CHAPTER II
LITERATURE SURVEY

2.1. Polymer Processing

The ability of a screw to manufacture products of good quality with high productivity and low cost is dependent on its performance. In the extrusion process, the certain geometry and process condition for the screw and the die affect the output rate. The operating point of the extrusion is therefore determined by the screw and die characteristics where equivalence output and pressure drop is formed for both screw and die (Wilczynski, 1989). It was found that the operating point was affected by Mw of the blends between HDPE and ultrahigh molecular weight polyethylene (UHMWPE). The UHMWPE induced the shift of the operating point of the blends which was predicted by Criminale-Ericksen-Filbey (CEF) equation and also supported by experimental data (Rosario *et al.*, 1992).

A study of effect of MWD on polymer processing were reported by Christensen *et al.* (1991). They mentioned that the MWD of commercial grade of polyolefin had an important effect on the output rate and pressure development in the extruder, thereby influencing productivity and product uniformity. For each polymer with the same melt flow index, the broad MWD sample had the advantage of the low melt temperature and low torque, while the narrow MWD sample had the high output rate.

Polymers are viscoelastic fluids, which are described by rheological properties. Viscosity is generally determined by capillary rheometer as the apparent viscosity of the melt. Meanwhile, elasticity is also determined by degree of die swell. Thereby, rheological properties have the effect on processibility. An increase in apparent viscosity and die swell is accompanied by increased processing difficulty (Liang, 1995). These properties are also dependent on the molecular parameter. Increase in Mw is accompanied with increasing viscosity and the broader MWD implies the greater the die swell. Thus, many researchers have to consider and explore the effect of these properties during extrusion.

The rheological properties and crystallization behavior affect on the HDPE melt during extrusion. Meanwhile, the process variable affecting the flow behavior are temperatures, shear rate, geometric parameters of the die, and pressure as reported by Ness *et al.* (1993).

The relationship between the rheology and processibility of polyethylene (PE) were determined by Utracki *et al.* (1985). They summarized that the changes of die geometry played a key role on the output rate. Moreover, linear low density polyethylene (LLDPE) with high Mw gave less amount of output rate in comparison with low Mw of LLDPE by using the same die.

The other parameters of homopolymer blending of high Mw with low Mw that must be considered is the technique of mixing. Boscoletto *et al.* (1997) investigated impact behavior and rheological properties of HDPE and UHMWPE mixtures. The main consideration was on the different types of mixing apparatus, a Brabender Plasti-Corder and internal mixer. The researcher also divided a Brabender into two function apparatus; i.e. extruder and mixer head. It was found that the general trend of impact strength increased with amount of UHMWPE in HDPE matrix. The blends with mixer head gave higher impact strength compare with its extruder and more dissolved of UHMWPE content were found in mixer head mixture. However, the mixtures with 2 types of Brabender also resulted to have higher impact strength in comparison with internal mixer.

Moreover, the detailed morphological investigation revealed that UHMWPE was only partially dissolved and acted as filler. Two phases were obviously shown with a digital scanning electron microscope. At higher than 3% by weight of UHMWPE, the incorporation of UHMWPE with HDPE was poor and behaved like separate particles in the matrix by using single screw extruder. This may due to high viscosity of UHMWPE which difficult to break their particles out.

Vadhar *et al.* (1987) reported that internal mixer resulted to poor mixing in comparison with sequential loading method of UHMWPE and LLDPE. The sequential loading method was a method which allowed the UHMWPE melting first at 250 °C and then cooling down to 180 °C to add LLDPE and blending until obtaining homogeneous mixture. Moreover, the blend with sequential loading method also resulted in tensile strength that varied from 1.8 to 5 N/m^2, whereas the sample from internal mixer showed tensile strength in range of 1.2 to 3 N/m^2.

The effect of mixing rate on the mechanical properties of the blends of UHMWPE and HDPE were also studied by Tincer *et al.* (1993). Increasing mixing rate enabled a better incorporation of high concentration of UHMWPE within HDPE and also resulted in higher applied stressed in the polymer melt. At low concentration of UHMWPE, the yield strength decreased with increase in the weight percentage of UHMWPE in the blend. Meanwhile, the ultimate tensile strength and elongation at break of the blends were in contrast to yield stress. This was due to UHMWPE dispersed in HDPE as segregated particles with incomplete incorporation as seen by low heat generation during mixing.

The research work of Baker *et al.* (1993) studied the effect of processing on molecular characteristics which were MWD and Mw of LDPE. The polymer was sheared in single-screw and twin-screw extruders, and in a high speed melter/mixer (Gelimat) and then diluted in trichlorobenzene and in p-xylene. Gel Permeation Chromatography (GPC) was used to study the changes of Mw and MWD. They concluded that a specimen of LDPE had been sheared in various processing instruments without significant change in the polymer MWD. A mild exception to this occurred in a sample sheared in the Gelimat mixer, where very slight reductions in Mw were observed.

2.2. Mechanical Properties

The relationship between molecular structure and mechanical properties is very complicated, compared with that of solution properties. However, most polymers are used in the solid state. It is very important to control or predict mechanical properties at the stage of polymerization. Polymers vary widely in their mechanical behavior depending on the degree of crystallinity, degree of crosslink, and the value of T_g and T_m (Odian, 1993). It is also known that the service properties of polymers, especially rheological and processing properties, depend on the average molecular weights and their distribution, and on the content of fractions with very low or very high molecular weights (Cholinska *et al.*, 1993). In general, a higher Mw increases all of mechanical properties (Billmeyer, 1984).

The trying to prove an empirical equation between mechanical properties and Mw was done by Ogawa (1992). In this article, he discussed tensile and flexural properties of crystalline polypropylene as a function of Mw, based on eq. (2.1)

$$P = A + B/M \tag{2.1}$$

Where P stands for mechanical properties, M molecular weight, and A and B are constants. He found that, the properties of tensile strength and elongation at yield gave a negative value, and the elastic modulus in tension and flexural properties gave a positive value. When B was positive, mechanical properties decreased with increase of Mw, while the tendency was reversed, when B was negative. This fact suggested that tensile properties increased with Mw, while compressive properties decreased with it. Furthermore, strength and elongation at yield increased with Mw, while elastic modulus in tension decreased with it. He also suggested that it was possible by using B value to compare the difference of Mw dependence among polymer species. However, the comparison should be conducted by taking into account the difference of Mw for equal degree of polymerization. He also tried to apply eq. (2.1) for tensile strength and elongation at break. However, no satisfactory result was obtained. Factors such as thermal history in preparing test species may be more predominant than Mw. In the case of copolymers, it was due to the content and sequence length of the comonomer in a polymer chain governed more strongly mechanical properties. Therefore, it was certain that a simple equation did not hold in copolymers.

Part of polymer with high Mw improved mechanical properties in homopolymer blending of polypropylene (PP). Adding high Mw PP at 3% of blend composition enhanced tenacity, yield stress and initial modulus for PP fiber grade (Deopura *et al.*, 1986).

Flood *et al.* (1990) studied on the PP samples possessing three different MWD ranging from narrow to broad, but having the same melt flow rate. They found that as the MWD became broader, the tape modulus and tenacity increased slightly and the percent elongation and shrinkage decreased slightly. These effects were attributed to decrease in molecular mobility and increase in the number of tie molecules present in broad MWD resins.

Tensile property data for polystyrene (PS) samples of varying MW were related with the way to prepare sample. The large difference value was due to the injection molded and compression molded. The results for narrow MWD polystyrene showed that tensile strength increased with Mw. The value of these property by injection-molded was showed higher than the value by compression molded. This difference was due to more orientation in injection molded bars compared with compression molded which was isotropic property. However, effect of MWD on this property were also studied. The conclusion was that the broad MWD samples increased the scatter in data and resulted in a slightly lower quality value compared with narrow MWD (Bersted *et al.*, 1990). Furthermore, the research work of Schlund *et al.* (1987) also indicated that the mechanical stability of the very broad MWD resin of LLDPE was found to be the poorest.

The effect of the Mw on the fracture behavior of PP homopolymer was studied by Van Der Wal *et al.* (1998). The fracture behavior was determined by a tensile test on notched Izod specimen. The observations were found that sample with highest Mw had the highest modulus, yield stress and impact strength.

The influence of Mw on the tensile drawing behavior of PP has been studied by Wills *et al.* (1980). Molecular weight, however, still played an important role in determining the strain hardening characteristics of the materials of their results. The higher the molecular weight of the sample, the faster the rate of strain hardening and the higher the level of stress achieved for a given strain. Similar observations were made by Wang *et al.* (1990) regarding mechanical behavior of HDPE at various Mw. They found that the highest modulus achievable for polyethylene appeared to depend mainly on molecular weight. Moreover, they also proposed a formula to predict the maximum draw ratio (Dr_{max}). Dr_{max} increased with the square root of Mw by neglecting entanglement effect.

The effect of MWD on drawability and mechanical properties of UHMWPE was investigated by Liang *et al.* (1989). They concluded that the drawability of narrow MWD reached a lower draw ratio than a sample with a broader MWD. Furthermore, the narrow MWD showed a higher modulus than a broader MWD.

The miscibility and mechanical properties of mixtures of ultrahigh-molecular weight linear polyethylene (UHMWLPE) and a linear polyethylene of moderate molecular weight (LPE) were investigated by Ueda *et al.* (1986). UHMWLPE has useful mechanical properties but cannot be readily processed by conventional method because of its high melt viscosity. The mixtures of UHMWLPE and LPE exhibited interesting mechanical properties with the potential advantage of achieving conventional processibility. Tensile strength and strain at break were maximum by adding LPE at 0.6 wt fraction in UHMWLPE matrix. Similar observations were made by Sawatari *et al.* (1989) that the morphological and mechanical properties of blends film were dependent upon the compositions of low molecular weight polyethylene (LMWPE) in UHMWPE.

The final mechanical properties were found to be intermediate between that of parent polymers and also affected by processing condition.

However, the effect of MWD on the mechanical and rheological properties of a series of PP were evaluated by Tzoganakis *et al.* (1989). From their study, the impact strength decreased with low Mw, whereas extrudate had less swelling with narrow MWD and low Mw. The absences of very long polymer chains were mainly responsible for the reduced elastic properties of polymer melts.

Moreover, the research work of Wong (1998) also suggested that swelling was actually a function of time and the maximum swell was highly dependent on the MWD of a polymer. Their experimental data also indicated about melt flow index (MFI) which was much more susceptible to the L/D ratio than it was to temperature and applied load. It was apparent that the MFI decreased with increasing L/D ratio. It was understood by the fact that the greater shear resistance existed in the dies of larger L/D. From these results, it should be a guide to estimate the flowability and output rate in the polymer processing. One part of research work of Mantia *et al.* (1985) also showed about the relationship between MFI and Mw of HDPE, LDPE, and LLDPE. MFI were increased with decrease in Mw of all samples.

The aim of present work are covered on the effect of molecular parameters and processing performance. The molecular parameters are defined in terms of Mw and MWD. The performance parameters are variation of screw speed and geometry of dies. Temperature is controlled which means the control of viscosity of samples.

In the present work, twin screw extruder is employed to improve melt mixing of two polyethylenes having either different Mw or MWD's. In order to obtain the relationship between mechanical properties and processibility of HDPE homopolymer blends, the evaluation of results must consider composition dependence.