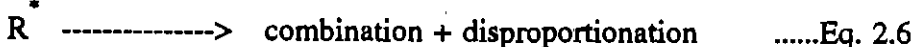
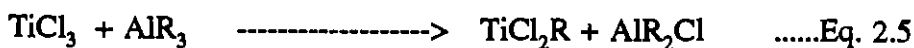
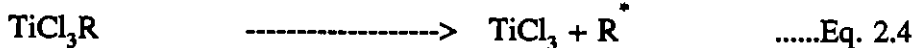
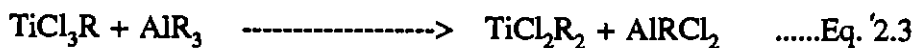
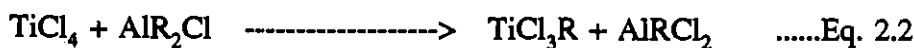


CHAPTER II

THEORY

2.1 Ziegler-Natta catalyst

Prior to 1950, the only commercial polymer of ethylene was a highly branched polymer called high-pressure polyethylene or LDPE. The technique for producing a linear polyethylene was discovered by using the stereospecific polymerization catalyst. Ziegler first recognized the importance of the catalyst and the novel type of polymerization. It induced especially for ethylene monomer[7]. Natta, at almost the same time, reported on a similar catalyst useful for a wide range of olefin, diolefin and acetylenic monomer. Then Ziegler and Natta were awarded the Nobel prize in 1963[8]. These catalysts are known as Ziegler-Natta catalysts. In general, these catalysts may be described as a combination of a transition metal compound from group IV to VIII and an organometallic compound of a metal from group I to III of the periodic table[9]. Most Ziegler-Natta components participate in a complex set of reactions involving alkylation and reduction of the transition-metal component by the Group I -III component as shown below for $\text{TiCl}_4 + \text{AlR}_3$:



Radicals produced in Eq.2.4 are capable of initiating radical polymerization with some monomers, for example, vinyl chloride.

Ziegler-Natta catalysts have been used for commercial manufacture of various polymeric materials since 1956. Together these polymers represent the largest commercially plastics as well as the largest commodity chemicals in the world. The resulting initiators exhibit a range of behaviors in terms of activity and stereospecificity. The term activity as used in the most literature references applies exclusively to the rate of polymerization. Activity is often expressed on terms of kilograms of polymer formed per gram of initiator component. Modification of an initiator system to increase activity has often come at the expense of stereospecificity.

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.

The polyethylene prepared with this catalyst had physical properties completely different from the conventional high-pressure product. This process produces polyethylene by polymerization at low pressure and ambient temperature using mixture of triethylaluminum and titanium tetrachloride as the cocatalyst.

High density polyethylene is linear polymer that was produced Ziegler-Natta catalyst, it has much lower degree of branching that result in higher crystallinity

High density polyethylene is linear polymer that was produced Ziegler-Natta catalyst, it has much lower degree of branching that result in higher crystallinity and higher crystalline melting temperature. Linear low density polyethylene is the linear backbone with short branches which is also produced by Ziegler-Natta catalyst. Table 2.1 exhibits the properties of HDPE and LLDPE.

Table 2.1 : The properties of HDPE and LLDPE

Commercial product	LLDPE	HDPE
Density range, g/cm ³	0.918 - 0.935	0.941 - 0.965
Approximate % crystallinity	54 - 63	70 - 90
Crystalline melting point, °C	120 - 130	133 - 138
Tensile strength, psi	1,900 - 4,000	3,100 - 5,500
Elongation, %	100 - 950	200 - 1,000

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2.2 Metallocene catalyst

Metallocene catalyst species is not new, it was discovered in 1951. Natta conducted the first metallocene-polymerization research during early Ziegler-Natta catalyst development. Because they were unable to get good activity with conventional activator, they were put aside in favor of the traditional Ziegler-Natta catalysts based on TiCl_3 and TiCl_4 . Consequently, metallocene catalyst development was dormant for 20 years until new work sparked interest. Metallocene is a more elegant replacement for the term “iron sandwich”, initially used to describe the structure of dicyclopentadienyl iron $[(\text{C}_5\text{H}_5)_2\text{Fe}]$. Its structure was described separately by Wilkinson and Fischer in 1954 (Figure 2.1) as comprising an iron atom (Fe) sandwiched between parallel planar cyclopentadienyl group, and the name is now applied generally to similar organometallic structure.

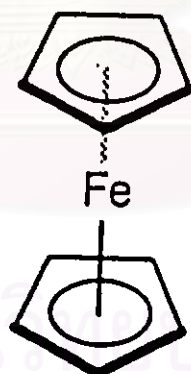


Figure 2.1 : The iron sandwich : The first metallocene

Ferrocene; Dicyclopentadienyliron; $(\text{C}_5\text{H}_5)_2\text{Fe}$

The level of industry research activity is tremendous and more than 50 metallocene catalyst families[10] have been discovered. Among these, the four basic metallocenes shown in Figure 2.2 appear to be the foundations for many other families. The upper two structures are nonstereoselective while the lower two structures exemplify the stereoselective families. The latter are known as "bridged metallocene" because the two cyclopentadienyl ligands are joined by a covalent bridge, in this case a methylene-center or isopropyl bridge. The bridge makes the structure rigid and enables the development of stereoselective catalysts. The left-hand system is isoselective and yields products, for example, that are similar to conventional isotactic polypropylene (PP). The other is syndioselective and is the first system developed that can produced highly syndiotactic (96-98%) PP, a new form of PP with several very interesting performance characteristics.

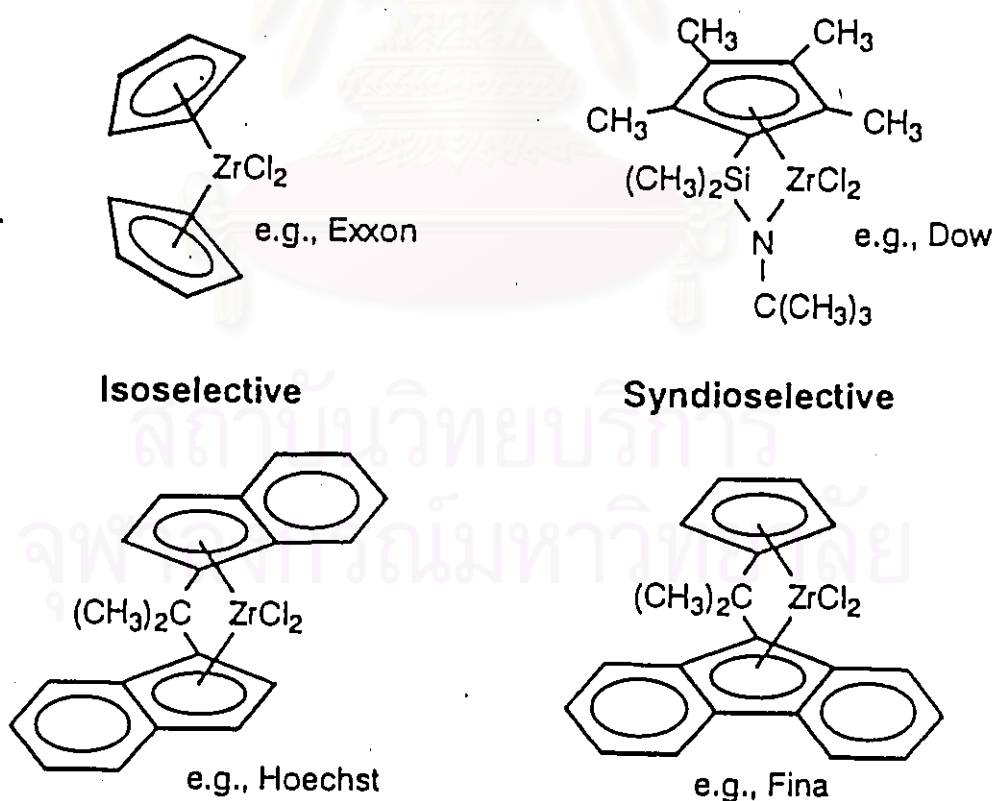


Figure 2.2 : Primary metallocene catalysts

The dichloride derivatives of the most common metallocene complexes are typically crystalline solids, stable in dry air, slowly hydrolyzed in moist air, and moderately soluble in toluene and polar organic solvents. They are not polymerization catalysts in themselves and must be activated with a cocatalyst. The most common cocatalysts are methyl aluminoxane (MAO), which are oligomeric compounds containing Al-O-Al linkages (Figure 2.3) prepared by hydrolysis of trimethyl aluminum (TMAL).

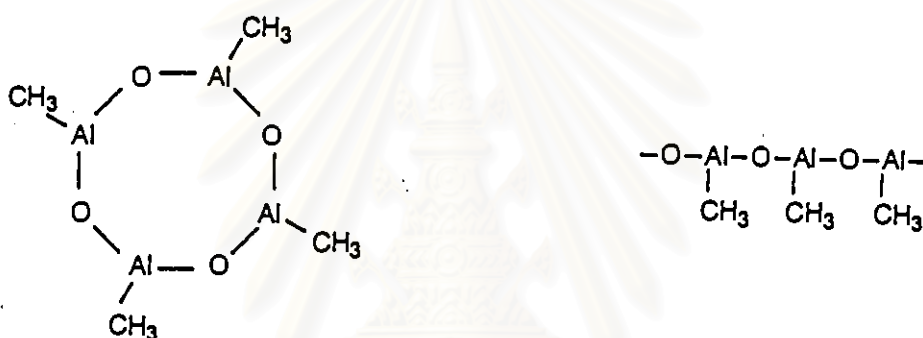


Figure 2.3 : Cyclic and linear methyl aluminoxane (MAO)

The behavior of a metallocene catalyst system is extremely sensitive to the geometry of the catalytic site at the transition metal, and thus to the chemical composition of the metallocene. For example, substitution of a particular hydrogen atom on the metallocene may change the catalyst from being highly stereoselective to having zero stereoselectivity, or from being highly active toward propylene polymerization to being almost totally inactive to propylene (but not to ethylene). This sensitivity to the molecular geometry of a single component of the catalyst system, the geometry of the catalytic site, can be designed to assemble precisely tailored polymer molecules from the appropriate reaction system.

Nowadays, metallocene catalysts can be defined as a compound consisting of a transition metal atom such as titanium and zirconium sandwiched between ring structures to form a sterically hindered site. It is the presence of these stereoselective catalytic sites that enable polymerization of almost any monomer even beyond the traditional C_3 to C_8 α -olefins in a precise manner. By the selection of proper metallocene catalysts, polymer molecular weight distribution and content, and tacticity can be independently controlled which otherwise was thought to be beyond control[5]. If one (high purity) metallocene composition is used, all the active polymerization sites are the same and each polymer molecule is therefore the same (within the limits allowed by the reactor configuration).

Metallocene catalysts have initiated a new era in polymer synthesis. These well defined catalysts now allow producers to design polymers with exact properties and to create as yet unknown material. Metallocene catalysts have proven to control properties such as polymer molecular weight, molecular weight distribution, comonomer distribution and content, and tacticity of the polyolefins in an efficient manner as compared to conventional catalyst. They tend to have features such as increased impact strength and toughness; better melt characteristics and improved clarity and higher puncture resistance in film.

The metallocene catalysts currently use for some production, polymerization takes place in a very defined pattern. It produces materials with narrow molecular weight distributions, and therefore a uniform comonomer distribution from one polymer chain to another resulting in more specific set of properties. One benefit of this single site catalyst process is that the outcome of polymerization is much more

predictable, which enables known effects to be more likely to repeat, and therefore from the basic of a more reliable modeling procedure.

2.3 Metallocene linear low-density polyethylene (MLLDPE)

The first material that used the metallocene catalyst is polyethylene, "Exact" from Exxon and "Affinity" from Dow, which introduced the material as a "Plastomer" and followed with a further series of materials called "Engage" which are true polyolefin elastomer[11].

Commercial grades of metallocene linear low density polyethylene (MLLDPE) have been available for some time, mostly in the US. Producers of polymer resins based on metallocene catalysts are pinning their hope on the packaging industry. Applications for MLLDPE are varied: packaging film should benefit from the material's improvement. It seem to agree with resin producers that the special properties of these resins could revolutionize the packaging industry.

MLLDPE differs from Ziegler - Natta linear low density polyethylene (Z-NLLDPE) in cooling and crystallization which firstly the crystal nuclei are formed, and then the crystals grow around these nuclei. Consequently, since the lamella thickness is determined by the high-density component, the lamellas are thick. In contrast, in the case of MLLDPE, these have not high-density component so uniform crystal nuclei form and grow, thus yielding thin lamella[12]. MLLDPE has an impact strength and tear strength two to three times greater than Z-NLLDPE. MLLDPE has excellent optical properties, especially in haze and gloss of the film, and lower melting point and offers a film that can be heat sealed at low temperature

due to the thin lamella. Because MLLDPE has a lower content of low-molecular-weight/low-density polymers than Z-NLLDPE, MLLDPE has excellent anti-blocking properties.

However, one major concern is the processability of MLLDPE. Due to its very narrow molecular weight distribution, MLLDPE is difficult to process. By comparison, rating of processability by rule of thumb has been set: from easiest to the most difficult as follows ; LDPE ranks 10, bimodal HDPE 8, LLDPE 4, typical MLLDPE 1. Terms of the processability debate changed in 1993 when Dow won a composition of matter patent on placing long chain branches in MLLDPE[13].



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2.4 Polymer blend

Polymer blend is a physical combining of two or more polymers without reaction[14]. The various types of property response of polymer A and B, when blended, are seen schematically in Figure 2.4. Incompatible blends produce lower than expected property response. Completely immiscible polymers represent the second category. When these polymer components are mixed in any proportion, the blend separates into distinct domains or phases, each containing an individual polymer. One polymer acts as the continuous phase and other is the discrete phase.

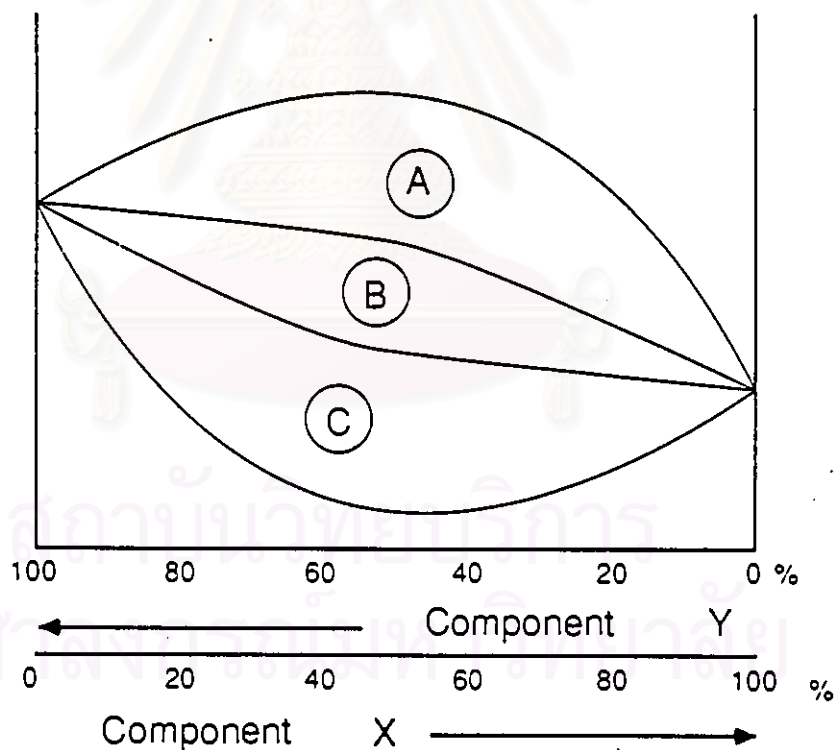


Figure 2.4 : Schematic of the relative effects of blending polymer. Region A represents synergism in properties. Region B represents simple property addition. Region C represents incompatibility in properties.

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.

2.5 Determination of polymer/polymer blend

There are several methods that can determine compatibility of polymer blend, 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 or microscopic techniques.

2.6 Literature reviews

Polyolefin blends are increasingly interested in terms of processability, producibility, production cost. The binary blend of high density polyethylene (HDPE) and linear low density polyethylene (LLDPE) in the range of composition from 100% HDPE to 100% LLDPE has been investigated for mechanical properties and the morphology by various works. However, the most of those works were used Z-NLLDPE and using the injection mold or compression mold to prepare the specimen for physical property testing.

A.K. Gupta and others [15,16,17,18] who were performed HDPE/Z-NLLDPE blend and investigated their mechanical properties such as flexural, impact and tensile, etc. including the morphology. They found that the properties of HDPE and Z-NLLDPE are distinguished by three-regions of blend composition, viz. (i) 0-30% Z-NLLDPE content (i.e., HDPE rich blend), (ii) 70-100% Z-NLLDPE content (i.e., Z-NLLDPE rich blend), and (iii) the middle zone. The cocrystallization of HDPE and Z-NLLDPE occurs at all compositions of their blend prepared by melt mixing

in a single screw extruder. Mechanical properties of the HDPE/Z-NLLDPE blend vary with the blending ratio and the variations are linear and nonlinear.

Hoseok[19] suggested that HDPE/Z-NLLDPE system was miscible blend in the crystalline and amorphous phase the same as A.K, Gupta's report.

Kim[20] had been considered the mechanical properties of blown HDPE film due to its most widely use. The most important mechanical properties of blown HDPE film are impact strength and tensile property. Blown films having a broad range of morphology were produced under several processing conditions. The mechanical properties of blown HDPE films are highly associated with their morphological feature, which are dependent on the overall characteristics of HDPE resins. Some correlations were found between the anisotropy of the tear and tensile properties of blown HDPE films and the state of orientation of the crystalline molecular chain axes and lamella stacks at the film plan.

Yu-T.[21,22] studied the influence of molecular weight distribution and extrusion processing variables on the morphological feature and orientation of HDPE uniaxially tubular films. The results shown that the final morphological structure and molecular weight distribution are a very important parameters in HDPE extruded film in influencing their properties.

There are many researches studied in the morphology or properties of MLLDPE, for examples, Starck-P[23] studied the amount and distribution of branching and compared with Z-NLLDPE by using DMA. It was found that

MLLDPE gave the highest tan delta intensity value which demonstrated the ease of incorporating higher comonomer amounts in the case of single site polymer.



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