-and-plate rheometer and the non-uniform shear flow in capillary rheometer, which involved the entrance and exit effects.

The effect of dispersed phase concentration on drop breakup and coalescence in polymer blends was studied by Sundararaj *et al.* (1995). Three different mixers, an internal batch mixer and two types of twin-screw extruders, were chosen in order to compare the efficiency of mixers. The study showed that a limiting dispersed phase particle size existed at very low concentration around 0.5 wt% for polymer blends mixed from three mixers.

The final particle size depended on the dispersed phase concentration, especially for uncompatibilized blends. Coalescence during blending process occurred at higher concentrations, resulting in larger particle sizes. Surprisingly, they found that breakup occurred even the viscosity ratio was greater than Taylor's and others predictions ($\eta_r = 4$).

Leon *et al.* (1996) investigated the deformation of polypropylene drops in polystyrene matrix with different viscosity and elasticity ratio (G_r) under a simple shear flow. The shear flow was generated by two counters rotating transparent disks, which was designed and machined for this laboratory. By adjusting the speed of one disk the drop center was fixed in the laboratory frame and deformation followed via high magnification video camera. They could observe the widening of drops perpendicular to the flow direction and found that the width of flattened drops depended on the difference in elasticity between matrix and drop, and was proportional to the difference of the second normal stress difference of both two phases. Nevertheless, no widening drop was observed for viscosity ratio greater than unity and elasticity ratio larger than 2. When viscosity ratio reached 5 and elasticity ratio was 14 the drop did not flatten, but rather formed a cylinder that folded and unfolded periodically in the flow field.

Minale *et al.* (1997) observed how the steady state morphology during shear of an immiscible polyisobutylene and poly(dimethylsiloxane) blend can be affected by the initial conditions. It was shown experimentally that there was a critical shear rate, identified as the cross value between breakup and coalescence limiting curves, above which a unique morphology was attained regardless of the initial conditions. This morphology resulted from the equilibrium between the two processes. Below this critical shear rate, 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 the blend. By changing

the viscosity ratio, they could summarize the applicability of three different coalescence theories. The accuracy of the fully mobile interface theory seemed to increase with decreasing viscosity ratio, whereas the opposite held for the immobile interface theory. The partially mobile interface theory described the various results equally well.

Moldenaers *et al.* (1998a) investigated further about the effect of processing conditions, essentially the flow conditions, on the morphological hysteresis of immiscible blend. They found that the critical shear rate decreased with increasing concentration of minor phase and led to vanishing of the hysteresis region. As expected, coalescence was enhanced by higher concentrations while droplet breakup was nearly independent of droplet concentrations. Elasticity of minor phase, nevertheless, seemed to facilitate breakup process.

Moldenaers *et al.* (1998b) derived the coalescence model to describe the experiments, based on the approach suggested by Chester in 1991. The coalescence process was not only was affected by blend concentration but also affected by two dimensionless parameters: strain and step down shear rate ratio, which were predicted by the coalescence model. Consequently, they constructed the master curve for each step down ratio by plotting the relative increasing in droplet size (the ratio between volume average droplet size at each step down ratio and initial volume average droplet size) versus the strain after step down multiplied by the square of concentration.

Mighri *et al.* (1998) examined the deformation and the critical breakup conditions of drops in elastic fluids systems under uniform shear flow. A variety of constant viscosity elastic (Boger) fluids were used to obtain drop/matrix combinations with approximately the same viscosity ratio and different elasticity ratio (in term of relaxation time ratio). The results showed that critical capillary number, Ca_c , increased dramatically with increasing in

elasticity ratio up to 4 and reached the maximum of 1.75 for elasticity ratio greater than 4.

A novel technique, spinning drop apparatus, was developed by Schoonenberg *et al.* (1998) to measure coalescence phenomena in polymer blends. In comparison, this technique is more rapid and more versatile in its control of the contact radius and coalescence force than the conventional method, the slow process of gravity driven collisions. The coalescence time was shown to increase with dispersed phase velocity, as expected by Chesters model (Chesters, 1991) based on partially mobile interfaces. They also found that in commercial polymers, the coalescence process can be considerably faster than for purified components because impurities could lead to premature coalescence through lubrication of the interface or by third-phase particles destabilizing the matrix film.

The approach of dispersed droplets in molten quiescent polymer blends from an initial distance comparable with their radii was analyzed by Fortelny *et al.* (1998). It was shown that a substantial flattening of the droplets appeared only at distances comparable with the critical distance for rupture of the matrix film between droplets. The time of coalescence was controlled by the film drainage between practically undeformed spherical droplets. The effect of viscoelasticity on the rate of coalescence was studied for the Maxwell model of the matrix. The theory of coalescence caused by Brownian motion or molecular forces could predict rates of coalescence, which were comparable with those determined experimentally.