

CHAPTER IV

EXPERIMENT

In this research, the ethylene polymerization with high activity homogeneous Ziegler - Natta catalyst, the experiment were divided three part :

1. Catalyst preparation
2. Ethylene polymerization
3. Characterization of polymer product

The details of the experiment were discussed in following.

4.1 CHEMICAL

The chemicals used in this experiment were normally analytical, but only critical chemical had to specified as follows.

1. Ethylene gas (98.5%pure) was supplied from Union Carbide Thailand Limited. It was purified by passing through a column packed with molecular sieve 5A size 11/6 mm. supplied from Union Carbide Thailand limited to remove traces of moisture.

2. Ultra high purity oxygen free nitrogen gas with oxygen and moisture content less than 3 ppm. was supplied by Thai Industrial Co., Ltd.

3. Aluminum sulfate octahexahydrate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) was manufactured by J.T. Baker.

4. Bis (cyclopentadienyl)zirconium dichloride (Cp_2ZrCl_2) was supplied by FlukaChemie AG, Switzerland, used as without further purification

5. Toluene (C_7H_8) used as polymerization solvent was supplied from E. Merck, Federal Republic of Germany. Toluene used in catalyst preparation was freshly reflux over sodium metal.

6. Trimethylaluminum ($\text{Al}(\text{CH}_3)_3$), 15% in hexane was supplied from Tokyo kasei without further purification.

7. Methanol (CH_3OH) was manufactured J.T. Baker used as quenched catalyst.

4.2 EQUIPMENT

All apparatuses were carried out in the polymerization and characterization instruments as follows :

4.2.1 Glass Reactor

The polymerization reactor was a modified glass bottle as used a cap having a septum for injection. It had total volume being 100 cm^3 . The reactor was operable in pressure range of 0-40 psi. and the temperature range 0 -100 °C.

4.2.2 Magnetic Stirrer and Hot plate

The magnetic stirrer and hot plate having solid ceramic top were impact-resistant, acid and alkali resistant. It was used to heat maximum temperature 530 °C, and provided to control of stirring speed 100-1000 rpm.

4.2.3 Cooling System

The cooling equipment as shown in Figure 4.1 was used in preparing cocatalyst. As initial preparing cocatalyst reaction, the reaction temperature was immediately increased. Following the reaction was reduced so can be control the temperature. Cooling system was divided into 3 part, one coil for refrigerating, temperature control, and pump. It was conduct another coil for cooling be prepared cocatalyst.

4.2.4 Gas Contribution System

The system consisted of : ultra high purity nitrogen feeding lines and ethylene feeding lines. For the investigating of ethylene consumption rate, a storage ethylene tank was used and connected to the line of ethylene cylinder. The storage tank was equipped with a pressure gauge to measure the amount of consumed ethylene during polymerization. A pressure gauge (0 - 235 psig) was used for indicating the reaction pressure.

4.2.5 Syringe, Needle and Septum

The syringe and needle were 20, 10, 2, 1 and No. 22, 25, respectively. The septum was a silicone rod. It was used for prevent surrounding air when transfer a solvent or cocatalyst

4.3 CHARACTERIZATION INSTRUMENTS

The instrument used to characterization the polyethylene products were specified in the following.

- Fourier Transformed Infrared Spectroscopy (FT -IR)

It was employed to study the microstructure of polyethylene.

- Ubbelohde Viscometer.

The molecular weight of the polyethylene was determined by viscometer. The flow time of the fluid that flowed through the capillary was used to determine intrinsic viscosity was measured from the aliquot of diluted solution of polyethylene by Ubbelohde viscometer, Figure 4.2

- Scanning Electron Microscopy (SEM)

As show in Figure 4.3, It was applied to investigate the morphology of the polyethylene particles. After, the polymer sample was coat with gold by Ion sputtering device, Figure 4.4.

4.4 PROCEDURE

4.4.1 Methylaluminumoxane Cocatalyst

It was also to know to prepare oligomeric mixture of aluminumoxanes having a degree of oligomerization between 2- 12 by reacting trimethylaluminum with copper sulfate containing water of crystallization ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$). However, in this case the yield was only approximate 30% relative to

the trimethylaluminum employed. A further disadvantage was that, as a result of reduction of reduction reaction, traces of copper always remain in the aluminoxane thus prepared, and these color these product yellow to red. Before being used as a component of the catalyst in the polymerization of olefins, It must be filtered, purified and recrystallization, since otherwise the polymerization was interfered with and the quality of the polymer was adversely affected. Since aluminum salt was containing water of crystallization. It was preferably that $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ used instead of copper sulfate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

In a 100 ml, modified bottom equipped with a magnetic stirrer and magnetic bar were place 4 g of fine $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and 8 ml of hexane. 40 ml of a 15% in hexane solution of trimethylaluminum were added dropwise at 0 °C. After 2 hr. reaction the temperature was slowly raised to 20 °C. Stirring was maintained for 40 hours. The solution was separated from aluminum salts and used as a stable cocatalyst solution for the production of the soluble Ziegler - Natta catalyst.

4.4.2 Catalyst Preparing

Bis(cyclopentadienyl) zirconium dichloride was added to 10 mg. to the vial with a septum cap under nitrogen atmosphere. Toluene solvent was filled in the vial 10 ml by syringe. Shaken the catalyst until to clear solution, it was used a catalyst for production of soluble Ziegler - Natta catalyst.

4.5 POLYMERIZATION

The polymerization of ethylene was carried out in the 100 ml of glass reactor. It was operated under a constant pressure. Modified bottom and magnetic bar were dried in oven at 110 °C for several hours before used in the ethylene polymerization. In each experiment, glass reactor was purged with nitrogen and toluene 50 cc. was filled in its. Then, the cocatalyst which prepared by method described in section 4.4.1 was injected in the reactor by syringe. Next, the catalyst which prepared by method described in the section 4.4.2 was add in the reactor. The catalyst was then activated at room temperature and it was mixed by magnetic stirred and control temperature set point was requirement. The ethylene gas was pass into the reactor and constant pressure. The rate of polymerization was determine from ethylene consumption rate measured by the decrease of pressure in ethylene tank.

By stopping admission of ethylene gas and depressurization, the polymerization reaction was quenched. The 50 ml of methanol was poured into the polymerization mixture for a while to deactivate the catalyst and the polymer was then separated and dried 110 °C for 12 hours.

The studied of ethylene polymerization on high activity homogeneous Ziegler - Natta catalyst was divided into two parts. Firstly the suitable polymerization condition and their effects on ethylene polymerization were studied on bis(cyclopentadienyl) zirconium dichloride- methylaluminoxane catalytic system. As the optimum condition was selected, the experimental

investigation of condition and effects on the polymerization were conducted as follows :

4.5.1 The Effect of Catalyst Ratio

The catalyst ratios were varied from 700 - 8800. The reaction temperature was 0 - 80 °C and reaction time 1.5 hr. The ethylene partial pressure was 20 psi. The zirconium metal in catalyst suspension was fixed at 34×10^{-6} moleZr/l.

4.5.2 The Effect of Ethylene Partial Pressure

The polymerization conditions were used at the selected resulting condition (i.e. Al/Zr mole ratio, Cp_2ZrCl_2 concentration, temperature). The partial pressure of ethylene was varied from 10 to 40 psi.

4.5.3 The Effect of Temperature

The ethylene polymerization was further studied by varied temperature at the condition of suitable selection from the previous part. The temperature was varied 0 - 80 °C.

4.5.4 The Effect of Cocatalyst

The ethylene polymerization was usually carried out in bis (cyclopentadienyl) zirconium dichloride/methylaluminoxane catalytic system. The methylaluminoxane cocatalyst was replaced with other cocatalyst. In this experiment, ethylaluminoxane was prepared as for the new cocatalyst.

4.6 CHARACTERIZATION OF THE POLYETHYLENE PRODUCTS

The polyethylene product possess remarkable chemical inertness, particularly at ordinary temperature, to most chemical, including acid and alkalies. Chemical analysis used to characterize polyethylene was a few. As a result this, a quantitative measurement of physical properties and determination involving chemical and physical structure have increased important. In this work the polyethylene polymer products were characterized as described in the following.

4.6.1 Microstructure Determination

Infrared spectroscopic techniques are suited for quantitative determine microstructure of polymer such as methyl groups, unsaturation and carbonyl. In practice, conversion of infrared adsorption intensities to concentration values are made by use of adsorptivities calculated from model compound. Figure 4.5 shows the polyethylene spectrum. There are three very strong bands at 2950, 1460, and 720/730 cm^{-1} . These are assignable to the C-H stretching, deformation and rocking modes of CH_2 groups. At 1378 cm^{-1} is generally presence amount of chain branching in the polyethylene.

In addition to chain branching there is a second type of defect structure, occasional double bonds. These are readily identified by out-of-plane deformation mode. polymer made by the Phillips process one end of chain terminated by vinyl group which give the sharp band at 910 cm^{-1} . Low density polyethylene from high pressure polymerization contain vinylidene group, which absorb 890 cm^{-1} , while polymer prepared with a Ziegler - Natta

catalyst frequently have a mixture of three types of unsaturation, the two already mention together with trans CH=CH- , characterized by band at 985 cm^{-1} .

4.6.2 Molecular Weight

The viscosity of polyethylene solution has a relationship to its viscosity- average molecular weight. It is applicable to a reasonable wide spectrum of ethylene polymer having density 0.910 to 0.970 g/cm^{-3} . Elevated temperature, 135 °C is employed because of the insolubility of polyethylene at room temperature. The method test was referred in ASTM 1601. The viscosity-average of molecular weight (\bar{M}_v) of polymer is obtained by the Mark-Houink-Sakarada equation

$$[\eta] = k\bar{M}_v^a$$

Where $[\eta]$ = intrinsic viscosity

k, a = 2.3×10^{-4} , 0.82 respectively

4.6.3 Morphology

The term of morphology was refer to the shape, texture, or form of such a polyethylene. The polymer sample was coated with gold plate by ion sputtering device in Figure 4.4. Scanning Electron Microscopic technique was the effective method to investigate these morphologies.

4.6.4 Rate of Polymerization

The ethylene consumption during the polymerization time was expressed as a curve of gmole at room temperature of ethylene consumed versus time.

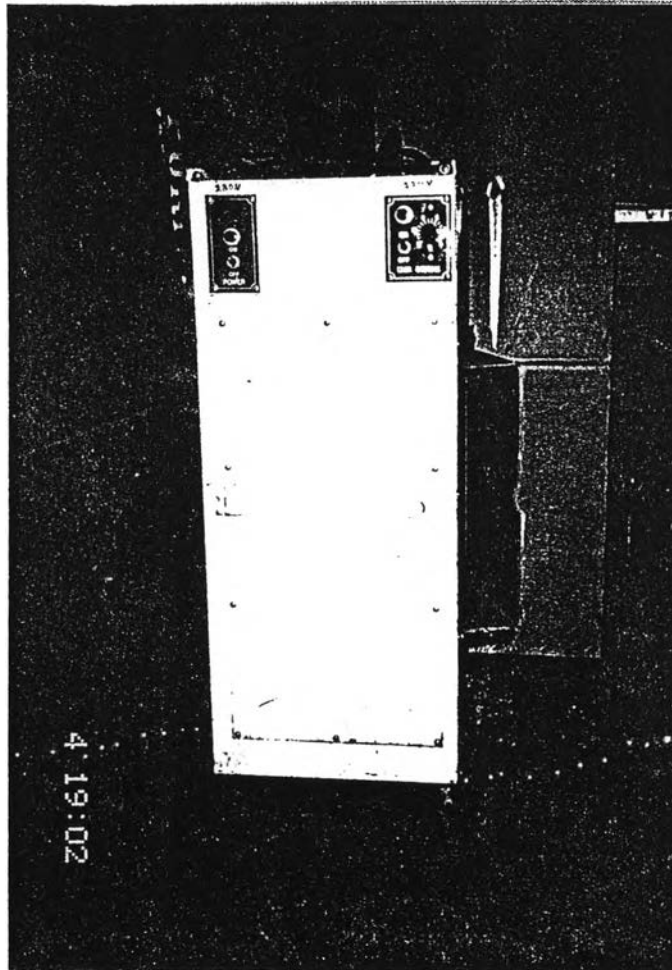


Figure 4.1 Cooling system

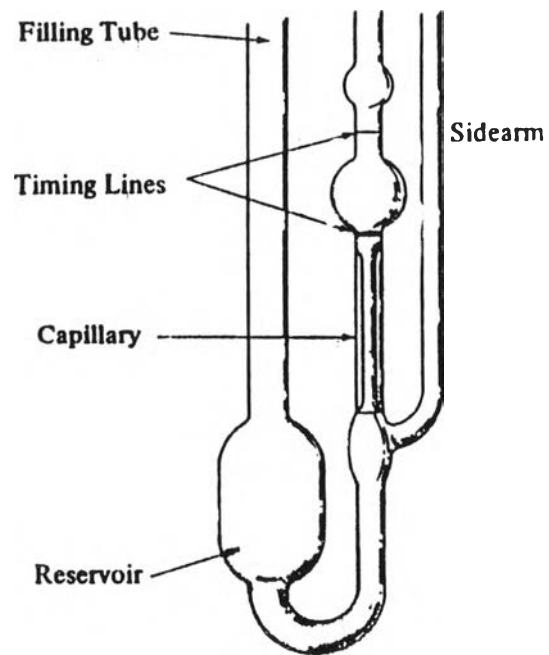


Figure 4.2 Ubbelohde viscometer

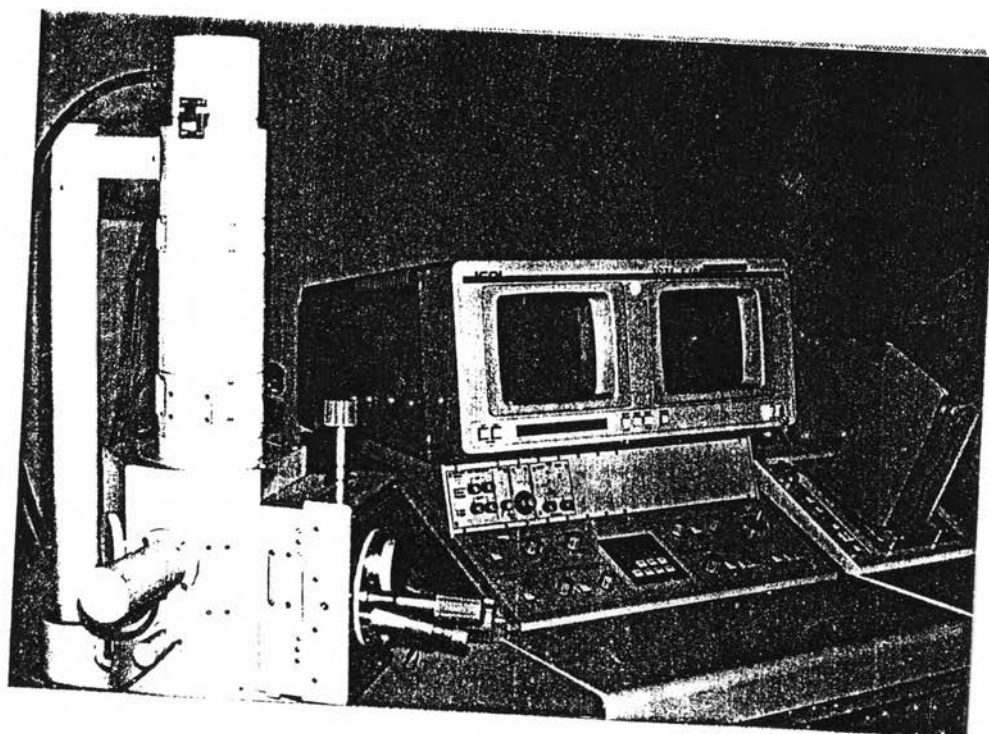


Figure 4.3 Scanning Microscope



Figure 4.4 Ion sputtering device

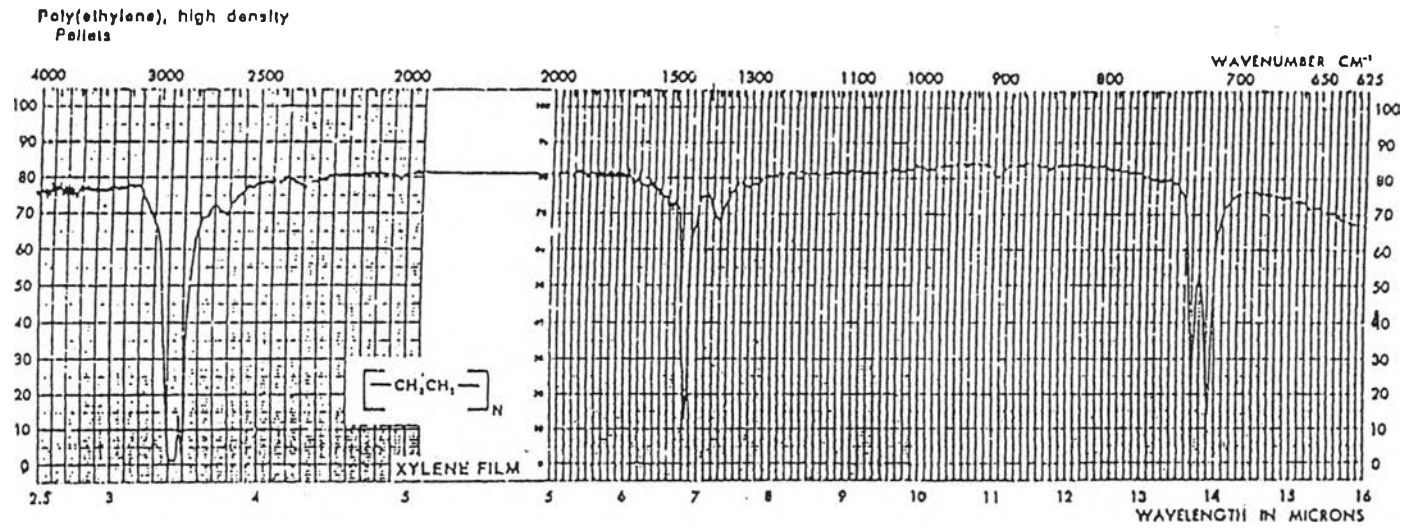


Figure 4.5 Infrared spectrum of high density polyethylene