CHAPTER II
LITERATURE REVIEW

2.1 Polyethylene (PE)

2.1.1 Basic Structure and Properties

Polyethylene (PE) is almost certainly popular plastics in the world. It has a very simple hydrocarbon structure. A molecule of PE is nothing more than a long chain of carbon atoms, with two hydrogen atoms attached to each carbon atom. Occasionally it is a little more complicated. Some of the carbons, instead of having hydrogen attached to the main chain, have long chains of PE attached to them. This is called branched whose variations modify the nature of the materials. Branches, in solid state, limit a crystallinity level of the PE. Chains that have few branches or short chain branch (SCB) tend to have a high degree of crystallinity and vice versa. The overall density of PE is mainly depended upon the crystallinity degree as regards to the good packing of crystallinity region (Peacock, 2000). Therefore, many type of PE exists with broad spectrum of physical properties employed in various applications. The principal classes of PE are as below:

2.1.1.1 High Density Polyethylene (HDPE)

The closest chemically structure to pure PE is high density polyethylene. It consists of linear chain with an extremely low level of packing hinder such as very small amount of short side chains. This microstructure can be produced via low-pressure polymerization process. As it's named, the density range is 0.94 – 0.97 g/cm^3, quite high crystallinity which performs the highest stiffness, best chemical corrosion resistance and lowest permeability among all types of PE. Moreover, the ultra-high molecular weight (UHMWPE), (MW $\geq$ 1,000,000), can be prepared with the same production process as well. UHMWPE is typically used to produce high strength fiber products. As its high crystallinity, the linear PE is much stronger than branched PE. The main market uses of HDPE are the household product container and liquid containment applications, pipes for water and natural gas transportations. Molded part is another linear PE application due to the high abrasion resistance.

2.1.1.2 Low Density Polyethylene (LDPE)

When a numerous of branches incorporated into the PE structures, they substantially obstruct the crystallization process, resulting in low density of the PE. It is produced via high-pressure polymerization which generates the random of LCB along the backbone. The range of its density is 0.90 – 0.94 g/cm^3. LCB provides desirable processing characteristics such as melt strength with relatively low viscosity during the manufacturing. Therefore, this type of PE is used primarily in flexible films, shrink-wrap films, low-load commercial and retain packaging applications.

2.1.1.3 Linear Low Density Polyethylene (LLDPE)

Linear low density polyethylene (LLDPE) is one of the most developing polyolefins produced under low pressure conditions. It can be defined as a rather linear PE with very short branch-like pendant groups resulting from the addition polymerization based on ethylene monomer in a presence of alkenes comonomer (α-olefins) such as butene, hexene, and octene. Such amount of comonomer ranges from 1 to 10% on a molar basis; therefore, it can be classified as either a homopolymer or copolymer. Few of LCB can be incorporated as well which, therefore, reduce the density of overall materials to approximately 0.90 – 0.94 g/cm^3. It is used as films applications with high tear strength, superior toughness and puncture resistance required. Tubes, pipes, or wire insulation are also made from LLDPE where the as high stiffness as HDPE is not required. Moreover, very low density polyethylene (VLDPE) which is another form of LLDPE whose short chain concentration is very high resulting in high level of disorder that crystallization is largely suppressed. The density of VLDPE ranges from 0.86 to 0.90 g/cm^3. VLDPE is used when softness, clarity, toughness and strain recovery are specific requirement for such applications including medical tubing and meat packaging.

2.1.1.4 Ethylene Vinyl Ester Copolymers

This is a type of the so-called copolymer obtained via high pressure reactor production, with a presence of polar comonomer such as that of acetate groups. Both SCB and LCB with acetate groups hinder the crystallization. The most common polymer in this class is ethylene-vinyl-acetate (EVA). Depending upon the level of their incorporation, it performs similar to those of LDPE when the degree of acetate group is low. At high acetate chain concentrations, it becomes like an elastomeric material with low modulus and greater chemical reactivity than HDPE, LDPE, and LLDPE. Since oxygen is incorporated, EVA exhibits higher density at a specified crystallinity degree than hydrocarbon PE. The major applications of this copolymer are packaging films or a component of adhesives.

Since almost applications of mentioned PE is the film market, it usually involves the production of thin film such as chill-roll casting, film blowing, wire coating, film coating or lamination. However, to produce a thin film with high production rate and also keep away from the processing difficulty that would result from very narrow die, a high level of melt stretching is required (Hernandez *et al.*, 2000). The property of molten polymer that can achieve a high ability to stretch during the film production is melt strength behavior. Generally, there are quite a few molecular characteristics of molten polymer that affects on a rise in melt strength such as broad molecular weight distribution (MWD), LCB or graft, and slight cross-link structures. Therefore, the molecular structure modification is one of the main processes to be applied.

Regardless to ethylene-vinyl ester copolymer, the chemical structure of PE is only hydrocarbon without any reactive species. HDPE, LDPE, and LLDPE become inert to other materials. To diminish the difficulty in blending or improve the interaction among the different phases, the addition of reactive sides onto the hydrocarbon backbone is practical. In addition to the bulk modification, the surface modification is widely practiced to improve its performance as a substrate for printing and painting.

There is a variety of method used to modify the surface of PE. The first one is chemical modification or chemical etching which is applied to irregularly shape molded part and also interior surfaces. Using strong acid as etchant, it is preferable to attack at the non-crystalline regions then oxidized and physically etched the PE surface. This is too slow process to be of great commercially practice. The second, flame treatment is primarily used to oxidize the surface of bottle or other thick-molded part prior to printing. However, the flame treatment is not much used on films due to the risk of overheating them. Another important one is corona discharge treatment. It is performed by passing the film between electrodes where the discharges are and the treatment occurs. This process can modify the PE surface within a second and widely used in the film industry nowadays.

2.1.2 Polyethylene for Breathable and Agricultural Film Applications

PE film markets is divided as, at least, food and non-food packaging films, stretch-wrap, and agricultural films. Specific functions are required depending on its intended applications (Briassoulis, 2004). Such as the breathable films requires the high rate of oxygen permeability through the films. This is also necessary for such a film in agricultural applications. (Feldman *et al.*, 2001)

According to the consumed quantity, planting is the main purpose of PE in agricultural film applications, such as greenhouses, small and high tunnels, mulching, and temporary coverings of structures for fruit trees (Dilaral *et al.*, 2000; Demetres, 2005). The function to enhance the growing and production of agriculture products is required. For baby plants, in general, oxygen is needed due to the high respiration rate during the growing stage; thus, the film with high oxygen permeability is necessary (Marais *et al.*; 2002). Therefore, being a barrier to liquids and insect attack while maintaining the oxygen permeability is the key function for planting plastic.

Nowadays, the high oxygen permeability, so-called breathable film can be produced via microporous creation inside the films. The common way to produce the microporous film is to use 43-52% w/w $CaCO_3$ in polyolefins compound, both PE and PP. (Mitchell *et al.*, 1991) This compound is then stretched during the solidification process of thin sheet extrusion. The microvoids can be initiated at the interface of $CaCO_3$ and the polymer matrix. However, the breathable film prepared by $CaCO_3$ routes is opaque which is not suitable for planting purpose. Moreover, the bio-degradation of agricultural film is in need of sufficiency and sustainability. Therefore, the film of LLDPE and natural product such as natural rubber (NR) was invented due to the meet of both physical and mechanical merit. Moreover, blending can be done easily resulting in rapid and simple way to develop new materials with low cost.

Multiphase blending is classified into thermodynamically miscible and immiscible blends depending upon the temperature, pressure, and material composition, etc. Regarding to the macroscopic scale, the compatibility of the blend mostly depends on the chemical composition among phases. If ones have the same microstructure or tend to have the interaction, the mixture is homogeneous and defined as a compatible blend. Since the blend morphology influences significantly on the blend product performance, another phase is usually added in order to improve the interaction in the system.

Among the natural products, NR is the one of agricultural products which has become a useful material nowadays. It has a tendency of photo-degradability due to the UV absorption of long chain natural macromolecules. Fortunately, the chemical structure of NR which is *1,4-cis*-polyisoprene which can be quite compatible with microstructure of PE. Blending of PE and NR has been studied in term of both stability and mechanical properties. According to the planting application, NR/LDPE blending systems, both with and without commercial stabilizers, were studied to investigate the photo-oxidation stability. The blend system containing no stabilizer was very rapidly degradation under tropical level of UV intensities exposures (Bhowmick *et al.*, 2001).

Additionally, another rubber phase was introduced to the system of PE and NR. The addition of liquid natural rubber (LNR) was believed to be used as a compatibilizing agent for the blend (Dahlan *et al*, 2002). The active terminals of LNR was expected to induce some chemical bonding both within the rubber phase and the rubber and plastic phases interface, consequently improved in physical properties of the blend products.

Another derivative of NR which was extensively examined was epoxidized natural rubber (ENR) (Seng-Neon *et al.*, 1997). The epoxidized modified NR possesses some excellent properties i.e. good oil resistance, low oxygen permeability due to containing the polar groups. Commercially, there are two grades of ENR which were 25 mol% and 50 mol% of epoxidation (Liau, 1999). Increasing epoxide degrees led to decrease the resilience and reduced oxygen and nitrogen permeability of cured ENR while the stiffness increased (Hanafi *et al.*, 2000; Poh *et al.*, 2001). NR, without epoxidation, had the highest solvent uptake, on the other hand, the solvent uptake decreased with increasing epoxidation. The transport behavior, mechanical properties, the gas permeability through the blend of NR and

ENR were considered by Johnson *et al* (Johnson *et al.*, 1999; 2000). The reaction occurred after the ring opening of epoxide provided the chemical bond that enhanced the mechanical properties of the products. (Seng-Neon *et al.*, 1997) Therefore, ENR has been, currently, introduced to the blends or composites system as well (Varghese *et al.*, 2003; The *et al.*, 2004).

2.2 Reactive Processing

Reactive processing is the melt-conducted process that involves a chemical reaction. On the other hand, it is the polymer processing of which the reaction occurred during the process. According to this definition, many processes can be classified as reactive processing such as post-reactor molecular modification, graft-copolymerization, polymer mixing and blending (Xanthos, 1992).

2.2.1 Post-Reactor Molecular Modification

Without the innovation of catalyst system and polymerization process, the modification of single-phase polymer via reactive processing is intended to produce structural changes that improve the properties of the modified material such as enhanced elongation, adhesive strength, and other mechanical properties. Moreover, the rheological change resulting from the development in molecular characteristic is to optimize the ease in plastic processing and to satisfy specific applications.

Polyolefins were the first base polymer used in reactive processing study. Most of those showed the result of chain extension for PE, not chain degradation due to the lack of tertiary carbon backbone like PP which had a tendency to chain degradation upon reactive processing. The chain scission process conducted at high temperature in melt-phase processing of PP had become known as controlled rheology PP for ease of processing (Tzoganakis *et al.*, 1988). In case of PE, the chain combination reaction results from the generation of radical sites on the polymer backbone, followed by macroradicals coupling (Mengge *et al.*, 2005). However, different intended application requires different levels of chain combination which finally influences on the end-use products. The degree of branching or crosslinking strongly depends on the amount of peroxide added.

2.2.2 Preparation of Carboxyl-Containing Polymers

In addition to the reactor-copolymerization, grafting of various chemical species onto the PE backbone can be done via post-reactor processing, especially for grafting of polar monomers wherein the original PE contained an appended branch of polymerized monomers or individual carboxyl-containing polymers. The reaction proceeds with creation of macroradicals on the PE backbone in the presence of grafting species. The main purpose of carboxyl-containing polymer preparation is, mainly, to increase the chemical reactivity, especially to be a masterbatch for further multiphase blending. For example, grafting of maleic anhydride (MA) onto the PE provided PE-g-MA which can perform as a compatibilizer for blending with reactive sites containing polymer. The MA graft polyolefins can be prepared by adding MA into the melt state of PE (Chaoqin et al., 2003), credited to reactive processing, solution state preparation (Machado *et al.*, 2001), mechanical-force grafting (Wulin *et al.*, 2005), or irradiation-initiated grafting (Zhanhai *et al.*, 2007). Most of them require the source of radical or reactive site generations. Other grafting agents such as acrylic acid, ethyle acrylate, and butyl acrylate were prepared in order to modify the inert characteristic of PE as well (Premamoy *et al.*, 1997: 1998, Zhanhai *et al.*, 2007).

2.2.3 Polymer Reactive Blending

On economically basis, reactive processing is primarily applied to produce new polymers by the modification of existing polymers. It is less expensive to develop the specific polymer properties than to develop new ones based on new synthetic routes. In the multiphase system, the mixture of chemically different polymers can be more homogeneous when they are subjected to the reactive blending with the presence of small amount of reactive coagents or some chemical initiators. Therefore, the reactive combination of one polymer with another was occurred (Moad, 1999). In addition, the occurrence of *In-situ* grafting which acts as a compatibilizer to improve the overall properties of immiscible blend can be done via the reactive processing as well (Osman *et al*, 2003; Dongyan *et al.*, 2005).

Various works have dealt with the effect of reaction temperatures as well as the kinds and content of the initiators and coupling agents on the bulk properties of the modified PE (Vale'ria *et al.*, 2004). Up till now, there were a large number of publications and the commercialization of reactive processing applications. It has become the potential method which, in conclusion, involves the free-radical modification of polymers. (Suwanda *et al.*, 1993). Many organic molecules decompose to generate free radicals that can abstract hydrogen atoms from PE to initiate chain combination. Organic peroxide initiators are the most typically used class of chemical free radical initiators such as benzoyl peroxide (BPO) and dicumyl peroxide (DCP) (Vale'ria *et al.*, 2004). In general, peroxide groups decompose homolytically under the influence of heat to generate a pair of oxy radicals, each of which can abstract a hydrogen atom from a PE molecules. Macroradicals can react with each other to form covalent carbon-carbon bond or react with other available radical species. The reaction scheme is simplified as follows:

Formation of the free radical: $\mathrm{ROOR} \longrightarrow 2\mathrm{RO}^{\cdot}$ (1)
Radical transfer: $\mathrm{RO}^{\cdot} + \mathrm{PE} \longrightarrow \mathrm{ROH} + \mathrm{PE}^{\cdot}$ (2)
Grafting/Cross-linking: $\mathrm{PE}_x^{\cdot} + \mathrm{PE}_y^{\cdot} \longrightarrow \mathrm{PE}_{x+y}$ (3)

2.3 Plasma Surface Treatment of Polymer: Principle and Applications

2.3.1 Plasma Chemistry

Plasma is an ionized state of matter and often referred to the fourth state of matter. Generally, the transformation from solid to liquid state or from liquid to gaseous state is achieved by supplying energy such as heating. Nevertheless, to reach ionized state, the neutral gas must be given sufficient energy. When the energy is applied to the process gas molecules, the resulting species produced by the inelastic collisions of electrons and gas molecules are a mixture of electrons, free radicals, and highly excited ions consisting of fragmented portions of the parent molecules. Additionally one has to take the plasma UV-radiation into account. The fluid-like properties of plasma are derived from the long-range interaction between charged particles. Thus, the technical plasma is an ensemble of randomly moving charged and uncharged particles with a sufficient charged particle density to remain electrically neutral on average. Since plasma contains electrically charged particles, their charges are in equilibrium on a macroscopic scale which is generally described as quasi-neutral property of plasma (Fridman *et al.*, 2004).

The sufficient energy required to separate electrons from the nuclei to which they are bound can be of various processes such as thermal, irradiation, and so on. However, the most popular and convenient means of plasma generation is through electrical discharges where electrons are energized in an ambient electric field and made to collide with atoms to produce ionized species.

Regarding to above definition, the plasma covers a wide range of phenomena which has been used in very diverse applications. It has more attracted attention to be used in many industries due to its highly reactivity making it useful for a number of chemical processing applications (John, 2005). However, there are two types of plasma as defined by the temperature of gas and temperature of electrons. One is equilibrium plasma which temperature of both gas and electron are almost the same ($T_e \cong T_n$), therefore, the kinetic of electrons and neutral species are the same. Another is non-equilibrium plasma which the kinetic of neutral species is much lower than that of charged species. The difference between these two qualitatively different types of electric discharges is primarily related to different ionization mechanisms. At atmospheric pressure, the equilibrium plasma can be generated at very high temperature (10,000 – 20,000 K), therefore, this is called thermal plasma while the non-equilibrium plasma is so-called non-thermal or cold plasma The latter plasma type can be explained as much lower of gaseous temperature than that of electron ($T_e \geq T_n$). It can be utilized as an effective industrial tool since the plasma environment facilitates many chemical reactions simultaneously without the over-thermal effect.

Plasma used in material processing is usually weakly ionized. The charged particle density is much smaller than the neutral density. Numerous applications involve both inorganic materials and organic polymers which become most interesting in terms of macromolecular plasma-chemistry (Ferencz *et al.*, 2004).

2.3.2 Plasma Surface Treatment Applications

One of the important applications is polymer surface modification via plasma. The principle of plasma surface treatment is that the energetic species in the gaseous plasma would bombard and interact with the polymer surface, and then transfer their energy to the solid polymer. Cracking of the organic molecules occurs when the attacked energy is greater than the bond energy of covalent bond; consequently, free radicals are created on the polymer surface (Iwata *et al.*, 1988). The interesting point of polymer surface activation is the intermediate species on the surface which are free radicals or further peroxides formed by reaction of radical sites and atmospheric oxygen (Chan *et al.*, 1996). The mechanism is believed to be the creation of radicals on the polymer surface and then subsequent coupling of these radicals with active species from the plasma environment. Depending on process gas, a large variety of chemical groups can be incorporated into the surface (e.g., hydroxyl, carbonyl, carboxylic, amino or peroxyl groups). Several reactions after peroxide occurrence are crosslinking, etching, grafting, and functionalization. Plasma treatments offer an unprecedented spectrum of possible polymer surface modifications (Masayuki *et al.*, 2007). The schematic of plasma surface modification is shown in Figure 2.1.

Such discharges provide chemically mild, environmental friendly and mechanically non-destructive means of altering free radical generation. Also plasma technology can effectively achieve modification of topmost layers region without affecting the desirable bulk properties of a polymer.

Nowadays, most of plasma surface modifications use the so-called processing mode to improve printability, adhesion, and wettability of final products, especially for chemically inert polymers as polyolefins (Changquan *et al.*, 2006). There are numerous publications involved the plasma surface modification of polymers. Most methods have been employed to treat the polymer surface via the down stream plasma process. Moreover, modification of the surface via plasma technique to suit the required surface property can be controlled and achieved by, firstly, generating the radicals and then creating the proper surface with the particular species on the polymer surface depending that specific properties required. Since the plasma can modify all types of polymers regardless to their structure or chemical reactivity. Various types of polyolefins were treated in film/sheet or fiber form including LDPE, HDPE, PP (Chan *et al.*, 1996). A variety of carrier gases can be used in plasma processing. Using air, the gaseous plasma can modified the surface with the introduction of both nitrogen and, mainly, oxygen based functional groups (Rajesh *et al.*, 2003).

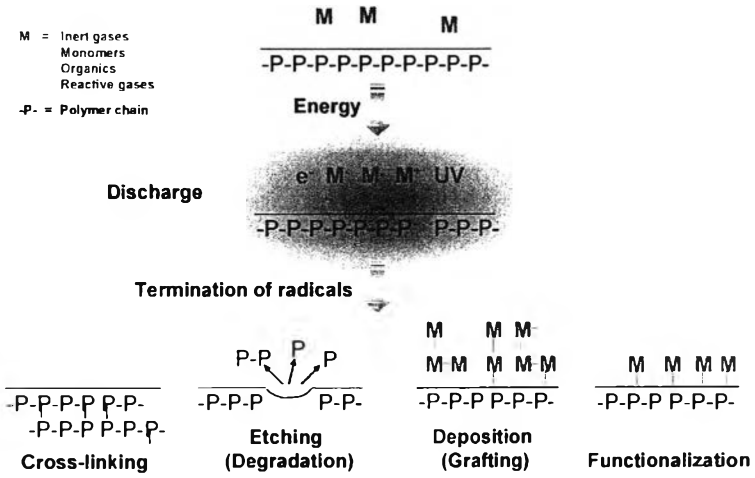

Figure 2.1 General principle of plasma surface modification.

2.3.3 Total Radical Concentration Measurement

Principally, the intermediate species revealed on the surface of plasma treated materials are the radicals or further peroxides as shown in Figure 2.1. Therefore, determination of total concentration of these species become necessary, especially for this research, to define the optimum condition for the intended application. There are a lot of researchers trying to set up the suitable determination method. Electron spin resonance was selected by Hollander *et al.* to measure both qualitative and quantitative radicals (Hollander *et al.*, 1999). Laser-induced fluorescence was tried by Ono *et al.* (Ono *et al.*, 2000). A method of chemiluminescence detection was adopted to quantify the radicals by Massines *et al.* and Tahara *et al* (Tahara *et al.*, 2003).

However, the limitation of those techniques was the specific operating conditions which sometimes were probably not appropriate to the plasma treatment process. Therefore, the conventional method being popular to determine the radical concentration on the surface was the chemical labeling by quenching the free radicals with radical scavenger such as *1,1*-Diphenyl-*2*-picryhydrazyl (DPPH), followed by spectroscopic methods like UV-absorption spectroscopy. The use of DPPH in benzene solution to detect the existing radicals was introduced by Suzuki *et al* (Suzuki *et al.*, 1986). It was liquid-phase radical trapping, so-called DPPH method, cooperated with the colorimetric chemical titration.

This procedure has been selected in a number of related works to determine the radicals generated on the plasma treated surface. The plasma treated materials were kept in a 1.0×10^{-4} mol/l benzene solution of DPPH at 70°C for 24 h to decompose the radical formed on/near the surface. The amount of DPPH consumed was measured by the difference of UV-visible light absorbance spectrum at 521 nm between the pristine and plasma treated materials (Suzuki *et al.*, 1986).

2.3.4 Atmospheric Pressure Plasma Processing

Plasma processing can be categorized into two types as defined by the condition of generation are low-pressure and high- or atmospheric pressure plasma. For low-pressure plasma, the ionization can be initiated and sustained easily but the operating system is quite expensive due to vacuum system requirement, and the size of materials to be treated is extremely depended on the size of vacuum chamber (Marian *et al.*, 2003). It is difficult to replace batch processes by continuous processes. Another type is high-pressure or atmospheric pressure plasma which has been greatly investigated nowadays. This system can overcome the disadvantages encountered in low-pressure plasma. The use of atmospheric pressure plasma can greatly expand the current scope of materials processing because the surface modification process can be more flexible due to longer life time of treated-film.

Regardless to the power supply system, there are several types of atmospheric pressure plasma apparatus used for the purpose of surface modification such as Corona Discharge, Atmospheric Pressure Plasma Jet (APPJ), and Dielectric Barrier Discharge (DBD).

2.3.4.1 Corona Discharge

The corona discharge is characterized as non-homogeneity of the field obtained through small diameters of one or both the electrodes. The electrode configuration is most often point to plane. It is practically used in the film industry nowadays. For polymer surface treatment, the bright filaments extending from a sharp high voltage electrode towards the substrate to be treated is low plasma density therefore, the multi-pin to plate or wire to cylinder is developed.

2.3.4.2 Atmospheric Pressure Plasma Jet (APPJ)

To expand the current scope of material plasma processing, the remote treatment by which the material to be treated is not subjected between the electrodes has been developed. The plasma jet operated at at atmospheric pressure is recognized as a plasma device of excellence in remote processing due to large-volume 2D/3D cold plasma generation. It performs like a continuous non-thermal arc since the treated material is not supposed to operate as an anode, so-called non-transferred arc. The arc is generated in a conical gap and pushed out of opening orifice (jet nozzle) by the gas flow, consequently creates a stable, homogenous, and uniform discharge (Wang *et al.*, 2007). Design of the electrodes and flow of process gas can be various, i.e. from micron-diameter jet to more than centimeter-diameter jet, single-jet/multi-jet (Andreas *et al.*, 1998).

2.3.4.3 Dielectric Barrier Discharge (DBD)

This type of atmospheric pressure device is defined by a pair of parallel plane electrode of homogeneous geometry with either one or both electrodes are covered by dielectric layer (Borcia *et al.*, 2003). When the electric field is supplied to the electrodes, the dielectric barrier prevents the glow to arc transition and leads to the formation of a large number of micro-discharges randomly distributed in space. However, it is also possible to form a diffused version of this micro-discharge. Since, the dielectric barrier discharge always generates nonuniformly random or diffused micro-arcs, it is so called silent discharge (Wagner *et al.*, 2003).

According to the plasma phenomena, positive ions, negative ions, and super-excites neutrals i.e. ion-molecular bonds in complex ions which are usually less strong than regular chemical bonds, but stronger than intermolecular bonds in neutral clusters, can also be formed. Plasma becomes a powerful chemical tool. However, excitation and dissociation by plasma electrons with broad energy distribution are not selective. The large variety of reactive species present in a plasma system leads to a large number of reactions and it is almost impossible to be controlled. Therefore, plasma processing is highly sensitive to the system, both the device itself and the process parameters. The process conditions developed for one system usually cannot be adopted for others (Fang *et al.*, 2007). Optimization of the processing parameters with respect to achieving a desired uniform treatment outcome for a given material is of importance for DBD utilization (Chaozong *et al.*, 2006).

2.4 Polymer Rheology

Rheology is the study dealing with the deformation of materials when forces are applied to them. "Stress" as a measure of force and "strain" as a measure of deformation are the two keywords in this definition. Various rheological measuring techniques are applied under two aspects. One is the use to observe the processing behavior of polymer melts. Another is done with respect to the polymer molecular characterization. Hence, the detection and characterization of branching has mostly been on focus to understand the viscoelastic behaviour of branched PE in the melt, subsequently for the prediction of their processing behaviour. In some case, the number of LCB is too small to be detected by solution-based chromatography or spectroscopy methods such as Size Exclusion Chromatography (SEC) and Nuclear Magnetic Resonance (NMR) (Janzen *et al.* (1999). However, they still show a significant influence on processing properties (Helmut *et al*, 2005). Various works have dealt with the rheological test of PE to investigate the molecular characteristic and flow behaviour of melt.

2.4.1 Small Amplitude Oscillaratory Rheometer

Dynamic measurement involves the response of polymer to an imposed sinusoidal stress or strain on a parallel plate or cone-and-plate instrument. The viscoelastic behavior of polymeric materials leads to out-of-phase stress and strain because of the time dependence property. The results of an oscillaratory shear experiment can be presented by means of plots of the amplitude ratio and the phase shift as functions of frequency as shown in the following equations (Dealy *et al.*, 1990).

$$\sigma(t) = \gamma_0(t) \,[\, G'(\omega) \sin(\omega t) + G''(\omega) \cos(\omega t) \,] \qquad (1)$$

$G'(\omega)$ and $G''(\omega)$ can be described as real and imaginary components of a complex modulus ($G^*(\omega)$), respectively.

$$G^*(\omega) = G'(\omega) + iG''(\omega) \qquad (2)$$

The complex viscosity (η^*) also represents the respondance of a small amplitude oscillatory shear testing.

$$\eta^* = (G' + G'')^{1/2} / \omega \qquad (3)$$

Branching characterization has several benefits relating to the polymer processability since it influences the melt viscosity, temperature dependence of viscosity, melt elasticity, shear thinning (Premamoy *et al.*, 1997).

For a linear polymer, G' is much less than G" at low frequencies. LCB increases the storage modulus (G') value and shifts the crossover modulus to lower frequency. However, this was affected by MWD as well. It is quite difficult to separate the effects of molar mass, molar mass distribution (MMD), and LCB.

Increase in LCB enhances zero-shear viscosity (η_0) as well as shear thinning behavior (Gabriel *et al.*, 2002). Using only viscosity measurement cannot confirm the presence of LCB. A common method to investigate the presence of LCB in PE is the determination of the flow activation energy (E_a). Since flow is a thermally activated process, its temperature dependence of viscosity can be investigated using a conventional Arrhenius relationship.

$$\eta(T) = \eta(T_0) \exp(E_a/R\,(1/T - 1/T_0)) \qquad (4)$$

Therefore, it is considered to be a very reliable and sensitive measurement of LCB in PE. The increased length and content of the branches result in rising of Ea, which is not affected by MWD.

A peculiar effect of the LCB is the shear rate dependence of E_a. The E_a of LCB polymer decreases with increasing shear rate. E_a of linear polymers is independent of the shear rate. This behavior is attributed to the relaxation and disentanglement process of the branched chains. While higher (apparent) activation energy can be attributed to the presence of LCB, the absence of LCB cannot be inferred from constant activation energy. However, the enhancement in shear thinning and melt elasticity is not only influenced by LCB, but also Mw/Mn (Markus, 2001).

However, branched PE is often thermorheologically complex. Therefore, an apparent activation energy calculated from the time dependence of the zero shear viscosity, must in fact be used (Wood *et al.*, 2001). Nevertheless, the main problems are to get an accurate value of the zero-shear viscosity (η_0), especially when LCB is not small enough, which is not easily accessible because of very long relaxation times of branched molecules (He *et al.*, 2004).

2.4.2 High-Shear Rate using Steady State Capillary Rheometer

Another ways to determine the viscoelastic behavior of polymer material is by capillary rheometer that is capable of reaching the temperatures and shear rates typically used for a wide range of processing equipment. The main principle of this instrument is the measurement of the pressure required to extrude materials through a small cylindrical tube or rectangular slit at a known flow rate. A schematic of a typical capillary rheometer is shown in Figure 2.2. The polymer will be held in a cylindrical reservoir and heated to the desired temperature. The molten material is then forced to flow down the barrel and through the die by a motor-driven piston and its flow rate is determined by the speed of that piston. When the pressure reaches equilibrium it will be recorded and the piston speed may be changed to measure the material at different rates.

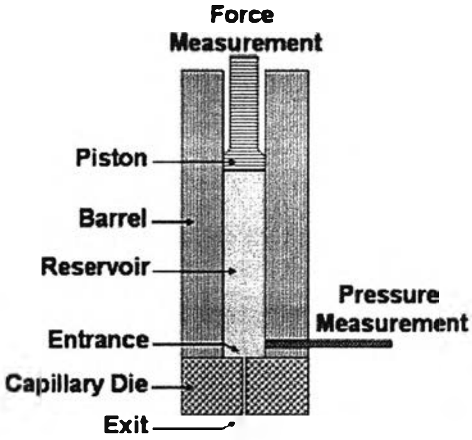

Figure 2.2 Schematic of a capillary rheometer.

Molten polymers are rheologically complex materials which can show evidence of both viscous and elastic properties. To investigate this phenomenon, both force and deformation must be measured quantitatively. Assuming that no-slip at the wall, fully developed flow with zero radial velocity, incompressible fluid of polymer, and steady isothermal flow, the flow profile is simplified for the analysis of flow testing in capillary rheometer. To obtain the rheological data, a continuous deformation rate or shear rate must be determined as a measure of how fast the shearing process is occurring. Once the deformation is determined, the force or stress (force applied to a unit area) causing the deformation must be measured. The viscosity which can be defined as the resistance to flow of the molten polymer is determined from the ratio of stress and the deformation rate (Dealy *et al.*, 1990). The equation generally used for rheological test in capillary rheometer are as given,

Shear rate: $\dot{\gamma} = d\gamma/dt = 4Qr/\pi R^4 = 4vr^2/R^3$ (s^{-1}) (5)

Shear stress: $\tau = F/A = Pr/2L$ (Pa or N/m^2) (6)

Shear Viscosity: $\eta = \tau/\dot{\gamma} = P\pi R^4/8QL$ (Pa.s) (7) where Q is the volumetric flow rate of material that relates with the piston speed (v) in the unit of mm/s. Pressure can be symbolic as P, L is the capillary length, r and R are radius in mm of barrel and capillary, respectively.

It is true that the viscosity of polymer cannot remain constant over the range of deformation, as a result, it depends on the deformation rate owning to property of non-newtonian fluid. As the viscosity is a function of shear rate, especially at intermediate level, most polymers behave like pseudoplastic or shear thinning that shows the decrease in viscosity when shear rate increases. Due to the shear thinning behavior, the equations used to calculate the viscosity are not exactly correct, thus the Rabinowitch correction has been developed using the slope (s) of apparent shear rate and shear stress. The smaller the s value, the more shear thinning is generated with that polymer and then the larger of shear rate correction is required.

$$\text{Slope (s)} = d\,[\log(\tau)]\,/\,d\,[\log(\dot{\gamma}_{app})] \qquad (8)$$

Then, the real shear rate will be given as follows:

$$\dot{\gamma}_{real} = [(3s + 1) / 4s]\ \dot{\gamma}_{apparent} \qquad (9)$$

In addition to the pressure drop due to the flow through the die (ΔP), the entrance and exit effects also add an extra pressure drop (P_e) to the measured pressure (P_m). Therefore, determination of this P_e is needed to avoid the high error due to the P_e component. The principle of Bagley correction which has been developed to solve this problem is whatever pressure still remains after ΔP is removed is the pressure due to entrance and exit effects. Using various die length while keep die diameter constant, the entrance and exit effects of each shear rate can be determined. This correction allows real shear stress to be calculated. Once shear rate and shear stress have been corrected, the final true viscosity can be obtained. When capillaries are relatively short ($L/R < 50$), the Bagley correction is necessary to account for the excess pressure drop, P_e, at the capillary entry.

As mentioned earlier, to achieve practical ways in drawn film processing, sufficient strength to resist high strain induced by drawing device is necessary. Melt strength of polymer is considered as an elongational deformation of molten polymer during the fabrication process. Extensional or elongational viscosity is the resistance of a fluid to extend. Measurement of elongational viscosity is considerably more difficult than measurement of shear viscosity. One of the devices used involves extrusion from a capillary and subsequent stretching with the help of a pair of rollers. To examine melt strength, the instrument should be capable to both stretching and measurement of force used to draw the melt until the failure. The maximum force required to break the extruded strand is referred to melt strength. However, it should be noted that this test is sensitive to many variables including dieswell, cooling rate, operating and ambient temperatures.

In practice, the terms extensional viscosity and melt strength are sometimes confused.. The excess pressure encountered in flow from a large reservoir to a smaller diameter capillary is due to elongational viscosity. In fact, Cogswell has developed a method for measurement of elongational viscosity from excess pressure drop (i.e., the Bagley correction). Melt strength is more of an engineering measure of resistance to extension.

Many reactive processing works have selected the rheological test to investigate and/or confirm the slight cross-linking or grafting structure as such polyethylene occurs dominantly via radical reaction during reactive processing. It was found that both shear and elongational viscosity increased with the amount of peroxide (Vale´ria *et al.*, 2004). Additionally, shear thinning behavior became more evident upon reactive processing. The E_a for flow was able to apply for high steady shear flow as well (Sobha *et al.*, 2002).