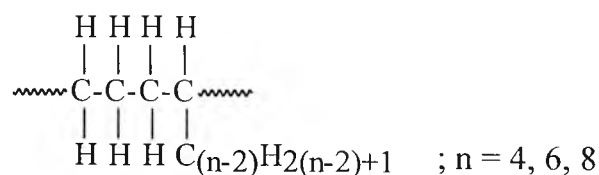# CHAPTER I

INTRODUCTION

Synthetic polymers are widely used, but a single polymer has limited properties for commercial applications. Synthesis of a new material with required properties is not always feasible and possible. To improve the range of polymer properties, without attempting synthesis of a special polymer, blending of two or more polymers is one solution. Although this is a simple approach to improve polymer properties, a common problem arises because of limited miscibility. Thus it is generally necessary to try some method of compatibilization such as addition of block or graft copolymers, addition of reactive polymer, or reactive blending (Folfes and Hope, 1993). The addition of block or graft copolymers is extensively studied but is an expensive method (Braun *et al.*, 1996). Reactive blending provides a suitable compatibilizer in a cheaper and more effective way. However, many different reactions may occur within processing equipment and lead to produce a variety of reaction products. The occurrence of these reaction products will depend on processing conditions and on the blend composition. Knowledge of the relationship between processing conditions and reaction products is fundamental to understanding how to control the ultimate polymer properties.

Linear low density polyethylene (LLDPE) is a commercial plastic that is mainly used for film applications and packaging. Its limited properties in elasticity and the difficulty to control its thickness cause some problems in processability. In this work, blending of LLDPE and natural rubber (NR) with maleic anhydride (MA) as a compatibilizer in the presence of DCP is studied. Maleic anhydride (MA) is widely used as a compatibilizer for reactive blending. Sometimes, only using maleic anhydride does not give the

best results. Many researchers have tried to use different types of peroxide to achieve the highest amount of grafted maleic anhydride onto polyolefins and other polymers (Gaylord *et al.*, 1987, Samay *et al.*, 1995). Many types of reaction products including graft copolymer and cross-linked gel may occur. Graft copolymer is the preferred product because it can locate at the blend interface and therefore act as a compatibiliser. The analytical methods that have been widely applied to determine the amount of graft copolymer are titration of the anhydride groups, and FTIR spectroscopy. There is abunant literature on the use of FTIR for quantification of grafted MA on polypropylene (Roover *et al.*, 1995, Sclavon *et al.*, 1996, 2000), polyethylene (Samay *et al.*, 1995 and Kelar *et al.*, 2000), and ethylene-propylene copolymer (Wu *et al.*, 1991). Moreover, including of various characterization techniques such as FTIR, TGA and tensile properties can reveal effect of reactive products on properties of the blends. Attemps made to correlate the graft copolymer or grafted MA polymer to mechanical properties of the blends. Content of graft copolymer and grafted MA products varied with processing condition to verify their influence on final morphology and mechanical properties.

1.1 Linear Low Density Polyethylene

LLDPE is a short chain branching polyethylene, which is synthesized from copolymerization of ethylene and other alpha olefins. The comonomers that commercially used are 1-butene, 1-hexene, and 1-octene. The molecular weight of LLDPE resins is in range 10,000 − 100,000. The melt index can range from 0.5 − 15 g/10 min. A general structure of LLDPE is shown in Figure 1.1

$$
\begin{array}{c}
\text{H H H H} \\
\text{| | | |} \\
\text{\scriptsize ww}\text{C-C-C-C}\text{\scriptsize ww} \\
\text{| | | |} \\
\text{H H H}\ C_{(n-2)}H_{2(n-2)+1} \quad ; n = 4, 6, 8
\end{array}
$$

Figure 1.1 Molecular structure of LLDPE.

LLDPE is a hard, tough thermoplastic material that extremely versatile. The other properties of LLDPE can be described as chemically inert, good resistance to solvents, acid, and alkalines, good dielectric characteristics and barrier properties. The outstanding strength properties make LLDPE resins applicable in many applications includeing films, coatings, mold articles and extrusions.

1.2 Natural Rubber (NR)

There are many types of rubber trees in the world. The only commercially interested rubber tree is the para rubber tree, *Hevea brasiliensis*, which shows several excellent properties in vulcanized and unvulcanized states.

Raw natural rubber mainly contain cis-1,4-polyisoprene which is about 93-95 %, 2-3% proteins, 2% acetone-soluble resins, water, small amount of sugars, and a little mineral matter. The chemical structure of cis-1,4-polyisoprene is shown in Figure 1.2.
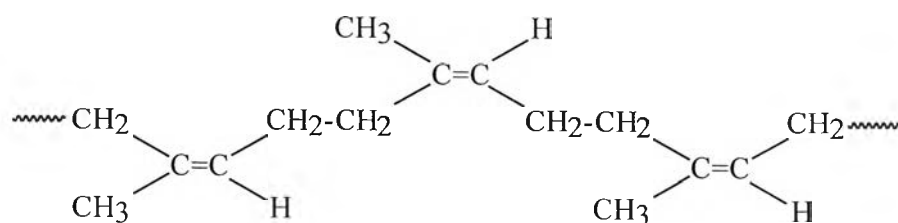
Figure 1.2 The chemical structure of cis-1,4-polyisoprene.

NR has molecular weight in the range of 10^4 to 10^7. The mastication can reduce the molecular weight of NR. Due to naturally occurring, properties of NR are depending on growing condition such as climate, seasons, and soil condition.

1.3 Polymer Blend

Polymer blend is a mixture of at least two polymers or copolymers. Blending of polymer will combine the excellent properties of more than one existing polymer. Moreover, the advantage of polymer blend is the wide range material properties obtained by changing the blend composition. Polymer blend can be prepared with processing machines such as twin-screw extruder, two-roll mill, and Banbury internal mixer. There is either homogeneous and heterogeneous polymer blending. For homogeneous blends, each blend component loses their unique properties and the blend properties are about the average of both blend components. For heterogeneous blends, the properties of each blend component still present. The poor properties of one component can be improved by the strength of the other blend component. There are several of morphologies of heterogeneous blends. The most frequently founded are i) a dispersion of one

polymer in the matrix of another polymer and ii) a co-continuous two-phase morphology. The type of morphology that will obtain depends on the characteristic of the blend component.

1.4 Compatibilization of Polymer Blends

The weak and brittle blends are obtained due to uncompatibilized blends. During melt mixing, the interfacial tension is lower than in the solid state. In the solid state, the presence of the dispersed phase in a matrix brings about stress concentration and weak interfaces. There are many methods for compatibilization. The most widely used are the adding of the third component, or by *in situ* chemical reaction, which leads to lower the interfacial tension. The lower interfacial tension brings about higher deformation and stretching of the dispersed phase so that the small size of particles is obtained and the blend properties is improved. Moreover, the presence of compatibilizer molecules at the interface will prevent the particles coalescence during processing.

The method of compatibilization can be broadly divided into 4 types:

1. Achievement of thermodynamic miscibility.
2. Addition of block and graft copolymers.
3. Addition of functional/reactive polymers.
4. *In situ* grafting/polymerization (reactive blending)

1.4.1 Thermodynamic Miscibility

The miscibility between polymers can be determined by Gibb's free energy of mixing:

$$\Delta G_m = \Delta H_m - T\Delta S_m \qquad (1.1)$$

where ΔG_m is the Gibb's free energy of mixing

ΔH_m is the enthalpy of mixing

ΔS_m is the enthalpy of mixing

T   is temperature.

The homogeneous miscible blend requires a negative free energy of mixing ($\Delta G_m < 0$) and then $\Delta H_m - T\Delta S_m < 0$. For polymer, the entropy of mixing is very low. Thus to achieve the negative free energy, the mixing must be exothermic. This requires the specific interactions between the blend components such as hydrogen bonding, ion-dipole, dipole-dipole, and donor-acceptor interactions. In fact, only the Van der Waals interaction will normally occurs in the reactions.

1.4.2 Addition of Block and Graft Copolymer

The addition of block and graft copolymer is a typical research approach to compatibilize polymer blends. For good compatibilizers, the emulsification of polymer blends is achieved as seen by the finer morphology and better properties. Normally, block or graft copolymers contain segments that are similar to the blend component. Block or graft copolymer are mostly located at the blend interfaces as shown in Figure 1.3.

GRAFT   BLOCK
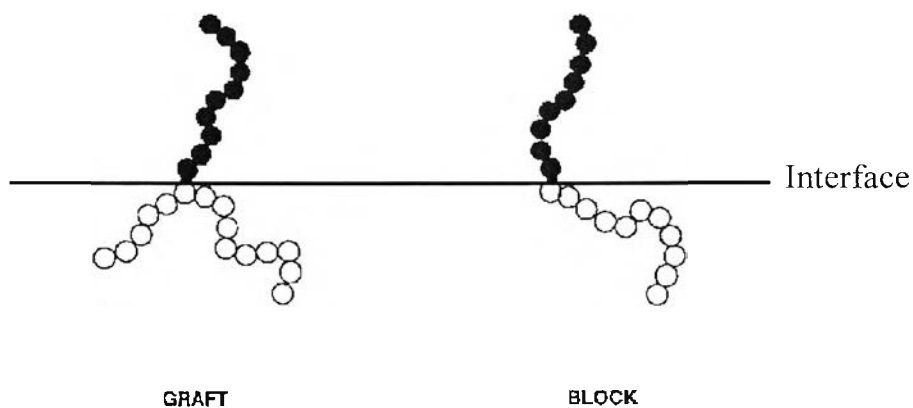
Figure 1.3 Block and graft copolymer that located at the interface.

1.4.3 Addition of Reactive Polymer

The reactive polymer is consisted of a polymer that miscible with one blend component by chemical modification to have some functional

groups capable to react with the second blend component. The reactive polymer will generate block or graft copolymer only at interface through the chemical reactions (Folfes and Hope, 1993). Moreover, this type of compatibilizer consumes a shorter processing time than the premade block or graft copolymers due to relatively higher diffusion rate of shorter chains moving to the interfaces.

1.4.4 Reactive Blending

Reactive blending allows chemical reaction occurring within processing equipment. In general blend components can be chosen for the modification by reactive compatibilizer. This method produces compatibilizer via *in situ* formation of copolymers or interactive polymers. The chemical that is most widely used for modification of polymer is maleic anhydride.

1.5 The Reaction of MA with Polymer.

Maleic anhydride has its dual functionality which are "ene" or radically active double bond size and the nucleophilically reactive anhydride as shown in Figure 1.4 (Burlett and Lindt, 1993).
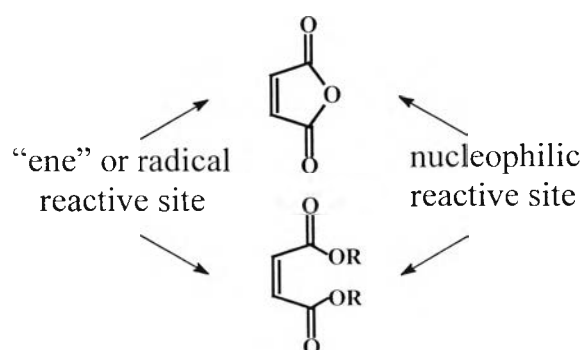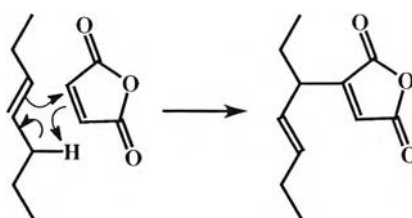

Figure 1.4 Maleic anhydride and its dual functionlity-"ene" or radical active site and nuccleophilic site.

The reaction of MA with polymers, maleation, can occurs in 2 ways:

1.5.1 Maleation via Diel-Alder Reaction

This Diel-Alder reaction occurs with unsaturated polymer molecule at high temperature. The mechanism of this type of reaction is shown in Figure 1.5.

Figure 1.5 Diels-Alder reaction of maleic anhydride with NR.

1.5.2 Maleation via Radical Species

The free radical can be generated from a radical generating species or mechanochemically generated radicals. The maleation can occur with both saturated and unsaturated polymer. This type of reaction requires lower temperature than the Diels-Alder type. However, this may cause problem with crosslinking and degradation in the elastomers. The mechanism of MA with NR via a free radical reaction is shown in Figure 1.6.
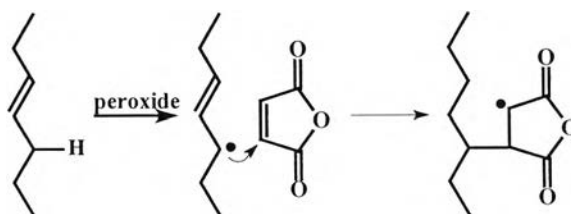
Figure 1.6 Maleation of maleic anhydride with NR in presence of free radical.

For polyethylene, a free radical initiator is needed. However, the use of high temperature for melting polymer can affect on the decomposition of the initiator. Thus it will be better if using the initiator that has long decomposition time. Under appropriate condition, the reaction yields a polymer containing append of succinic anhydride and MA. The mechanism of MA with polyethylene via a free radical reaction is shown in Figure 1.7.
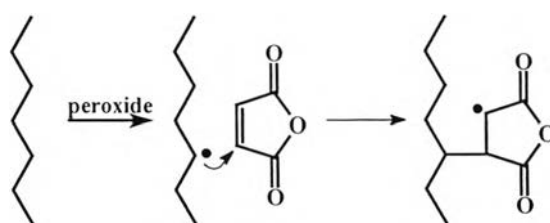
Figure 1.7 Maleation of maleic anhydride with LLDPE in presence of free radical.