CHAPTER I
INTRODUCTION

Polymer blending has attained considerable interest as a very suitable and economical alternative way to achieve the optimized properties of materials, without the need of complicated synthesis system. For each polymer blend, the properties of blend are important depending on its applications such as high impact strength for automotive applications, thermal stability for electronic parts, chemical and solvent resistance for paints and coatings, tensile strength and dimensional stability for building industry, barrier properties for food packaging industry (Utracki, 1989). Polymer blends are physical mixtures of different homopolymers, copolymers and terpolymers that can be homogeneous (miscible) or heterogeneous (immiscible), depending on the thermodynamics of mixing but most useful commercial blends are immiscible since they form a multiphase system with a deformed dispersed phase. Depending on the materials and the processing conditions quite different morphologies such as ellipsoids, fibers and plates are obtained. Since the final morphology from the mixing process can influence the properties of the final product, the control the size, shape of drop, and degree of size dispersion is required.

In order to control the morphology for the optimum properties, it is important to understand the mechanisms of drop breakup and coalescence under both shear and elongation flows during processing. Most fundamental researches are restricted to Newtonian (viscous) systems and focused on idealized systems: the systems consist of isolated drops of well-characterized model liquids at room temperature in simple flow fields. This is far from reality, considering that polymer blends are viscoelastic and that large deformations are encountered during the blending operation. Therefore the

elasticity of polymer should be a factor, which lead to a quite different mechanism of drop breakup and coalescence from the Newtonian one.

Up to now, theoretical and experimental studies indicate that viscosity ratio, interfacial tension, thermal and flow history, and composition play important roles in determining the morphology (Taylor, 1934; Rumscheidt and Mason, 1961; Grace, 1982; Favis and Chalifoux, 1987; De Bruijn, 1989; Wu, 1987; Sandararaj *et al.*, 1992; Sigillo *et al.*, 1997; Minale *et al.*, 1998). For the influence of elasticity on the drop deformation, most of the previous work focused on the fluids systems in which other the matrix or the drop phase was viscoelastic (Gauthier *et al.*, 1971; Flumerfelt, 1972; Tavgac, 1972; Elmendorp and Maalcke, 1985; De Bruijn, 1989). An interesting research involving the effect of normal stress difference on drop deformation in which both matrix and dispersed phases were viscoelastic was introduced by Levitt and Macosko (1996). They observed that the width of the flattened drops depended on the difference in elasticity between matrix and drop, and was proportional to the second normal stress differences of the two phases. The elasticity ratio defined as the ratio between the drop and matrix relaxation time was found to play a major role on the drop deformation in both elongation and shear flows. The drop deformation was shown to decrease with increasing drop elasticity whereas the matrix elasticity had the opposite effect (Mighri *et al.*, 1997, 1998).

The goal of this experimental study is to study the relation between the capillary number and the first normal stress difference ratio, defined as the ratio between the first normal stress difference of drop and matrix, $N_{1,d}$ and $N_{1,m}$, respectively, for viscoelastic polymer melt systems under simple shear flow.

1.1   Theoretical Background

1.1.1   Drop Breakup for Newtonian Fluids and Polymer Blends

The breakup of one fluid in another fluid is a process of considerable importance in many commercial mixing and dispersion operations. Although such processes are generally too complex for detailed analyses, it is possible to gain valuable insights into the underlying phenomena by studying the deformation and breakup of single drops in various well-defined flow fields. Most studies of this type have been limited to viscous Newtonian systems. G. I. Taylor (1934), the first pioneer, developed a four-roll mill and parallel band devices to study the deformation and breakup of a single Newtonian drop in hyperbolic extensional flow and uniform shearing flow, respectively. He discovered that at low deformation rates in both flow fields the drop deformed into a spheroid. At low stress in a steady uniform shearing flow the droplet deformation and possible breakup were controlled by two dimensionless groups, the viscosity ratio:

$$\eta_r = \frac{\eta_d}{\eta_m} \tag{1.1}$$

and the capillary number:

$$Ca \equiv \frac{\gamma \eta_m d}{\Gamma} \tag{1.2}$$

where η_m is the matrix phase viscosity, η_d is the dispersed phase viscosity, γ is shear rate, d is the initial diameter of the drop, and Γ is the interfacial tension. The capillary number is defined as the ratio between the viscous shear force and the interfacial force. He predicted that droplet breakup should occur when the interfacial force that resists droplet deformation can not balance the shear force that deforms the drop. The maximum droplet size

prediction obtained by balancing between two forces can be expressed as:

$$d = \frac{4\Gamma(\eta_r + 1)}{\gamma \eta_m \left(\frac{19}{4}\eta_r + 4\right)}$$ (1.3)

This relation is valid for small deformations in Newtonian fluids. Wu (1987) introduced a correlation relating the capillary number to the viscosity ratio as:

$$d = \frac{4\Gamma \eta_r^{\pm 0.84}}{\gamma \eta_m}$$ (1.4)

where the plus (+) sign in the exponent applies for $\eta_r > 1$ and the minus (-) sign in the exponent applies for $\eta_r < 1$. There is another mechanism proposed by Tomokita (1935) for dispersing a liquid in another matrix via the capillary instability of long cylindrical column. He found that the breakup process can be described by another two dimensionless parameter, critical capillary number (Ca_c) and dimensionless breakup time (t_b^*) by

$$t_b^* = \frac{t_b \gamma_c}{Ca_c}$$ (1.5)

where Ca_c is the value of Ca at which breakup occurs, t_b is the elapsed time between the startup of deformation and the first breakup of the drop, and γ_c is the critical shear rate. In general, the critical capillary number for droplet breakup is around 0.1-0.5, except for low-viscosity drops or high-viscosity ones with flow type close to that of a simple shear (Bentley and Leal, 1986).

1.1.2 Coalescence for Newtonian Fluids and Polymer Blends

During mixing, the dispersed phase progressively breaks down until a minimum drop diameter is reached, and the coalescence process can take place. Coalescence occurs when two droplets moving in an externally applied flow field collide and the duration of the collision is sufficient to allow completion of the coalescence process. Flow induced

coalescence of two Newtonian liquid drops can be modeled as a three-step mechanism (Allan and Mason, 1961) as shown in Figure 1.1. First, two drops come close to each other and the pair rotates in the shear field. The film of the matrix phase between the two drops drains, the film thickness decreases to a critical value, and rupture of the interface occurs, resulting in coalescence.
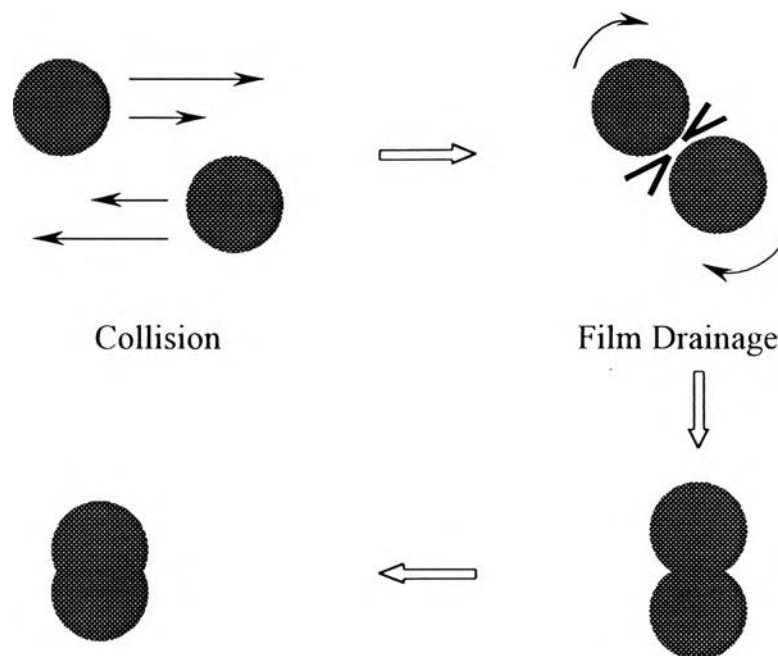
Collision　　　　　　　　　　　　Film Drainage

Figure 1.1 Idealized depiction of shear-induced coalescence of dispersed Newtonian droplets.

In simple shear flow, the collision frequency (C) of a drop as a function of shear rate and the volume fraction were estimated by Smoluchowski (1917) and Chesters (1991):

$$C = \frac{8}{\pi}\gamma\phi_d \qquad (1.6)$$

where ϕ_d is volume fraction of dispersed phase. Therefore increasing dispersed concentration and shear rates, which intuitively one would expect to decrease coalescence, actually increased the amount of coalescence (Roland and Bohm, 1984; Sundararaj and Macosko, 1995). Three different models of

matrix film drainage between the colliding drops were governed by the interfacial mobility: immobile, partially mobile, or fully mobile interfaces. The required drainage times was given by Janssen (1993) for immobile interfaces as

$$t_{drain} = \frac{3\eta_m R^2 F}{16\pi\Gamma^2}\left(\frac{1}{h_{crit}^2} - \frac{1}{h_0^2}\right)$$ (1.7)

for partially mobile interfaces as

$$t_{drain} = \frac{\pi\eta_d F^{1/2}}{2(2\pi\Gamma/R)^{3/2}}\left(\frac{1}{h_{crit}} - \frac{1}{h_0}\right)$$ (1.8)

and for fully mobile interfaces as

$$t_{drain} = \frac{3\eta_m R}{2\Gamma}\left(\frac{1}{h_{crit}^2} - \frac{1}{h_0^2}\right)$$ (1.9)

where h_0 is the initial film thickness between two colliding drops, h_{crit} is the critical film thicness before drop coalescence, R is drop radius, and F is the Stokes drag force acting on the drops ($\sim 6\pi\eta_m \gamma R^2$). The high polymer matrix viscosity should give rise to a relatively immobile interface that should result in long drainage time (van Gisbergen, 1991). However, Elmendorp and van der Vegt (1986) found experimentally that polymers had a high coalescence probability during mixing and concluded that polymers had fully mobile interfaces. Coalescence after mixing is an important area since manufactured polymer products are often annealed and coalescence may occur during annealing, resulting from the influence of temperature on droplet motion (Yang and Han, 1996).

Most coalescence studied in polymer blends has not used mechanical mixing. It has rather been studied in solvent-cast blends or melt blends under quiescent conditions (Park and Roe, 1991; Thomas and Prud'homme,1992). Considering the properties of polymers, coalescence in polymer blends is much more significant than expected and it is clear that coalescence in polymer system is not well understood.