CHAPTER II
LITERATURE SURVEY

History and Background

2.1 Polymer Blends

In 1995, Lee *et al.* studied reactive extrusion of polypropylene(PP)/natural rubber(NR) (90/10) blends which was conducted in the presence of a peroxide[1,3-bis(*t*-butylperoxy)benzene] and coagent (trimethylolpro-panetriacrylate, TMPTA). The increase and decrease of viscosity were interpreted in terms of crosslinking and chain scission of PP, which governed the rubber domain size and mechanical properties of the reactive blends.

Blends of natural rubber (NR) with linear low-density polyethylene (LLDPE) were prepared by melt blending in plasticorder mixer at various temperatures around the melting point of LLDPE and at various mixing rates. The optimum processing conditions were at temperature about 135°C and mixing speed of 55 rpm. The tensile properties, stress and strain, of the blend had improved significantly with the addition of liquid natural rubber into the blend (Ibrahim *et al.*, 1995).

Nikos *et al.* (1994) investigated effect or various PET/LLDPE blend ratios and ionomer contents. They found that the sodium ionomer of poly(ethylene-co-methacrylic acid) was an effective compatibilizer for melt-mixed and quenched PET/LLDPE blends.

2.2 Film Permeability

It has been considered so far that an increase in molecular orientation causes a decrease in gas permeability in polymers as a result of an increased packing efficiency of the polymer chains.

Kajitani *et al.*, (1997) investigated gas permeability in the polystyrene films uniaxially drawn under CO_2 plasticizing. They found that gas permeabilities in the

hot-drawn PS films were closed to those in the untreated film and decreased slightly with an increase in orientation. Gas permeabilities in the samples oriented by CO_2-plasticizeding drawing were larger than those in the hot-drawn samples over the whole range of f studied in this work, and increases with an increase in orientation. The enhancement of permeability in the films oriented by CO_2- plasticized drawing was interpreted from an increase in inter-chain distance.

Sharon *et al.* (2001) estimated the mass transfer coeffcient (h) of fumigant compounds across agricultural film. The h is a measure of the resistance to diffusion. It is a combination of film chemistry and independent of the concentration gradient across the film. This method used static sealed cells; fumigant vapor was spiked to one side of the film and the concentrations on bothsides of the film were monitored until equilibrium.

Ng *et al.* (2000) investigated the biaxial drawing of poly (ε-caprolactone)(PCL). PCL films were fabricated using solution casting and melt-pressing methods, and biaxially drawn to a draw ratio of 3x3. The solution-cast films have higher gas permeabilities than melt pressed films. Permeability was reduced in the melt-pressed films and oxygen was found to permeate three times faster than nitrogen. Biaxial drawing increased the gas permeability slightly but selectivity remained unchanged.

In 1966 Gontard and co-worker studied influent of relative humidity and film composition on oxygen and carbon dioxide permeabilities of edible films. For film permeability measurement, the oxygen and carbon dioxide permeabilities were measured at 25 ^{0}C in a controlled-temperature room using a standard isotactic method. Their specially designed permeability cell contained two circular (8 cm diameter x 0.5 cm deep) 25 mL chambers separated by the film sample, of which 50 cm^2 was exposed to both chambers and sealed with an O-ring. They found that carbon dioxide permeates through plastic polymer more rapidly than other atmospheric gases such as oxygen.

2.3 Molecular Oreintation

The theory related to infra-red dichroism is useful to determine molecular orientation. Dichroism depends on the fact that electromagnetic radiation can be absorbed by a molecule when the frequecy is equal to that of a normal mode of vibration of the molecule. In the case of a uniaxially drawn polymer, by taking measurements with polarized radiations having the electric vector either parallel or perpendicular to the draw direction, it is possible to characterize the degree of molecular orientation. The effect of anisotropy on a selected absorption band of the in frared spectrum of the sample is reflected by the dichroic ratio (Bokobza, 2001). The dichroic ratio can thus be defined in terms of the absorption index

$$D = A_{\parallel} / A_{\perp}$$

The absorption index A is closely related to the absorption coefficient α and K. Spectrum obtained from the Kramers-Kronig analysis resembles the absorbance spectrum obtained in transmission. For uniaxially drawn material, the orientation function (f) is retated to the dichroic ratio D by:

$$f = \frac{(D-1)(D_0+2)}{(D+2)(D_0-1)}$$

where D_0 is the dichroic ratio of a perfectly oriented sample. The latter is related to the angle α between the polymer chain axis and the transition moment of the particular vibrational mode under consideration by: (J. Guevremont et al., 1995)

$$D_0 = 2\cot^2\alpha$$

Birefringence is a method for measurements of orientation. Usually, birefringence is defined as the difference in the refractive index between two principle axes.

$$\Delta n_{12} = n_1 - n_2$$

The plane birefringence Δn_{12} is the refractive index difference between principle axes lying in the plane normal to the axis of microscopes. The monochromatic wave of light is divided into two parts, polarized along the 1 and 2 principle directions where they travel at different velocities v_1 and v_2

$$R = (2\pi h/\lambda)(1/v_1 - 1/v_2)$$

where R is retardation, λ is wavelength and h is thickness.

Birefringence is proportional to the stress exerted in the material.

$$C = \Delta n/\sigma$$

where C is stress-optical coefficient, σ is the true stress,

The relation between birefringence and the second-order moment of the orientation function is given by the expression:

$$[\Delta n] = [\Delta n]_0 <P_2(\cos\theta)>$$

where $[\Delta n]_0$ is the intrinsic birefringence characteristic of the polymer.$[\Delta n]_0$ maybe called the maximum birefringence because the perfect orientation corresponds to $<P_2(\cos\theta)> = 1$

Choudhury *et al.* (1989) studied natural rubber-polyethylene blends by differential scaning calorimetry (DSC), X-ray Scattering and dynamic mechanical. They found that the decrease in crystallinity with the addition of natural rubber is due to the addtion of amorphous component which migrates into the crystalline phase of pure PE.

Kate *et al.*, (2002) investigated the morphology of hexene linear low density polyethylene (LLDPE) blown film in the undrawn and drawn states. Wide-

angle x-ray scattering showed the orientation of the crystals with respect to the draw direction throughout the film. Initial extension of the film caused the crystallites to orientated with the draw direction.

Chuan *et al.*, (2001) studied the crystal orientation function of poly(trimethylene terephthalate) by wide-angle x-ray diffraction. A wide-angle X-ray diffraction method for measuring poly(trimethylene terepthalate) (PTT) crystal orientation function was described. It was based on Wilchinsky's treatment of uniaxial orientation.

2.4 Epoxidized Natural Rubber

The chemical modification of natural rubber (NR) has been studied for many years, both as a means of changing the nature of the polymer and as a route to useful applications such as bound antioxidants, novel crosslinking systems, comb grafting, and rubber-silica coupling agents. Epoxidation was initially intended for the latter uses, but it soon became apparent that when carried out cleanly, it could lead to interesting new forms of NR. The epoxidation of NR and other unsaturated polymers is not novel although many of the early materials contained the products of subsequent ring-opening reactions, resulting in complex mixtures that were neither useful nor reproducible. Recent work has shown that under carefully controlled conditions, these secondary ring-opening reactions can be avoided to give a clean modification of NR with any desired level of epoxidation (Baker *et al.*, 1984).

The chemistry of epoxidation of unsaturated compounds and subsequent ring-opening reactions has been extensively studied. Epoxidation is a stereo specific process, and its rate is governed by the substituents on the double bond. The ease and position of ring opening of epoxides is again controlled by neighboring groups (Gelling, 1984).

Baker *et al.* (1984) reported that higher levels of epoxidation will give better oil resistance, but such grades of ENR would become expensive and their ability to strain crystallize is reduced with consequently lower strength properties. As it stands with ENR-50, the new polymer shows equivalent oil resistance to the NBR, with much inproved tensile strength and fatigue properties. The second

substantial change in properties brought about the epoxidation is the reduction in gas permeability of NR. ENR-50 has been found to undergo strain crystallization like NR, but with oil resistance similar to a medium acrylonitrile NBR and gas permeability similar to butyl rubber.

Sukkaew *et a.l* (2000) investigated the optimum conditions to give the best impact strength of polymers blended in twin screw extruder. ENR/PVC of the composition 20/80 resulted in the best impact strength of 1218 J/m, whereas the best impact strength of NR/ENR/PVC system was 751 L/m for the 10/10/80 comsition. Both systems exhibited higher impact strength than NR/PVC. Rubber in both ENR/PVC and NR/ENR/PVC sytems that gave good impact strength was about the same amount of 20%. It was found that an equal amount of NR and ENR in the NR/ENR/PVC system provided better properties than the system with constant 10% ENR by weight added to NR/PVC system.

2.5 Linear Low Density Polyethylene (LLDPE)

Linear low density polyethylene is made by a low-pressure catalyst similar to the HDPE process, but with longer and more branches. LLDPE would typically have 16 to 35 branches per 1000 backbone carbons whereas HDPE would typically have 1 to 2 branches per 1000 backbone carbons. This branching in LLDPE is sufficient to prevent close-packing of the molecules. Therefore, LLDPE has low density like LDPE but a linear structure much like HDPE.

Major applications include blown and cast packaging films, injection molding goods, medical devices, automotive application, wire and cable coating, electrical cables, adhesives, and sealants. Other applications include blow molding goods, pipe and conduit, rotomolding, foams for sporting goods and houseware goods (Prasad, 1999).

The molecular interaction between LLDPE molecules are different from either LDPE or HDPE and yet are related to both. The effects of lack of crystallinity and low density are obviously found in both LLDPE and LDPE, while the linear shape of LLDPE molecules is similar to the shape of HDPE molecules. These similarities and differences result in LLDPE properties which are generally between

the properties of LDPE and HDPE. For instance, the strength of LLDPE is about 15% higher than LDPE. The stiffness of LLDPE can be as much as 25% greater than LDPE, and impact toughness is about 10% higher in LLDPE over LDPE (Strong, 1996).

The major contribution to shrinkage is the close packing of the molecular structure of the plastic as it crystallizes. Therefore, the shrinkage rate of a thermoplastic primarily depends on its percentage of amorphous to crystalline structure. Since the amorphous structure is not as compact as the crystalline structures, thermoplastics with high percentage of crystalline structure exhibit the highest shrinkage rate and are particularly prone to thermal shrinkage while amorphous materials tend to shrink less. On the other hand, the close packing into spherulites takes time and it occurs to the greatest extent when the material is cooled slowly. Hence, the extent of shrinkage is controlled by the rate of cooling. i.e., slow cooling causes large shrinkage whereas fast cooling causes lesser shrinkage (Pop-lliev, 2001).

Wang *et al.*, (2001) prepared maleic anhydride grafted polyethylene (maleated polyethylene)/clay nanocomposites by simple melt compounding. The exfoliation and intercalation behaviors depended on the hydrophilicity of polyethylene grafted with maleic anhydride and the chain length of organic modifier in the clay. When the number of methylene groups in alkyamine (organic modifier) was larger than 16, the exfoliated nanocomposite was obtained. When maleic anhydride grafting level was higher than about 0.1 wt%, exfoliated nanocomposite were formed for clay modified with dimethyl dihydrogenated tallow ammonium ion or octadecylammonium ion. The pure LLDPE showed only the intercalation, which did not depend on the initial spacing between clay layers.