



## CHAPTER I INTRODUCTION

Linear Low Density Polyethylene (LLDPE), a commercial plastics, has been widely used for engineering applications. Unlike conventional LDPE it has linear structure with remarkable absence of long chain branching. It becomes increasingly important as a replacement for conventional low-density polyethylene (LDPE) due to its superior mechanical and thermal properties. However, different molecular structure between the two polymers makes LLDPE generally more difficult to process. An important parameter in processing, so called melt strength, is defined as the force at the break point and is an indicative of the relative extensional performance of polymer melts. LLDPE has relatively low melt strength. LLDPE thus has a limit of extensibility and its thickness is difficult to control. Increasing molecular weight ( $M_w$ ) or molecular weight distribution (MWD) was shown to solve this weak property. Entanglement was a key factor associated with high  $M_w$  and MWD to hold the molecules while being stretched. LLDPE possesses short chain branching which is not capable to resist extending force while blowing. In industry, low density polyethylene which contains long chain branching is blended with LLDPE to enhance blow and draw abilities, i.e. melt strength. Blending LLDPE with natural rubber (NR) can result in more entanglement in the material. This is due to branched molecules of NR. But due to difference of their chemical structure the polymer compatibility must be concerned. Over the years different techniques have been developed to alleviate this problem. However, the phenomenon of compatibility can be induced into an immiscible polymer-polymer pair by introducing a third component that will either interact chemically with both phases or have specific interaction or

physical interaction with each other. This work, in fact, deals with the reactive compatibilization technique by the addition of maleic anhydride (MA).

MA has been used as a compatibilizer in immiscible blends due to its high reactivity. Reactive processing involves in situ reaction of components to form functionalized polymer and/or block or graft copolymers at the interface between the phases. In situ compatibilization of polymer blends in general is a complex process, which is governed by a large number of variables. On the other hand, the chemical structure (chemical composition of polymer backbone and number and type of functional groups), the physical structure (molecular weight distribution and branching of the blend components) and the blend composition are of importance. In addition, the processing equipment (twin screw or internal mixer) and the processing conditions (screw speed, residence time, and temperature) also play an important role. Variations in these adjustable parameters affect the miscibility, the chemical kinetics and conversion, and the interfacial tension of the system. These phenomena, in their turn, affect the interfacial tension and thickness, and the morphology of the blend (the morphology being a balance between particle break up and coalescence). Chemistry and morphology will continuously and mutually interact, not only during blend production but also during all subsequent processing steps.

## **1.1 Polymer Blends**

Polymer blend is a mixture of at least two polymers or copolymers. Polymer blends can be divided into two major classes based on their thermodynamic phase behavior.

### 1.1.1 Miscible Blends

It is well known that due to thermodynamic limitations, only a few polymers form truly miscible blends, characterized by a single  $T_g$  and homogeneity at the molecule level. When two polymers, A and B form a homogeneous mixture, many properties of the blend are additive (Olabisi, 1979 and Paul, 1980). A thermodynamic condition for miscibility involves an appropriate balance of the enthalpy and entropy terms in the Gibbs free energy of mixing, i.e., the free energy of mixing  $\Delta G_{mix}$ , must be negative (Olabisi, 1979):

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

If  $\Delta G_{mix} < 0,$  (1.2)

Then  $\Delta H_{mix} - T\Delta S_{mix} < 0,$  (1.3)

Where  $\Delta H_{mix}$  is the enthalpy of mixing,  $\Delta S_{mix}$  is the entropy of mixing and  $T$  is temperature. Equation (1.3) implies that exothermic mixtures ( $\Delta H_{mix} < 0$ ) and athermal mixtures ( $\Delta H_{mix} = 0$ ) will mix spontaneously, whereas for endothermic mixtures ( $\Delta H_{mix} > 0$ ) miscibility will only occur at high temperatures (Folkes and Hope, 1993)

Thus for a miscible blend, the favorable entropic contribution must be large enough to yield a negative free energy of mixing. For the enthalpic part negative, zero or small positive  $\Delta H_{mix}$  values are required for miscibility.

### 1.1.2 Immiscible Blends

Most polymers are immiscible because of their small combinatorial entropy of mixing and their positive enthalpy of mixing when specific interactions between components are absent. An immiscible mixture of polymers shows multiple amorphous phases as determined, for example, by presentation of multiple glass transition temperatures. A thermodynamic

condition for immiscible blend is that the free energy  $\Delta G_{mix}$ , will be positive (Olabisi, 1979).

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} , \quad (1.4)$$

where  $\Delta G_{mix} > 0$ . (1.5)

If  $\Delta H_{mix}$  is positive, phase separation can occur.

Blends of immiscible polymer have complex properties composition that are rarely additive (Olabisi, 1979 and Paul, 1980). Most properties are dramatically influenced by the spatial arrangement of phases in the final blend. The morphology is strongly affected by processing history and a change in morphology can become undesirable during fabrication steps since it is a dynamic structure. Properties like stiffness or heat distortion temperature are dominated by the component forming the continuous phase and show a spinoidal shape versus composition owing to the phase inversion (Keitz, 1984 and Shaw, 1982).

The poor mechanical behavior of phase separation blends is usually the consequence of inadequate adhesion between phases that does not allow efficient transfer of stress across the interface. One method to improve the interfacial characteristic of immiscible blend is to add a small quality of a third component as a “Compatibilizer” (Paul and Newman, 1978).

## 1.2 Reactive Compatibilizer as a Compatibilizer for Immiscible Blends

A reactive compatibilizer, before reaction, is not a real compatibilizer because it tends to dissolve preferable in one phase during melt blending. After the reaction, graft or block copolymers formed *in situ* contain chains or segments that are identical to, or miscible with each of the blend components. For this reason, a reactive compatibilizer can be considered a non-specific compatibilizer because the structure and content of the eventually formed copolymers vary with processing conditions. Generally, blend components

containing chain-end reactive functional groups are more suitable for *in situ* compatibilization (Kuo and Chang, 1994). When the blend components contain highly reactive groups within the macromolecular chain, a cross-linked network may be the result of a reactive compatibilization. It is important to control the extent and the degree of graft reactions. An excessively reacted and grafted copolymer is less efficient as a compatibilizer than a lightly grafted copolymer. It is possible to control the concentration of reactive functional groups to obtain the desired size of the dispersed phase.

The grafting of MA onto a polyolefin is usually accompanied by either chain scission or molecular weight loss (Minouri, 1969 and Gaylord, 1983). Therefore, an inverse relation exists between the level of MA grafted and the final molecular weight of the material. To overcome this problem, a grafted polyolefin of low molecular weight is often blended with a virgin polyolefin (Callais and Kazmierczak 1995) of higher molecular weight. The degree of grafting (i.e. MA content) of a polyolefin can affect the homogeneity of such blends (Keskkula and Paul 1995).

The goal of this study was to investigate the effect of *in situ* compatibilization in blends of NR and LLDPE with MA and without MA on thermal, mechanical and melt flow properties of the blends in a systematic and more integrated approach.