

## CHAPTER I

### INTRODUCTION

The name “*Nylons*” refers to the group of plastics known generically as aliphatic polyamides. It is derived from a diamine and a dicarboxylic acid. Due to a variety of diamines and dicarboxylic acids, there are several commercial nylon products such as nylon 6, 11, 12, 6/6, 6/10, 6/12, etc., providing an extremely broad range of available properties. For Nylon12 (polyamide12, PA12), it is a semicrystalline polymer produced by opening up a monomer containing both amine and acid groups known as a lauro lactam ring. Molecular chains of Nylon12 can be aligned under mechanical stretching for making fibers or films. This alignment is considered as crystallization, leading to an increase in material strength. Besides, with a lower concentration of amide groups than any other commercially available polyamide, Nylon12 has low water absorption, high degree of dimensional stability, excellent impact and non-impact strength, excellent chemical resistance to hydraulic fluids, oil, fuels, grease, salt water and solvents. Such properties make Nylon12 an excellent material for manufacturing many different products, including nylon tubes, aircraft interior parts, automotive exterior parts, wire insulation, flexible hosing, and nozzles. For application demanding high impact resistance such as bulletproof vest, the toughness of Nylon12 can be enhanced by incorporating an elastomer in it.

Natural rubber (NR) is one of elastomeric materials having the ability to return to their original shape after being stretched or deformed. NR is originally derived from the Pará rubber trees (*Hevea brasiliensis*); hence, it is a low-cost and more environmental friendly material. NR also has high resistance to tear and abrasion, strong bonding to metal parts, good low temperature properties, excellent dynamic properties with a low hysteresis loss, ease of processing, and especially good elastic properties. Owing to its high elasticity, NR is widely used as an impact modifier.

For polymer blends, they are mixtures of at least two polymers and/or copolymer which the minor component content exceeds 2 wt%. In general, not only the productions (polymerization, solution casting and melt mixing) but also the miscibility of polymer blends has played an important role in the improvement of

blend properties. Depending on the sign of the Gibbs free energy of mixing as shown in Equation (1.1), blends are either miscible or immiscible.

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} \quad (1.1)$$

where,  $\Delta G_{\text{mix}}$  is the free energy of mixing,  $\Delta H_{\text{mix}}$  is the enthalpy of mixing (heat of mixing),  $\Delta S_{\text{mix}}$  is the entropy of mixing, and  $T$  is the absolute temperature. The Gibbs free energy of mixing requires a negative value for the homogeneous miscible blend while the immiscible blend is associated with positive value of the free energy of mixing. For high molecular weight polymer blends, the gain in entropy is negligible. Hence, the free energy of mixing can only be negative if the heat of mixing is negative. This means that the mixing must be exothermic, which usually requires specific interactions between the blend components. These interactions may range from strongly ionic to weak and non-bonding, including hydrogen bonding, ion-dipole, dipole-dipole, and donor-acceptor interactions. For Nylon12/NR blend, there are no specific interactions between these two components. This is due to the polarity of amide groups in Nylon12 chains compared to the nonpolar structure of NR, resulting in the absence of adhesion and the incompatibility between two phases in the blend. As mentioned above, no favorable interactions between two phases mean that the enthalpy of mixing ( $\Delta H_{\text{mix}}$ ) is positive. Therefore, the  $\Delta G_{\text{mix}}$  is also greater than zero, indicating the immiscible polymer blend system. This leads to phase separation of Nylon12 and NR when they are blended.

To improve performance of the immiscible polymer blends, usually they need to be compatibilized by addition of a third component (a so-called "compatibilizer") or by inducing *in situ* chemical reaction between blend components (reactive blending). There are three aspects of compatibilization: (1) Reduction of the interfacial tension that facilitates fine dispersion, (2) Stabilization of morphology against its destructive modification during the subsequent high stress and strain processing, and (3) Enhancement of adhesion between phases in the solid state, facilitating the stress transfer, hence improving the mechanical properties of the blends (Ajji, 2002). The use of reactive compatibilizer containing maleic anhydride

(MA) such as SEBS-g-MA for Nylon6/PP blend was reported by Ohlsson *et al.* (1998); Wilkinson *et al.* (1999). The results revealed the reduction of interfacial tension and particle size of dispersed phase, relating to the increasing of impact strength. Carone *et al.* (2000) showed that the addition of MA to NR at room temperature prior to blending with Nylon6 led to an *in situ* graft copolymer formation. MA molecules reacted well with both Nylon6 matrix and NR domains during processing. This grafting reaction reduced the particle size of rubber dramatically. Ajji (2002) also stated that the presence of compatibilizer (a block or graft copolymer) not only reduced the interfacial tension, but it changed the molecular structure at the interface. Hence, the reactive compatibilization may also affect the processability, the blend performance and the flow behavior. The rheological properties of Nylon6/PP blend using SEBS-g-MA and MA-g-PP as compatibilizers were reported by Holsti-Miettinen *et al.* (1994); Marco *et al.* (1997) respectively. They demonstrated that the chemical reactions occurring between the components of the blends upon compatibilization increased the viscosity of the system. Moreover, a positive deviation of the viscosity from a log additive rule was found in the compatibilized blends due to the enhancement of compatibility in these immiscible blends.

Based on the above considerations, the main objective of this research work is to prepare a tough material from natural rubber-modified Nylon12 (Nylon12/NR) for application demanding high impact resistance and low moisture absorption. The incompatibility between Nylon12 and natural rubber due to poor polymer-rubber interactions or mismatched polarity remains for consideration to achieve good mechanical properties. Hence, a compatibilizer (third component) is needed to increase the interfacial adhesion between the blend components and to stabilize the blend morphology. The graft copolymers of polystyrene/natural rubber (PS/NR) and polystyrene/maleated natural rubber (PS/MNR) are used as non-reactive and reactive compatibilizers for Nylon12/NR blend, respectively. These compatibilizers prevent the coalescence of rubber particles and improve the morphological stability of the compatibilized blends by the introduction of steric hindrance. Besides, the presence of benzene ring in polystyrene provides the compatibilized blends with high heat resistance and modulus of elasticity (stiffness). The correlation of flow properties

and phase morphology affecting mechanical properties of the blends has been further discussed as a function of compatibilizer loading.

A general introduction about the dissertation is given in Chapter 1 together with its significance and the objectives of the study. Chapter 2 discusses in detail material properties, polymer blends and their compatibility. This is followed by a literature review focusing on rubber-toughened plastics and compatibilization of polymer/rubber blends in the presence of third component (compatibilizer). Chapter 3 describes the various materials used in the present study and their basic features. The experimental methods and analytical tools used for characterization of Nylon12/NR blend via non-reactive and reactive compatibilization are also presented. Chapter 4 discusses in detail the use of polystyrene/natural rubber (PS/NR) copolymer as a non-reactive compatibilizer for Nylon12/NR blend. In this chapter, the influence of PS/NR copolymer loading on phase morphology and mechanical properties of the blends is studied. The preparation of functional copolymer (polystyrene/maleated natural rubber, PS/MNR) is discussed in Chapter 5. The effects of mixing procedure and maleic anhydride loading on gel content, morphology, thermal and mechanical properties are investigated. PS/MNR copolymer is further used as a reactive compatibilizer for Nylon12/NR blend. The melt rheology (shear viscosity, power law index, activation energy, and extrudate swell) and extrudate swell of [Nylon12/NR]/[PS/MNR] using capillary rheometry are explained in Chapter 6. The correlation of viscosity ratio and phase morphology affecting mechanical properties of [Nylon12/NR]/[PS/MNR] blends with various compatibilizer contents is then stated in Chapter 7. The ballistic resistance of the materials is demonstrated in Chapter 8. Finally, Chapter 9 presents the conclusion and the recommendations of the toughness enhancement of Nylon12 with NR via non-reactive and reactive compatibilizations.