

CHAPTER I INTRODUCTION



Inspiration of Work

The dispersal of one fluid in another immiscible fluid phase is important in industrial processes, such as emulsion formulation, polymer blending, and also to create interface for heat transfer, mass transfer, and chemical reactions. The size and size distribution of droplets in the matrix phase are crucial for controlling the reactivity of these processes and/or the properties of the final products. For polymer blends, the mechanical or physical properties of immiscible polymer blends strongly depend on the morphology of the blends. For example, the impact strength of a polymer blend is significantly improved when the size of rubbery dispersed-phase inclusions is smaller than a critical value (Wu, 1985). The final morphology of polymer blends mainly results from the deformation, relaxation, breakup, and coalescence of the dispersed phase induced by the flow field inside the processing equipment used to shape the polymer product. In addition, these behaviors of droplet phase can be affected by processing conditions such as shear rate and rheological properties of components such as viscosity of the drop phase, viscosity of the matrix phase, the viscosity ratio of the blend, the interfacial tension, etc, and for common high molecular weight polymers, elasticity is also important. Thus, an improved understanding of the effect of these processes on blend morphology would obviously be valuable for better controlling the final properties of polymer blends.

The investigation of deformation and breakup of an isolated Newtonian droplet in an immiscible Newtonian matrix was pioneered by Taylor (1932, 1934). He observed that droplet deformation and breakup of isolated droplets in a Newtonian blend under quasi-steady conditions (i.e., gradually increasing deformation rate) are controlled by two dimensionless parameters, namely the viscosity ratio (η_r), of the dispersed (η_d) to the matrix phase (η_m), and the capillary number (Ca), which is the ratio of matrix viscous stress to interfacial stress:

$$Ca \equiv \dot{\gamma} \eta_m r_0 / \Gamma \quad (1)$$

where $\dot{\gamma}$, r_0 , and Γ are shear rate, undeformed droplet radius, and interfacial tension between matrix and droplet phase, respectively.

For viscosity ratios near unity, the steady-state three-dimensional shape of an isolated deformed Newtonian droplet sheared in a Newtonian matrix can be represented by an ellipsoid having three different principal axes, the longest of which orients at an angle θ with respect to the flow direction, (Guido and Villone, 1998). When the matrix viscous stress ($\eta_m \dot{\gamma}$, where $\dot{\gamma}$ is applied shear rate) overcomes the interfacial stress (Γ/r_0 , where Γ and r_0 are the interfacial tension and the undeformed droplet radius, respectively), the droplet will break. This occurs when the ratio of the viscous to the interfacial stress which is the capillary number $Ca \equiv \eta_m \dot{\gamma} r_0 / \Gamma$ exceeds a critical value, Ca_{crit} . Ca_{crit} is a minimum when η_r is around unity (Grace, 1982; De Bruijn, 1989). The flow type (shear vs. extensional flow) was also found to effect the correlation between Ca_{crit} and η_r (Rallison and Acrivos, 1978; Bentley and Leal, 1986).

However, molten polymers are viscoelastic under normal processing conditions, and droplet sizes are expected to be different from those in Newtonian systems due to the influence of elasticity and shear thinning in the matrix and the dispersed phases. It has long been noticed, for example, that in blends of viscoelastic polymer melts, the steady-state average droplet size that results from breakup and coalescence of droplets under shear corresponds to a much higher capillary number than is seen in blends of Newtonian liquids at comparable viscosity ratios. Wu (1987) studied the steady-state average droplet size in extruded viscoelastic polymer blends containing 15% of dispersed phase and compared the results with those of Newtonian blends. Like the Newtonian blend, the minimum in Ca for these polymer blends was found at a viscosity ratio of around unity; however the value of Ca at $\eta_r = 1$ for Wu's polymer blends was around ten times greater than that of a Newtonian system.

Many experimental results on immiscible viscoelastic blends when either one phase or the other is viscoelastic have been reported in the literature (Flumerfelt, 1972; Elmendrop and Maalcke, 1985; Milliken and Leal, 1991; Tretheway and Leal, 2001). An unusual phenomenon, transient and steady-state droplet widening along the vorticity axis (Levitt *et al.*, 1996; Hobbie and Migler, 1999; Migler, 2000; Mighri and Huneault, 2001), was observed for a viscoelastic droplet sheared in a viscoelastic matrix.

Although most experimental data in the literature suggest that droplet-phase elasticity leads to less deformed, more stable, droplets relative to comparable Newtonian droplets, studies of droplet behavior when droplet elasticity is the sole manipulated valuable are rare, because in most previous work both droplet elasticity and viscosity ratio were varied simultaneously. Since the results for Newtonian blends show that droplet deformation and breakup is strongly influenced by viscosity ratio, it is quite crucial to control this parameter carefully in any attempt to study the effects of other factors, such as elasticity, on droplet deformation and breakup.

This research work is, therefore, devoted to the investigation of the influence of dispersed phase elasticity on droplet behavior and morphology of immiscible polymer blends in a shear flow using blend systems at fixed viscosity ratio of unity. The data and correlations obtained in this study will provide us with a better understanding between the blend morphology and corresponding viscoelastic properties, and therefore a guidance toward improving commercial product quality.

Scope of Work

The immiscible blends used in this work can be categorized in two main systems, i.e., blends of “Boger” fluids, and high-molecular-weight melt blends. The blends of “Boger” fluids are chosen as the representative blend systems for weak and moderate elastic dispersed phase. To take a further step towards understanding the behavior of commercial blends, the blends containing highly elastic and shear-thinning polymer melts for both the droplet phase and the matrix phase are also investigated. Although mostly commercial blends are concentrated and consisting of

drops of various sizes, it is also important to understand the behavior of a single droplet first as fundamental knowledge. Therefore, the study is done on both isolated droplets and concentrated blends containing 10% or 20% of dispersed phase.

In chapter II and III of this dissertation, the effect of weak and moderate droplet elasticity (Weissenberg number of dispersed phase fluids of blends up to around 3) on droplet behavior and morphology of immiscible blends is studied for blends of “Boger” fluids. Specifically, the steady-state deformed shape, the capillary number for droplet breakup (Ca_{crit}), for an isolated droplet in a matrix with the same viscosity as the droplet fluid, but different dispersed-phase elasticities were measured. The effect of weak and moderate droplet elasticity on the steady-state morphology of concentrated blends containing 10% or 20% of dispersed phase is also reported in these chapters. In addition, the quantitative correlation between droplet elasticity in terms of dispersed phase Weissenberg number (Wi_d) and critical capillary number for droplet breakup (Ca_{crit}) of isolated droplets is developed.

To take a further step towards understanding the behavior of commercial blends, the blends containing highly elastic and shear-thinning polymer melts for both the droplet phase and the matrix phase are studied and presented in chapter IV, and in Cherdhirankorn *et al.* (2003) (see also Cherdhirankorn (2003)). The transient droplet deformation, steady-state deformation, and also breakup of isolated elastic droplets sheared in elastic matrix are reported in Cherdhirankorn *et al.* (2003). Finally, the influence of elasticity contrast, as measured by the ratio of the first normal stress differences, $N_{1r} \equiv N_{1d}(\gamma)/N_{1m}(\gamma)$, between the dispersed and the matrix phases, on steady-state droplet size in a simple shear flow for concentrated polymer blends containing 20% of dispersed phase fluids was investigated and is reported in chapter IV.