



CHAPTER I INTRODUCTION

Blending of polymer is a popular method of improving their end-use properties. However, most polymers are thermodynamically incompatible and phase separated on blending.

For binary immiscible blends, it is widely known that the size and distribution of dispersed particles are the results 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 dispersed phases in the matrix is an important factor affecting the blend performance. 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).

Compatibilization of polymer blends is carried out to reduce the scale of dispersion and to stabilize the morphology. This can be achieved by addition of a pre-made block copolymer to the system or by carrying out an in-situ reaction between the complementary groups of the blend components. Both techniques promote dispersive mixing which leads to reduce particle size.

For multiphase polymer blends, one of the major targets is to understand and to control the phase morphology of these multicomponent blends. In this respect, the interfacial tensions between the individual phases and their relative viscosities are two predominant factors. In binary blends, the size of the minor phase depends on the interfacial tension and the viscosity (or torque) ratio of the dispersed phase with respect to the matrix. The interplay of these factors although more complex in ternary blends remains essential for the control of the blend morphology, in which each component, is either separately dispersed, or forms a core-shell structure (one minor

component forming shell around small domains of the second one) or an intermediate phase organization. The tendency for one minor phase to encapsulate the second minor component in ternary blends can be predicted by equation.

$$\lambda_{31} = \gamma_{12} - \gamma_{32} - \gamma_{13}$$

Where γ_{12} , γ_{32} and γ_{13} are the interfacial tensions for each component pair, and λ_{31} is defined as the spreading coefficient for component 3 (shell) to encapsulate component 1 (core). The index 2 refers to the matrix, λ_{31} must be positive for component 1 to be encapsulated by component 3. If λ_{31} and λ_{13} are negative, phase 1 and 3 will tend to be dispersed separately in the matrix of 2. Furthermore, in the particular case where λ_{21} is also negative, a partial engulfing morphology could occur. These different cases are represented in Figure 1.1

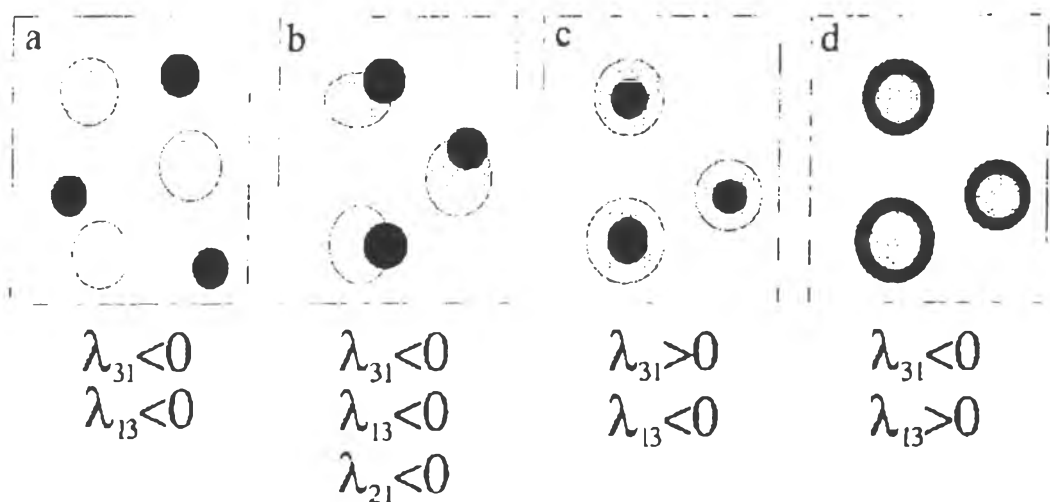


Figure 1.1 Schematic description of the different possible morphologies in a 1/2/3 ternary blend : (a) separate dispersion; (b) partial engulfing; (c) complete engulfing of phase 1 by phase 3; (d) complete engulfing of phase 3 by phase 1.

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

$$\Delta G_m = \Delta H_m - T\Delta S_m + S\gamma$$

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

$$\Delta G_m = \Delta H_m + S\gamma$$

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

$$\Delta G_m \approx + S\gamma$$

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:

$$W_e = (\eta_m d_n \dot{\gamma}) / 2\gamma_{12}$$

Where W_e is the critical number, η_m is the viscosity of the matrix, d_n is number average diameter of dispersed phase, $\dot{\gamma}$ is the shear rate, and γ_{12} is the interfacial tension. When a compatibilizer is added to a blend, the interfacial tension decrease. As a result, the dispersed phase size decrease. 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).

Another major target is to understand the rheological properties of these multicomponent blends. The knowledge of rheology can be used in processing. If correlations between rheological behavior and blend morphology could be established, rheology could be use as a sensitive tool to monitor and control morphological changes.

From previous research work, the morphology of blend depended on melt rheology and surface tension while the interface depended on surface tension. The

properties of blend depended on interfacial distance, total dispersion size and core size. So the morphology and interface played the major role in properties of blend.

In this work, Natural Rubber (NR) and Polyamide12 (Nylon12) are blended together with pre-made block copolymer (Polystyrene/Natural Rubber/Maleic Anhydride or NR/PS/MA). The possible reaction among maleic anhydride and polyamide that can take place during processing is represented in Figure 1.2

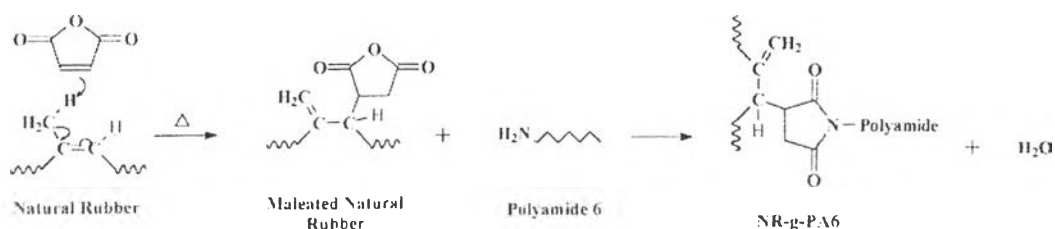


Figure 1.2 Possible reaction among maleic anhydride and Polyamide that can take place during processing (Carone Jr. *et al.*, 2000)

In this work, the morphology-rheology-interface-property relationships of Polyamide12 (Nylon12) (80%wt)/Natural Rubber (NR) (20%wt)/Compatibilizer were investigated. Styrene-ethylene-butylene-styrene block copolymer (SEBS), Styrene-ethylene-butylene-styrene block copolymer grafted by maleic anhydride (SEBS-g-MA), Polystyrene (PS)/Natural Rubber (NR), [PSNR], and Polystyrene (PS)/Natural Rubber (NR)/Maleic Anhydride (MA), [PSNRMA], reactive blend was used as the compatibilizer. Dicumyl peroxide was used as a free radical initiator to kick-off the reaction between polystyrene/natural rubber/maleic anhydride (PS/NR/MA) blends. The crosslink reaction may be involved which can be verified later by solvent extraction. For SEBS-g-MA, MA readily reacted with the amine group in polyamide. The effect of copolymer type and amount were studied on the blend morphologies, rheological properties and mechanical properties. The interface in Nylon12/NR/compatibilizer blends was also studied in order to obtain the relationship to the blend properties.