CHAPTER I

INTRODUCTION

For binary immiscible blends, it is widely known that the size and distribution of dispersed particles are the result of the competitive process between drop breakup and coalescence and difference polymer blend properties. The interfacial tension, shear rate of mixing, and viscosity ratio are factors controlling the degree of dispersion. For ternary immiscible blend system where two minor phases are dispersed in a continuous matrix, not only the particle sizes but also the morphology of the two disperse phases in the matrix is an important factor affecting the blend performance. In some ternary blend systems, the phase morphologies of blends having co-existing phases show that one of the minor components forms an encapsulated layer around the domain of another minor component. This is called the capsule formation morphology. In other systems, the two minor components stack on each other in the matrix phase so called the stack formation morphology. A third morphology is that the two minor components form independent where is called the isolated formation morphology as shown schematically in Figure 1.1. It has been known that morphological development of non-reactive ternary immiscible blends are mostly controlled by the balance of interfacial tension among the components (Horiuchi et al., 1997). The morphology can be observed by transmission electron microscopy (TEM) and scanning electron microscopy (SEM).
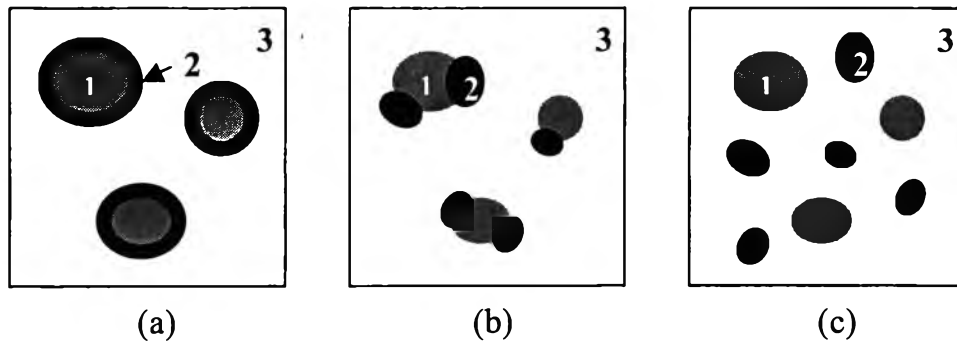
(a)   (b)   (c)

Figure 1.1 Schematic description of phase formation to appear in ternary immiscible polymer blends composed of polymer 1, 2 and 3: (a) "capsule formation" of 1 encapsulated by 2; (b) "stack formation" of 1 and 2 stuck together; (c) "isolated formation" of 1 and 2 dispersed separately.

The interfacial tension between components can be applied to predict the morphology in ternary blend systems in term of a spreading coefficient. From Harkin's equation for a binary matrix:

$$\lambda_{ij} = \gamma_j - \gamma_i - \gamma_{ij} \tag{1.1}$$

where λ_{ij} is the spreading coefficient of polymer i on polymer j. γ_i, γ_i, and γ_{ij} are surface and interfacial tensions of polymer i and polymer j. When the spreading coefficient of polymer i on polymer j is high, polymer i will spread on polymer j as illustrate in Figure 1.2a for a ternary blend with disperse phase of polymer1 and 2 and continuous phase of polymer3.

$$\lambda_{21} = \gamma_{13} - \gamma_{23} - \gamma_{12} \tag{1.2}$$

where λ_{21} is the spreading coefficient of polymer 2 on polymer 1. γ_{ij} are the interfacial tensions between components. The spreading coefficient is measure of the ability of one disperse phase component to displace the matrix from the surface of the second component as shown in Figure 1.2b (Hobbs *et al.*, 1988).
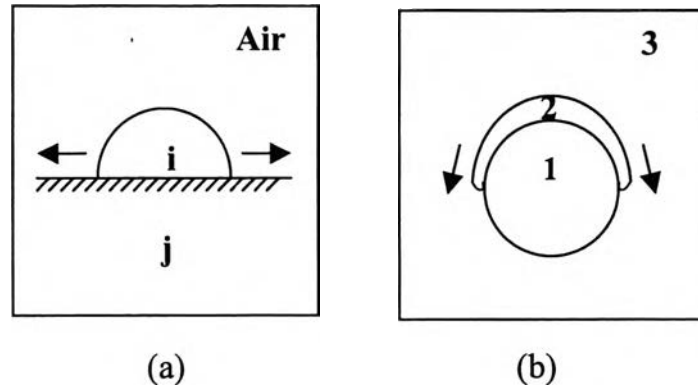
(a)   (b)

Figure 1.2 Schematic diagrams showing spreading behavior of: (a) liquid on solid substrate and (b) one polymer phase on another within a third component.

For polymer blend systems, the Gibbs free energy of mixing (ΔG_m) is given by the following equation:

$$\Delta G_m = \Delta H - T\Delta S_m + S\gamma \qquad (1.3)$$

where ΔH_m is the enthalpy of mixing, ΔS_m is the entropy of mixing, T is the temperature, S is the surface area, and γ is the interfacial tension. When ΔS_m is very small (high polymer), the equation becomes

$$\Delta G_m = \Delta H + S\gamma \qquad (1.4)$$

For an incompatible blends, ΔH_m is also very small, hence we may unite,

$$\Delta G_m \approx S\gamma \qquad (1.5)$$

so the lower the interfacial tension, the lower free energy of mixing (Paul, 1976, ch. 12).

The interfacial tension can be also related to the dispersed phase diameter using the Taylor's equation for droplet break-up:

$$W_e = \frac{\eta_m d_n \gamma}{2\gamma_{12}} \qquad (1.6)$$

where W_e is the critical number, η_m is the viscosity of the matrix, d_n is number average diameter of dispersed phase, $\gamma^{\bullet}$ is the shear rate, and γ_{12} is the interfacial tension. When a compatibilizer is added to a blend, the interfacial

tension decreases. As a result, the dispersed phase size decreases. At a particular compatibilizer loading, there is a balance of interfacial tension and particle deformation. However, when the compatibilizer level reaches the point that there is no further reduction in this particle size is observed, it means that the compatibilizer occupies the maximum interfacial area. Therefore, there is a maximum quantity of the compatibilizer required to saturate the blend interface and, beyond this level, further addition of compatibilizer will not reduce the particle size and may lead to undesirable micelle formation which very often reduces the total performance of the blend system (Asaletha and Thomas, 1995). The above discussions focuses only on droplet breakup. At typical volume fraction of the disperse phase, one must also made the influence of droplet coalescence. It is well established that the higher of droplet coalescence is slowly inhibited by addition of compatibilizer at levels for below that necessary to cause micelle formation. More recently, however, we have shown that there is correlation also between interfacial tension lowering by compatibilizer due to the inhibition of coalescence. Compatibilizer will absorb more strength to the interface are more effective at reducing coalescence.

For the blend properties, the interfacial adhesion between components can be increased by using a compatibilizer that enables higher interfacial stress transfer between dispersed and matrix phase. The dispersed phase size also affects the properties. The critical particle size of the dispersed phase depend on polymer type. In ternary blends having the core-shell morphology, some synergism of mechanical properties can be observed (Luzinov et. al., 1999).

In this work, the morphology-interface-property relationships of Polyamide12 (Nylon12)/Natural rubber (NR)/Compatibilizer were investigated. Styrene-ethylene-butylene-styrene block copolymer (SEBS), Styrene-ethylene-butylene-styrene block copolymer grafted by maleic anhydride (SEBS-g-MA) and polystyrene (PS)/natural rubber reactive blends

were used as the compatibilizer. Dicumyl peroxide was used as a free radical initiator for cross-linking in polystyrene/natural rubber (PS/NR) blends. For SEBS-g-MA, maleic anhydride (MA) readily reacted with the amine groups in polyamide. The effect of copolymer type and amount were studied on the blend morphologies and properties. The interfaces in Nylon12/NR/ compatibilizer blends were also studied in order to obtain the relationship to the blend properties.