CHAPTER II
LITERATURE SURVEY

History and Background

2.1 Polymer Blends

Mixing a polymeric material to a particular polymer is a simple method for combining the attractive features of each material into each other or for improving the deficient characteristics of the particular material. Recently, polymer blending has been employed to enable the reuse of recycled industrial waste and/or municipal plastic scraps. The production of new materials designed by blending implies lower cost and the shorter time scale. The mentioned technological, economical and ecological advantages resulting from polymer mixing processes led, over the last 10 years, to 10% annual increase in the production of polymer blends. It recently reaches about 20 % of the overall plastics production (Folke, 1993).

2.2 Polyethylene Film

Film is defined as flat unsupported sections of a plastic resin whose thickness is very thin and generally regarded as being 0.25 mm or less in thickness.

The largest volume of raw material for film is polyethylene. It is available in wide rang of types with different copolymers, molecular weight, and other factors. Blends of various types may also be used to optimize properties, processability and economics. Almost two-thirds of the volume of all polyethylene resins are used in film or sheet applications.

Low density polyethylene (LDPE), the original form of polyethylene, still has a large market share based on its high transparency, good tear resistance, impact resistance and moisture resistance. It has poor resistance to oils and grease, high temperature and is permeable to odors and gases. It is primarily used clear packaging of may items; such as bread, meat, poultry, seafood, frozen foods and garment bags. It is also used in industrial applications such as liners, stretched wraps, heavy-duty bags and shrink-wrap.

In the late 1980s, linear low-density polyethylene (LLDPE) became a significant resin in polyethylene film business. LLDPE obtained under low pressure reactor with many short branches seems to replace the conventional LDPE with long branches. LLDPE produces by coordination polymerization contains double bond at the chain end which is capable to react with some functional group; e. g. maleic anhydride (MA). It has a higher tensile strength, impact strength, elastic modulus, elongation at break, resistance to heat and stress cracking. The replacement goes on for film extrusion, blow molding, wire and cable coating.

The most obvious properties of LLDPE are high crystallinity, high melting temperature, narrow molecular weight distribution and narrow melting range. Polymerization plants for LLDPE are cheaper to build, easier to operate and maintain and have lower energy requirements. Thus, they are more attractive to operate than high-pressure plants. For these reasons manufacturing costs are reduced. LLDPE has been the most successful packaging material where clarity is not a major concern. It is often used as grocery sacks, stretched wraps, liners and mulch film. There is a growing market for its use in diapers for both infant and adult.

High density polyethylene (HDPE) also has a large market share. As molecular weight and density of polyethylene increases, tensile properties, chemical resistance and barrier properties of film production increase. Excellent abrasion resistance is also achieved. HDPE film has large market share of the grocery sack business. It is also used for cereal and snack food packaging where its resistance to moisture penetration is a prime concern. HDPE is manufactured by ethylene polymerization by either the Phillips process or the Ziegler-Natta process.

Polyethylene is expected to continue to be an attractive commodity polymer for many years because of its low cost, chemical resistance and mechanical properties. Especially with the ongoing development of metallocene catalyst, polyethylene can now be manufactured with a precise control of branch content and placement and thus allows its properties to be better.

2.3 Natural Rubber (NR)

The natural rubber is obtained in latex form produced by certain plants and trees. The commercial product is obtained exclusively from the tree _Hevea brasiliensis_. The hydrocarbon component of NR consists of over 99.9 % of linear cis-1, 4 polyisoprene. It is also known that only few percent of trans configuration, results in greatly different properties of cis polyisoprene. The average molecular weight of the polyisoprene in NR ranges from 200,000 to 400,000 with a relatively broad molecular weight distribution. This corresponds to about 3000 to 5000 isoprene units per polymer chain. As a result of its broad molecular weight distribution, NR has an excellent processing behavior.
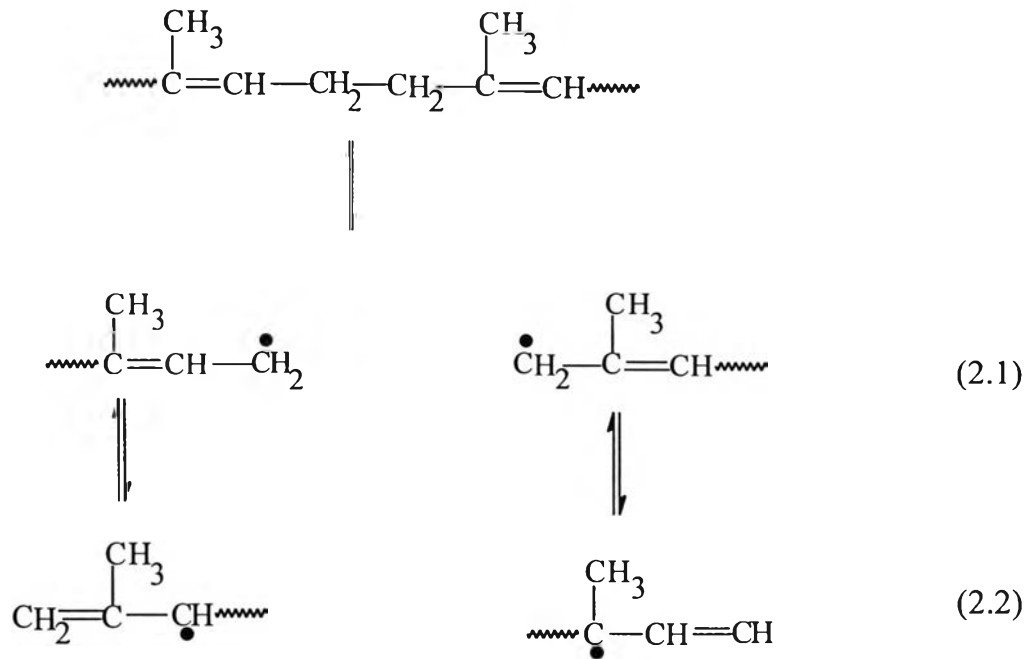
The chain structure of the polyisoprene depends on the biogenesis of NR. It was studied by gel permeation chromatography (GPC) that they could be a certain amount of long chain branching in high M_w molecules, depending on growing condition of _Hevea_ tree (Hofman, 1989).

There is one double bond for each isoprene unit. These double bonds and the α-methylene groups are reactive groups for vulcanization reaction with sulfur (Roger Hasen, 1996).

The double bonds can enter into additional reactions with oxygen or ozone to degrade the rubber. In high shear mixing process and under the presence of oxygen, a scission of polymer chain takes place. In the so-called mastication process, the molecular weight of a very tough crude rubber is broken down to facilitate its process ability.

The mastication of NR is required for making compounds, which are mixture of rubbers, fillers and other ingredients. Since NR is an unsaturated hydrocarbon, it can also react readily with oxidizing agent like peroxide or compatibilizing agent like maleic anhydride (MA).

It is known that during mastication, NR is undergone mechanical degradation. The molecule is pulled apart and broken by applied shear force leading to some production of free radicals as following.

$$\text{www}-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_2-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH\text{-www}$$

$$\downarrow$$

$$\text{www}-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-\overset{\displaystyle\bullet}{C}H_2 \qquad\qquad \overset{\displaystyle\bullet}{C}H_2-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH\text{-www} \qquad (2.1)$$

$$\updownarrow \qquad\qquad\qquad\qquad \updownarrow$$

$$CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}-\overset{\displaystyle\bullet}{C}H\text{-www} \qquad\qquad \text{www}-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\displaystyle\bullet}{C}}-CH=CH \qquad (2.2)$$

The outstanding properties of NR are good green strength and good building tack (tacky) that is particularly important for the manufacture of composite components. The favorable elastic properties manifest very low damping, low hysteresis and low heat build-up in dynamic deformations. This behavior combined with very short relaxation times, qualifies NR especially for products which function in dynamic applications; vibration and suspension elements and tires. The dynamic fatigue resistance of NR vulcanizates is also excellent (Werner Hofman, 1989).

2.4 Compatibilizer for Polymer Blends

The serious problem of polymer blends is immiscible in molecular level due to high interfacial tension and low interfacial adhesion between two phases. The presence of a third component is often required to overcome these problems.

Maleic anhydride is known to be a widely used for improving interfacial reactivity.

Maleic anhydride is prepared by high temperature air oxidation of benzene at high temperature, catalyzed by a vanadium compound. It is a preferable compatibilizer, since it has a low melting point (52.6^0C), more reactive and less water on esterification (Horiuchi, 1997).
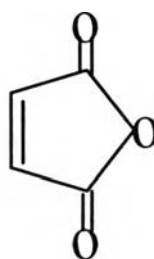
Maleic anhydride

2.5 Role of Compatibilizer in Polymer Blends

A compatibilizer for an immiscible polymer blend presents many similarities to low-molecular weight surfactants. It is well known that the dispersed phase size of an immiscible blend is reduced after the addition of surfactant (Noolandi, 1982). This is due to the ability of surfactant to reduce the interfacial tension between the phases. The quantity of surfactant that is required to emulsify a mixture depends on five variables;

- The affinity of the surfactant for the two phases,
- The degree and type of mixing,
- The size of dispersed phase,
- The rate of orientation of the surfactant at the interface and
- The stabilization of the interface against flocculation and subsequent coalescence.

For small molecules, the efficiency of a surfactant can be represented by means of an emulsification curve, where the dimension of the dispersed phase size is recorded against the concentration of the surfactant. The emulsification curve is characterized by an initial rapid decrease of dispersed phase size, followed by a plateau that represents the equilibrium value. For immiscible polymer blends, the emulsification curve has similar aspect as demonstrated by Matos (Matos *et al.*, 1995). At the beginning, the dispersed size dropped rapidly with the addition of a compatibilizer, as a consequence of the reduction of interfacial tension, and then a critical concentration value was reached. It was denoted as an optimum concentration for compatibilizing system, sometimes called critical micelle concentration (CMC), the same word used in emulsion.

Both phenolic-modified and maleic-modified polypropylene were used as compatibilizing agent for PP/NBR blends by George and co workers. They found that the addition of 1% MA-PP resulting in 35% reduction of NBR dispersed phase size, but further addition of compatibilizer did not allow extra reduction of particle size. On the other hand, addition of 10 % Ph-PP caused 77% reduction of NBR dispersed phase size. From this result it seemed that MA-PP compatibilizer was more effective than PP-MA compatibilizer.

2.6 Morphology of Polymer Blends

The structure of immiscible blends, defined as the interrelationship between blend morphology and flow conditions, have been extensively studied. The size and shape of the minor polymeric phase was affected by factors; such as the chemical structure of the components, component viscosity, dispersed-phase content and the type of stress experienced during flow. An increase in the minor-phase content led to greater coalescence of droplets and therefore, a large dispersed phase size was obtained (Santra, 1993). An extensional stress-flow field, such as one occurring during extruding in blown film and cast film or at the entrance of capillary rheometer, was more effective than shear-stress field to deform, elongate, and orient droplets of dispersed phase (Dumoulin, 1984). In a shear flow filed, dispersed droplets first elongated and then broken at a critical value of deformation rate.

2.7 Thermal Properties

Structural changes are usually associated with changes in heat absorption or emission and are measured using calorimeter. Calorimeter can also measure changes at constant heating or cooling rate. The difference in heat loss or gain between the sample and the reference cells are measured in differential scanning calorimeter.

A thermal scan of immiscible polymer blend typically exhibits the glass transition temperature (Tg) corresponding for each components as a result of the complete phase separation of polymers. On contrary, certain amount of compatibilizer, locating at the interface enough will result to exhibit a single Tg. The crystallization (Tc) and melt temperatures (Tm) of a crystallizable polymer,

which is present in an immiscible blend, may be altered by presence of second component (Theraya *et al.*, 1994).

2.8 Processing of Polyethylene

Although, plastic materials in principle can be processed in a variety of physical states (in solution, emulsion, melt). Melt processing is used almost exclusively with polyethylene.

Polyethylene is processed by a wide variety of technique most of which are blown film and chill roll cast film extrusion. There is sufficient space here to deal adequately with the principle and practice of these processes or even with the particular characteristics of polyethylene film fabricated by these processes.

2.8.1 Blown Film Extrusion

Blown film is the most important method for producing polyethylene film. It is estimated that some 90% of all PE films are produced on blown film lines. And it can be seen from the overall usage statistics for LDPE that blown film process is a dominant position. This process offers optimum efficiency and other advantages, like variability in the width and thickness dimensions and the outstanding mechanical properties obtainable by biaxial orientation (Rajen, 1994).
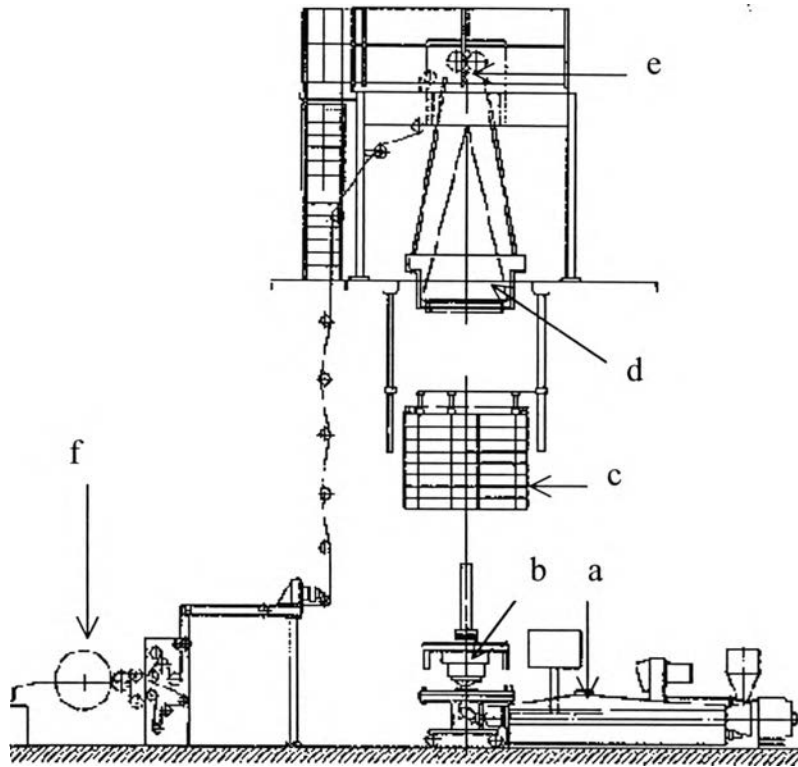
Figure 2.1 Schematic describing the film blowing process, a) extruder, b) rotating blow-head with internal air exchange system, c) calibration basket, d) bubble collapse, e) haul-off, f) contact winder with tension rolls and dancer rolls.

In the blown film process a polymer melt is extruded (usually in a vertically upward direction) and blown by air through the die head into the tube to obtain thin bubble. Then it is cooled, flattened out and wound up. There are three important parameters for blown film process, blow-up ratio, draw-ratio and freeze line distance.

a) Blow up-ratio (BUR)

Blow up-ratio mainly effects to molecular orientation in

transverse direction

$$BUR = \frac{R_b}{R_d} \qquad (2.3)$$

Where R_b is radius of film bubble and R_d is radius of annular die.

b) Draw-ratio (DR)

$$DR = \frac{V_s}{Q_v} \qquad (2.4)$$

Where V_s is speed of nip roll (m/s) and Q_v is extrusion rate (m/s)

c) Freeze line distance

Freeze line distance is defined as the distance between the die and frost line, which the extrudate becomes solidify and often be seen by appearing of haziness.

The effect of three parameters of tubular blown film found to be related to molecular orientation. Polyethylene molecules in the melt have a short relaxation time (measure of the time taken for molecules to coil after releasing of an applied stress). Thus, in the tubular film blowing process only molecules that are in melt state before the freeze line can be oriented and the orientation will be freezed after the freeze line. In addition, the molecular orientation during blown film operation is known to have a major effect on the mechanical and thermal properties of both amorphous and semi-crystalline polymers.

2.8.2 Chill Roll Cast Film Extrusion

Although a large proportion of polyethylene film is made by blown film process. Some film is produced by extruding flat film from slit die either into a water bath or on to chilled casting roll. The higher cooling rate that is possible in chill roll process is preferred. The products of high clarity will be obtained.

The production of film by chill roll casting is one of the classic extrusion processes. Films on flat film lines are mainly used in the packaging industry. Most thermoplastics can be processed on flat film lines. Quality of chill roll cast film can provide excellent optical and dimensional properties which are highly demanded permits high take-off speed influence the morphology of the film very favorably.
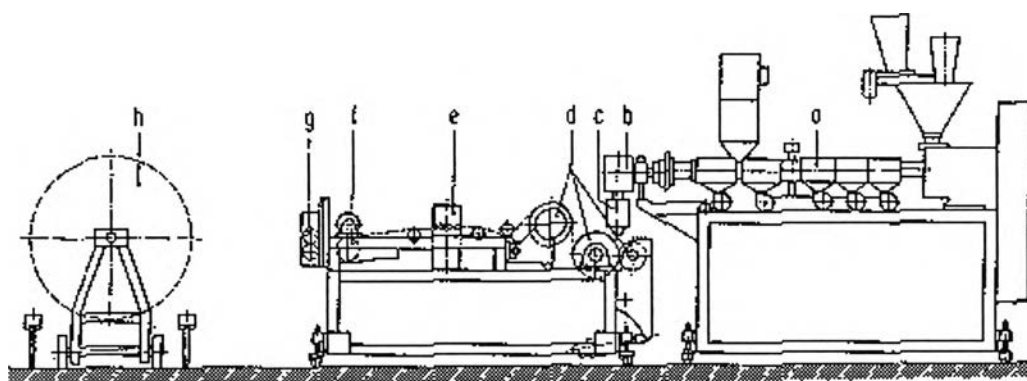

Figure 2.2 Schematic describing chill roll cast film line, a) extruder, b) adapter, c) die, d) cooling rolls, e) thickness scanner, f) take-off unit, g) edge trimming, h) winding station.

Chill roll cast film extrusion is based on the principle of shaping a melt that has been plasticated and homogenized in the extruder into a planar shape. Cooling and stabilizing this structure can be done by means of roll contact and then winding up after a trimming to obtain certain width. Depending on film thickness and application, a distinction is made particularly between fine film (10 to 50 μm), thicker cast film (100 to 400 μm) and thermoformable sheet (0.2 to 2.5 mm). The chill roll cast film has better transparency, gloss, crystallinity, rigidity, and thickness tolerance than blown films (mostly made of polyethylene) which offer advantages of higher tensile strength in both machine (MD) and traverse (TD) directions and simple alteration of film thickness by changing the blow up ratio.

2.9 Mechanical Properties

2.9.1 Tensile Properties

Tensile properties are determined by pulling a test specimen at a constant speed. The resulting stress (or load applied) is measured and recorded as a function of strain (or elongation). The stress and strain are defined mathematically by:

$$\text{Stress} = \frac{\text{Load supplied on specimen}}{\text{Cross-sectional area of specimen}} \tag{2.5}$$

$$\text{Strain} = \frac{\text{Increase in length of specimen}}{\text{Original length of specimen}} \tag{2.6}$$

Tensile strength is the maximum tensile stresses, which a material is capable to support. It is calculated from the maximum load carried during the tensile test divided by the original cross-sectional area of the specimen. The tensile test provides insight of the stress-strain behavior of a material under uniaxial tensile loading and distinguishes between brittle and ductile materials under a given set of test conditions. Tensile value is strongly influenced by temperature, strain rate, moisture level and fabrication conditions (Ward, 1990).

Flexible chain can be converted into highly oriented and extended conformation by drawing which causes substantial increase of tensile strength. The drawn process presents opportunities for significant advancement in mechanical properties for the common semicrystalline polymers. Many attempts have been made for obtaining the highest draw ratio (DR) and optimized tensile properties. For ultra-high molecular weight the maximum DR was achieved at 350. The drawn sample gave a tensile modulus of 210-230 GPa (Cole, 1994). Higashida *et al.* (1993) studied the mechanical properties of uniaxially and biaxially rolled PE and PP sheets. They found that the tensile strength of the rolled PP sheet reached almost 100 MPa which was three times larger than that of original resin. Chan *et al.* (1989) studied the properties of oriented PP laminates. They found that the strength and modulus of oriented PP in machine direction (MD) increased with an increase in draw ratio, however, the transverse direction (TD) properties remain relatively unchanged. This indicated that molecular orientation strongly influenced the strength of polymer.

2.9.2 Impact Strength

Impact resistance is a measure of the ability of material to withstand a sudden load without failure. The impact resistance of a structure is therefore a

complex function of geometry, mode of loading, cross head speed and material properties.

2.9.3 Tear Resistance

Tear resistance is a measure amount of the force required to propagate tearing across a film or sheet specimen. There are two types of specimens, a rectangular type and one with constant radius testing length. The Elmendorf-type tearing tester is the most widely used testing machine. In this type of testing machine, there is a pendulum swings through an arc, acting by gravity to tear the specimen from a precut slit. One side of specimen is initially gripped on one half by the pendulum and on the other half by stationary member. A pointer indicates the loss in energy of the pendulum. The scale indication is a function of the force required to tear the specimen. The average tearing force (i.e. the tear resistance) is then calculated using the following formula:

$$\text{Average tearing force, mN} = \frac{\text{average scale reading X pendulum constant}}{n} \quad (2.7)$$

Where n = number of plies of film used for each test run

Since there is not a direct linear relationship between tearing force and specimen thickness, data from this test method are reported as tearing force in milliNewton together with specimen thickness. Only sets of data from specimens of similar thickness are comparable.

2.10 Molecular Orientation

The orientation of macromolecules in fabricated polymer films plays an important role in determining their performance ranging from mechanical to optical characteristics.

If polymer molecules are oriented by stretching, the optical properties are anisotropy because the mobility of electrons within a polymer chain differs from those in tranverse direction to molecular chains. The molecular orientation is determined by measurement of total birefringence and infrared dichoism spectroscopy.

2.10.1 Infrared Dichroism

Infrared dichroism is a measurement of anisotropy of absorption of electromagnetic waves in a medium. The absorption of the electromagnetic wave occurs when the frequency of electromagnetic wave is equal to the natural frequency of electron. This natural vibration affects the transition moment vector. In the infrared wavelength ranges, the vibrations are associated with the molecular orientation.

The absorbance of light passing through a sample is defined as :

$$A = log\left(\frac{I_0}{I}\right) \tag{2.8}$$

Here, I_0 is the incident beam intensity and I the transmitted beam intensity. The value A relates to the extinction coefficient (e) for light of a specific wavelength , the density of the material (ρ), and the thickness of the sample (b) as follows:

$$A = eb\rho \qquad (2.9)$$

For infrared dichroism study, the incident beam is polarized successively in the sample machine direction and right angles to it. The ratio of the absorbances is the dichroic ratio at certain frequency (or wave number). Specific absorbances are determined by degree of interaction between the infrared light and the molecules composing the sample. The orientation of the crystalline and amorphous was defined by the "Hermans orientation function (f)" (Russo *et al.*, 1996).

$$f = \frac{3\cos^2\theta - 1}{2} \qquad (2.10)$$

in which θ represents the average angle between the chain axis in a particular phase and a reference axis that usually the drawn direction.

The average orientation function which account for overall orientation of the crystalline and amorphous phases, is defined as

$$f_{av} = \phi_c f_c + (1 - \phi_c) f_{am} \qquad (2.11)$$

in which ϕ_c is the volume fraction of crystalline phase given by

$$\phi_c = \frac{d - d_{am}}{d_c - d_{am}} \qquad (2.12)$$

where d is density of the sample, d_c and d_{am} are density of crystalline and amorphous phases. For LLDPE crystalline and amorphous densities were taken as 1.002 and 0.855 g/ml respectively (from sorption measurement as reported by Pezzutti, 1985).

Infrared dichroism is widely used to determine molecular orientation. The intensity of an infrared absorption band depends upon the angle between the transition moment and chain direction. Interaction or resonance produces a transition in the molecules. The orientation function f for the species undergoing transition is given by:

$$f = \frac{(D-1)(D_0+2)}{(D+2)(D_0-1)} \tag{2.13}$$

Where $D = \dfrac{A_\parallel}{A_\perp}$; $D_0 = 2\cot^2\psi$. The angle ψ is angle between the transition moment and chain direction. Value of angle ψ of HDPE is 87-90^0 as reported by Wedge wood. Cole *et al.* (1994) reported the angle of 0^0 for linear low-density polyethylene, Russo *et al.* (1996) determined the angle to be 18^0 for polypropylene.

2.10.2 Birefringence

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

$$\Delta n_{12} = n_1 - n_2 \tag{2.14}$$

Note; 1, 2 denote first and second principal axes.

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

$$R = \frac{2\pi h}{\lambda}\left(\frac{1}{v_2} - \frac{1}{v_1}\right)$$ (2.15)

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

Birefringence is proportional to the stress exerted in the material.

$$\Delta n = c\sigma$$ (2.16)

where c is a constant.

Recently Pezzutti *et al.* (1985) determined intrinsic birefringence for both crystalline and amorphous phases of LLDPE to be 0.057 and 0.043 respectively. Picot (1984) studied the molecular orientation of PE film when take-up speed was varied over the range of 50 to 120 m/min. He found that the crystalline orientation function f_c was slightly negative below take up speed of 50 m/min and rose to value of 0.4 at 120 m/min when cooling system was quench bath temperature of $37.8\ ^0C$. White *et al.* (1989) showed that for melt spinning of polyethylene and polypropylene fibers, stress during solidification induced crystallization to occur (i.e., very low stress permitted spherulite formation while

high stress yielded a lamella structure with lamellae perpendicular to draw direction). There were many parameters that affected to molecular orientation, i.e. not only process variable such as draw ratio and blow up ratio, but also processing conditions, internal stress, cooling rate, die temperature, melt temperature and die gap. Overall orientation stress strongly depends on draw ratio but higher operating temperature reduces the overall orientation (Chan *et al.*, 1985). Faster cooling rates and lower die temperatures cause the increase of surface orientation while the core orientation remains almost unchanged (Sakellarides, 1985).