

CHAPTER II

THEORY

2.1 . Polyethylene properties

The melting temperature, extent of crystallinity, modulus, and mechanical behavior depend on the method of manufacture and the addition of comonomers, as well as overall molecular weight. Polyethylene is manufactured by several major processes: The high-pressure, free-radical polymerization, the Ziegler process, and the newer metallocene-catalyzed polymers and the metallocene- Ziegler processes shown in Table 2.1.

Table 2.1 Synthetic methods for polyethylene manufacture

Method	Polyethylene properties
High pressure (free radical)	Broad molecular weight distribution, both short and long branches along chain, low melting, low density
Ziegler process (coordination catalysts, titanium tetrachloride/triethyl aluminum)	Broad molecular weight distribution, few branches, high density, linear polymers, high melting, comonomers control crystallinity levels
Metallocene catalysis (bis- cyclopentadienyl metal complexes)	Relatively narrow molecular weight distributions, controlled levels of branching, improved control of comonomer distribution
Metallocene-Ziegler	High comonomer incorporation

Various polymers are named based on their density shown in Table 2.2. The densities of the polyethylenes decrease with increased side group mole fraction [4].

Table 2.2 Polyethylene properties

Polymer	Designation	Degree of branching, CH ₃ /100C	Density range, g/cm ³	Melting temperature range, °C
Low-density polyethylene	LDPE	2 - 7	0.915 - 0.94	100 - 129
High-density polyethylene	HDPE	0.1 - 2	0.94 - 0.97	108 - 129
Ziegler linear low-density polyethylene	zn-LLDPE	2 - 6	0.91 - 0.94	99 - 108
Metallocene linear low-density polyethylene	m-LLDPE	3 - 7	0.90 - 0.92	83 - 102

LDPE containing long chain branching in the order of 1 – 3 per 1000 carbon atoms as well as 10 – 30 short chain branching per 1000 carbon atoms shows low tensile strength and modulus, medium impact and tear resistance (MD tear strength > TD tear strength).

HDPE is the most crystalline polyethylene, since its chains are linear and contain very little branching. It shows high modulus, medium tensile properties, poor impact and tear resistance (high TD tear and extremely low MD).

LLDPE have a wide range of short chain branching, depending on the type of catalyst (zn-LLDPE and m-LLDPE) and comonomers (butane, hexane or octane) added to reduce the crystallinity of the product, it generally has good tensile, impact and tear resistance (superior tear resistance with TD tear > MD tear resistance) [3], the type and amounts of short chain branching have a significant effect on the physical properties. These various compositions are modeled in Figure 2.1 [4].

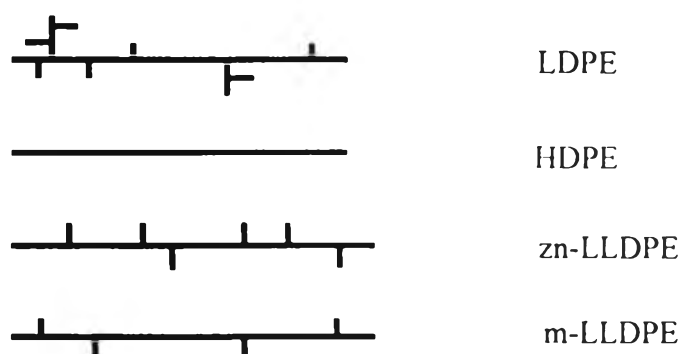


Figure 2.1 Model structure of polyethylenes, illustrating the various types of regularity of side chains.

2.2 Characteristics of metallocene and Ziegler-Natta catalyst LLDPE

Metallocene catalyst is a “single-site catalyst” (SSC) because it has a uniform active site that has a high polymer productivity per transition metal to produce a “pure” LLDPE with very narrow molecular weight distribution. This catalyst produces very few unwanted low-molecular weight, low density product [5].

Ziegler-Natta catalysts is a “multi site catalysts” (MSCs). Ziegler-Natta catalysts give polymers of much broader molecular weight distribution and compositions vary not only from one molecule to another, but also between molecules of different molecular weight. This is because most high performance Ziegler-Natta catalysts are heterogeneous and contain many different catalyst active sites (multi active sites) with different characteristics [6].

Because metallocene catalyst has a uniform active site in contrast with ziegler-natta catalysts, non uniform catalyst, metallocene catalyst produces LLDPE with uniform length polymers, and thus has very narrow molecular weight. Metallocene catalyst also makes it possible ethylene to copolymerize with bulky comonomers such as higher α -olefins, cyclic olefins and styrene that were difficult by ziegler-natta catalysts

systems, and produces polyolefins with low density and that are extremely tough. Mostly used α -olefins for the production of m-LLDPE are hexane-1 and octane-1 [5].

Because m-LLDPE has narrow molecular weight distribution, it forces high torque in the extruder during processing and die pressure becomes high. It also permits melt fracture at low shear rate showing poor processability.

2.3 Polymer blend

By definition, any physical mixture of two or more different polymer or copolymers that are not linked by covalent bonds is a polymer blend. Development of a new polymer to meet a specific need is a costly enterprise. If the desired properties can be realized simply by mixing two or more existing polymer, there is an obvious pecuniary advantage.

A number of technologies have devised to prepare polymer blend. It so happens that most polymers are not compatible. Rather, they separate into discrete phase on being mixed, although an increasing number of completely miscible blends are being developed. Differences between the two types are manifested in appearance, miscible blends are usually clear, immiscible blends are opaque and in such properties as glass transition temperature, miscible blends exhibit a single T_g intermediate between those of the individual components, whereas immiscible blends exhibit separate T_g s characteristic of each component. Miscibility is by no means prerequisite to commercial utility.

Homogeneous polymer blends are more convenient from the standpoint of being able to predict properties of processing characteristics. If additive are used, for example, there are no problems of migration from one phase to another. Physical or mechanical

properties usually reflect, to a degree, the weighted average of the properties of each component.

In general, the properties of a blend are usually determined by the miscibility of the polymeric constituents. Miscibility implies that a single phase is produced. The most difficult polymer blend category to clearly describe is that of the partially miscible system. The most common system is one in which two completely immiscible polymer are made compatible with a third organic agent, called a compatibilizer. The compatibilizer usually increases the interfacial adhesion between the two polymers blend.

Miscible polymer blend is a polymer mixture which is homogenous down to the molecular level. Thermodynamically, this is associated with the negative value of the free energy of mixing i.e. $\Delta G_m \cong \Delta H_m \leq 0$; where ΔG_m is the Gibbs' free energy of mixing and ΔH_m is the enthalpy of mixing. Miscible polymer blend has a single phase, in contrast, immiscible blend polymer is a polymer mixture in which polymer-A forms a separate phase from polymer-B. The thermodynamically immiscible blend is associated with the positive value of the Gibb's free energy of mixing i.e. $\Delta G_m \cong \Delta H_m \geq 0$.

The compatibility of a polymer-polymer system determines a polymer system properties. In general, compatible polymer blends is a homogeneous polymer mixture to the eye with physical properties. Polymer blends that are heterogeneous on a macroscopic level are called incompatible polymer blends [6,7].

2.4 Determination of polymer/polymer miscibility

There are several methods that can determine compatibility of polymer blends, each method has a limit of useful range. A variety of experimental techniques have been used to determine the compatibility of polymer blends. Some techniques, such as calorimetry, thermomechanical, dynamic mechanical procedures, are based on the determination of the number and the location of the glass-transition temperature; T_g . Other techniques are based on scattering of microscopic techniques.

2.5 Blown film extrusion process

Blown film extrusion is a continuous process in which the polymer is melted, the melt is forced through an annular die, and the resulting tube is inflated with air into a “bubble” and cooled. Air is always blown on the outside of the bubble to cool the film; to increase production rates, internal bubble cooling can also be used. The film is stretched in the longitudinal and circumferential directions during production, resulting in biaxial orientation. The circumferential stretching is inherent in the blowing process. Longitudinal stretching is imparted by drawing of the film between the extruder and the nip rolls.

The properties of the film are determined by the blow-up ratio and the linear line speed. The blow-up ratio is the ratio between the diameter of the final tube of film and that of the die. The internal air pressure that expands the tube into the bubble is typically supplied through a port into the mandrel, the interior part of the die. Once the process is running steadily, little air is usually lost, so make-up requirements are small. When internal bubble cooling is used, air is constantly being exchanged inside the bubble.

The travel of the film through the blown film tower is aided by various guiding and sizing devices. The film turns from molten to semi-solid at the “frostline” but is still easily deformed as it moves up the tower. However, the orientation of the film is generally complete at this point. When the film is cool enough, the bubble is collapsed by plates and rollers (pinch rollers), and wound up, with or without slitting, gusseting or other treatment [8]. Thus, the blown film process can produce tubular as well as flat film (shown in Figure 2.2).

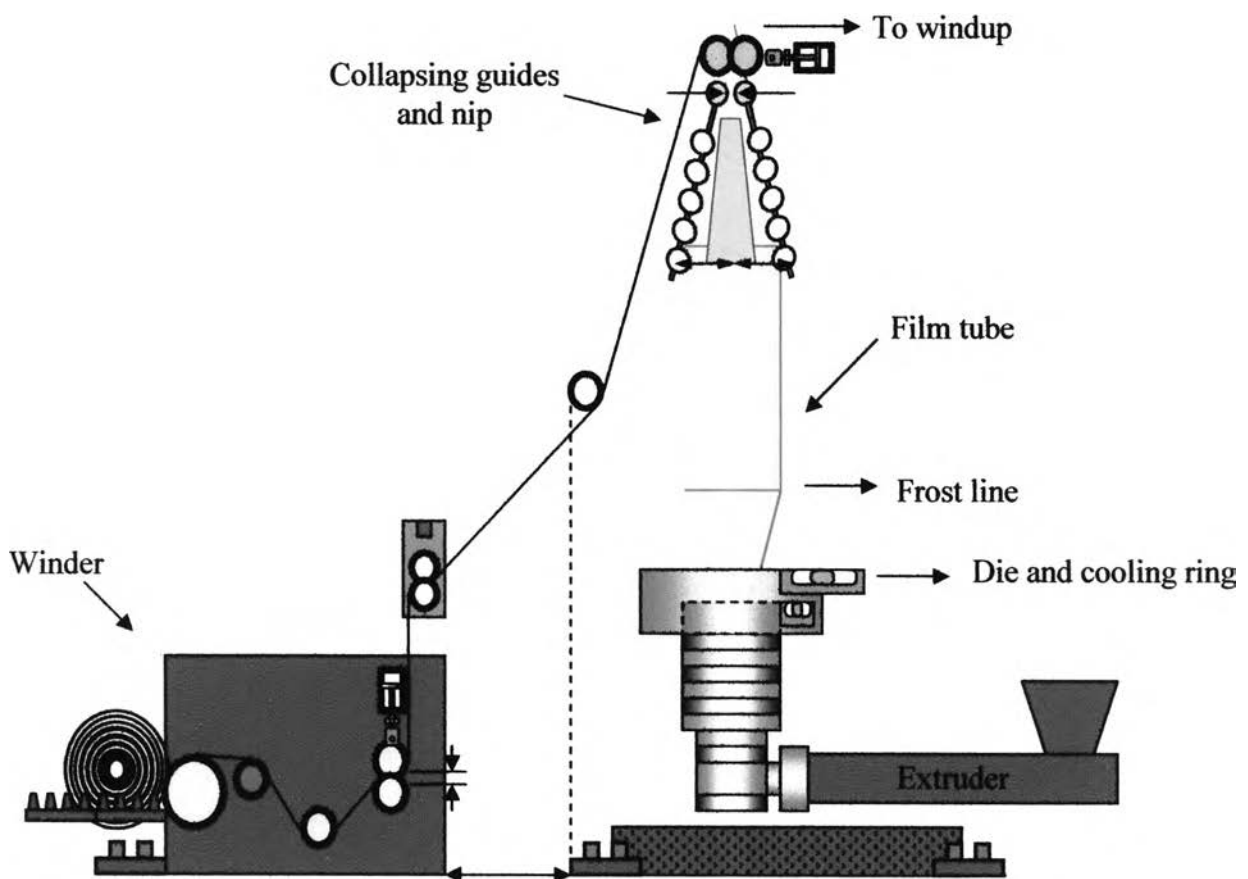


Figure 2.2 Blown film extrusion.



2.6 Literature reviews

K. Cho et al [9] reported the HDPE/LLDPE blend was miscible in the melt, but the LLDPE/LDPE and HDPE/LDPE blends exhibited two crystallization and melting temperatures, indicating that those blend phases separated upon cooling from the melt. The mechanical properties of the HDPE/LLDPE blend conform to the rule of mixtures.

H. Parichattakul [6] studied the properties of HDPE/m-LLDPE film for industrial bag applications (typically in the thickness of 15 – 40 μ) by comparing with HDPE/zn-LLDPE. The investigation were in the range at 0-40% LLDPE of the blends. She was suggested for HDPE/m-LLDPE blends were miscible in the crystalline phase but immiscible in the amorphous phase. The mechanical properties of HDPE/m-LLDPE films were superior to HDPE/zn-LLDPE films.

N. Utairatana [7] studied for thermal, mechanical properties, seal strength and film clarity from blown films of HDPE/m-LLDPE by comparing with HDPE/zn-LLDPE. The results indicated the HDPE/m-LLDPE and HDPE/zn-LLDPE blends were miscible in both crystalline and amorphous phases. The mechanical properties of HDPE/m-LLDPE films were superior to HDPE/zn-LLDPE films at the same condition. The downgauging of HDPE/m-LLDPE film at 90% of m-LLDPE with 150 or 165 micron, and then zn-LLDPE films thickness at 180 micron. And studied mechanical properties of blown films HDPE/m-LLDPE, HDPE/zn-LLDPE with medium-density polyethylene (MDPE) at the same melt flow index (MFI) and density. The results that the equivalent mechanical properties of HDPE/m-LLDPE films, HDPE/zn-LLDPE films to MDPE films of the same thickness can be achieved.

J.F. Zhengang et al [10] studied the effect of branching characteristics of LDPE on its melt miscibility with HDPE. There were using molecular simulation. The level of

branch content for LDPE above which the blend is immiscible and segregate. The melt was found to be around 30 branches/1000 long chain at the chosen simulation temperatures. This value is significantly lower than that of LLDPE (40 branches/1000 carbons) in the blends with HDPE computed by one of the authors. The major is difference between LDPE and LLDPE models. The each modeled LDPE molecule had three long chains while each modeled LLDPE molecule had one long chain. The present results together with those of the LLDPE/HDPE blends suggest that the long chain branching may have significant influence on the miscibility of polyethylene blends at elevated temperatures.

R. Mingtao et al [11] studied nonisothermal crystallization and melting behavior of m-LLDPE/zn-LLDPE/LDPE ternary blends. The weight percentage of LDPE in ternary blends is usually 20%, remainder vary weight percentage of m-LLDPE and zn-LLDPE. Each ternary blend in this study shows different crystallization and melting behavior due to its different m-LLDPE content. The crystallization of the ternary blends rises with increasing m-LLDPE content and m-LLDPE improve the crystallization of the blends at low temperature. The fixed small content of LDPE made little influence on the main crystallization behavior of the ternary blends and the crystallization behavior was mainly determined by the content of m-LLDPE and zn-LLDPE.

R.Pérez et al [12] studied miscibility and blown film of m-LLDPE/LDPE blends at same composition. Viscosity results and time-temperature superposition results reveal that all the considered m-LLDPE/LDPE blends, except 47.5% m-LLDPE/52.5% LDPE blend, are miscible in the molten state. Miscible blends with a high LDPE content and immiscible 47.5% m-LLDPE/52.5% LDPE blend, show 'melt fracture', but not 'sharkskin'. The latter is observed in miscible blends of a high m-LLDPE content. 'Sharkskin' is postponed in 87.5% m-LLDPE/12.5% LDPE blend, a result which is associated to the elongational viscosity enhancement, due to the presence of long chain

branches. This profitable effect of long chain branched molecules has not been noticed in blown film extrusion experiments, since m-LLDPE and 97.5% m-LLDPE/2.5% LDPE, 95% m-LLDPE/5% LDPE, 92.5% m-LLDPE/7.5% LDPE and 87.5% m-LLDPE/12.5% LDPE blends show a similar performance.

A.H. Ibelwaleed et al [13] studied influence of branch content and composition distribution of hexane LLDPE on its miscibility with LDPE were used to study the melt miscibility using rheological tools. They were investigated m-LLDPE two grades have the same weight-average molecular weights. The different a high and low branch content, and zn-LLDPE have low branch content will disclose the influence of catalyst type. The composition distribution of LLDPE had influenced its miscibility with LDPE. The zn-LLDPE blend with LDPE was founded to be more miscible than an m-LLDPE of the same weight-average molecular weights and similar branch content. A high branch content m-LLDPE was founded to be more miscible with LDPE than a low branch content m-LLDPE of the same weight-average molecular weights and molecular weights distribution. The high branch content m-LLDPE blends with LDPE were partially miscible and immiscibility to develop in LDPE- rich blends.

A.K. Gupta et al [14,15,16] who performed HDPE/zn-LLDPE blend investigated their mechanical properties such as flexural, impact and tensile strength, etc. including the morphology. They found that the properties of HDPE and LLDPE are distinguished by three regions of blend composition, viz. (i) 0-30% LLDPE content (i.e., HDPE rich blend), (ii) 70-100% LLDPE content (i.e., LLDPE rich blend), and (iii) the middle zone. The cocrystallization of HDPE and LLDPE occurs at all compositions of HDPE/zn-LLDPE blend prepared by melt mixing in a single screw extruder. Mechanical properties of HDPE/LLDPE blend with vary the blending ratio are sufficiently linear at small deformation and nonlinear at large deformations.

U. Yilmazer [17] studied effects of blending LDPE with LLDPE (0-100%) on extrusion blown films and test mechanical properties and haze. He was founded the LLDPE had higher tensile strength and elongation at break than the LDPE in both directions. The impact energies of the LLDPE and the LDPE were approximately the same, but tear strength of the LLDPE was lower than the LDPE in the machine direction. Haze undergoes a maximum between 20 and 40% LLDPE content. And he was comparative mechanical properties strongly depend on the processing conditions such as; blow-up ratio and draw-down ratio, and structural parameters such as the molecular weight and molecular weight distribution of materials. there were studied at 20/80 (LLDPE/LDPE) ratio. Tensile strength, elongation at break, and tear strength in both directions became equalized. The impact energy decreased as the blow-up ratio and draw-down ratio approached each other.

J. Lu and H.-J. Sue [18] studied morphologies of films blown from a LDPE, a LLDPE and blend. The LLDPE film has a relatively random crystal orientations. The film made from the LDPE/LLDPE blend possesses the highest degree of crystal orientation. The LDPE film has the greatest amorphous phase orientation. Cocrystallization between LDPE and LLDPE occurs in the blowing process of the LDPE and LLDPE blend. An unusual effect of blending on film morphology has been found. This effect results in undesirable anisotropy in mechanical properties of the blended film. The underlying mechanisms of morphology development due to blending and strategies for minimizing the undersirable anisotropy in LDPE/LLDPE blend film have been proposed.

A. Majumdar and D.D. Kale [19] studied mechanical properties from blown films of different% of zn-LLDPE, m-LLDPE (octane-based both LLDPE) and LDPE. Tensile strength, dart impact strength, hot tack strength, heat seal strength, and the

barrier properties of these films were measured. They founded a film produced from blend composition of 75% LLDPE and 25% LDPE, replacement of zn-LLDPE by even 25% of m-LLDPE showed significant improvement in mechanical and heat sealing properties. The barrier properties also showed good improvement. Considering all the properties replacing zn-LLDPE by m-LLDPE in the range of 25-50% is adequate in getting superior properties.