

## CHAPTER III EXPERIMENTAL

### 3.1 Materials and instruments

#### Materials

- Magnesium ethoxide (commercial grade, Degussa). An average particle size is 700 micron in diameter.
  - Toluene (analytical grade, Mallinckrodt Chemical) was kept under molecular sieve 4 Å and stripped with N<sub>2</sub> before use.
  - Ethanol (analytical grade, Merck) was dried over preactivated molecular sieve 4 Å.
  - Carbon dioxide (99.999 %, Lab center).
  - Titanium tetrachloride (commercial grade, Ti oxide UK Limited).
  - Heptane (processing grade, IRPC Public Company) was distilled and kept under molecular 4 Å sieve and stripped with N<sub>2</sub> before use.
  - Hexane (commercial grade, IRPC Public Company) was from high density polyethylene plant and stripped with N<sub>2</sub> before use in polymerization.
- Ethyl benzoate (GC grade, 99.8%, Fluka).
- Dicyclopentyl dimethoxysilane (DCPDMS) (99.99%, Xiangyang).
  - Ethyl aluminium sesquichloride (EASC) and triethyl aluminium (TEA) (commercial grade supplied by Chemtura) were diluted by dried hexane.

Ethylene, hydrogen and nitrogen gas of polymerization grade, supplied by IRPC Public Company.

### **Instruments**

- 2-liter autoclave stainless steel for polymerization (Buchi).
- Particle sizer analysis (Sympatec particle sizer, HELOS/KF, Oasis and Gradis system).
- FT-IR spectrometers (Perkin Elmer, 1760X).
- Thermogravimetric analyser (TGA) (Perkin Elmer, 7DX).
- Scanning electron microscope (SEM) (JEOL, JSM 6031F).
- Gel permeation chromatograph (GPC) (Polymer Laboratories, PL GPC 220 high temperature chromatography).
- Melt flow indexer (Gottfert, MPX 62.92).
- Cone & plate rheometer (Physica MRC 301).

### **3.2 Preparation and characterization of magnesium ethyl carbonate**

Magnesium ethyl carbonate was formed by suspending 0.25 mol of magnesium ethoxide in 0.25, 0.5, 0.75 and 1 mol of ethanol medium and 400 ml of toluene, adding carbon dioxide 40 psig at ambient temperature until the magnesium ethoxide was dissolved. Magnesium ethyl carbonate was precipitated from the solution as discrete spheres by treating with 0.125 mol of ethyl aluminium sesquichloride (EASC). The agitation speed was varied to 300, 400, 500, 600, and 700 rpm in order to control the particle size of the support.

Magnesium ethyl carbonate was characterized by FTIR and TGA. Its particle size was determined by particle sizer.

### 3.3. Preparation and characterization of catalyst

#### 3.3.1. Preparation of catalyst

The magnesium ethyl carbonate prepared above was reacted with chlorinating agent: ethyl aluminium sesquichloride  $\text{Al}_2\text{Et}_3\text{Cl}_3$ . Titanation reaction is performed by dropwise adding of  $\text{TiCl}_4$  (with varying ratio of Mg to Ti at various temperatures) over 4 h. Agitation speed and treatment time were varied at treatment temperature of  $110^\circ\text{C}$ . After that, the motor was stopped and catalyst was settled down. Mother liquor was siphoned off and a new portion of fresh hydrocarbon solvent was introduced. The temperature was controlled over  $65^\circ\text{C}$ . The catalyst was washed several times until the titanium content in mother liquor was lower than 10 mmol/l. Finally the Ti content in the catalyst was determined. The catalyst was used for ethylene polymerization.

The following reaction parameters were studied. Each optimum molar ratio found was used in next experiment.

1. The effect of molar ratio of chlorinating agent (EASC) to magnesium component
2. The effect of molar ratio of Ti:Mg (2, 3, 4, and 5 )
3. The effect of number of titanation with  $\text{TiCl}_4$  (using the optimum ratio from 2)
4. The effect of heat treatment time at  $110^\circ\text{C}$  for 2, 5, and 10 h (using the optimum ratio from 3)
5. The effect of molar ratio of EB:Mg (using the optimum ratio from 4)

6. The effect of aging time after addition of EB (using the optimum ratio from 5)
7. The effect of dicyclopentyldimethoxysilane as binding agent during support preparation

### 3.3.2 The metal contents in catalyst

The metal contents in the catalyst were determined by following methods.

#### A. Titanium concentration

100 ml 2N sulfuric acid and about 5 ml of zinc amalgam were filled in a 300 ml conical flask with ground stopper place. During reaction, the sample was pipetted into the conical flask, shaken vigorously for 10 minutes. The zinc amalgam was separated via the connecting rubber tube into the small test tube, where the system is completely filled with water. This method ensures perfect removal of the zinc amalgam. Then 10 drops of diphenylamine solution were added and titrated with 0.2 N  $\text{Ce}(\text{SO}_4)_2$  solution.

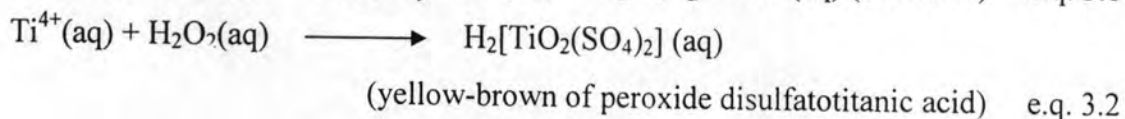
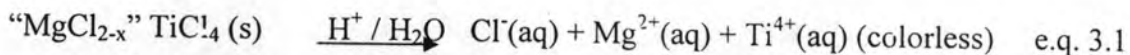
#### Calculation of Ti concentration

Ti concentration (mmol/l) = (consumption of 0.2 N  $\text{Ce}(\text{SO}_4)_2$ ) \* (1000) / ml sample

#### B. Percentage of titanium content in catalyst

100-150 mg of the solid catalyst was dissolved in 40 ml of 30% of sulfuric acid. The adjusted volume was performed by water in 100 ml volumetric flask. Then, 2 ml of  $\text{H}_2\text{O}_2$  was added to form color. The sample was analyzed by using visible spectrophotometer at  $\lambda = 410$  nm. The percentage of Ti in catalyst is calculated by the standard calibration curve.

The Ti content in catalyst containing quadrivalent ( $Ti^{4+}$ ) and trivalent ( $Ti^{3+}$ ) titanium is hydrolyzed with dilute aqueous sulfuric acid. The Ti was then oxidized by  $H_2O_2$ . The Ti content were analyzed by using visible spectrophotometer ( $\lambda=410$  nm) (see equations 3.1 and 3.2)



### C. Magnesium concentration

60 ml of 2N sulfuric acid was added in a 250 ml Erlenmeyer flask with stopcock. The catalyst sample was put into the conical flask and washed with acetone. It was stirred for 3 h. The volume was adjusted by using water in 250 ml volumetric flask. 20% NaOH was added into the sample to make pH adjustment to be about 4-6 for Ti precipitation from the sample. The precipitated Ti was filtrated from the solution. The sample was divided into two parts. The first part was kept for determination of magnesium concentration whereas the second part was used for determination of chloride concentration.

200 ml of the solution was pipetted and made volume by using water in 500 ml volumetric flask. After that 50 ml of prepared solution was pipetted into an erlenmeyer flask. A tablet of indicator-puffer tabelete, 5 ml of Triethanolamine, and 1 ml of 25%  $NH_4OH$  was added in the solution respectively, then treated with 0.1M EDTA.

$$\text{Mg concentration (mmol/l)} = V_n/F$$

$V$  = consumption volume of EDTA (ml)

$n$  = concentration of EDTA

$F$  = dilution factor (0.002)

#### D. Percentage of magnesium content in catalyst

The catalyst, 150-200 mg was dissolved in 2 ml of HCl and 50 ml of water. The pH of the catalyst sample was adjusted by adding 40 ml of buffer (pH = 10) and 0.5 ml of Na<sub>2</sub>S. Then the temperature was raised to 55°C. After that 0.5 g of Eriochrome black T (indicator) was added and then titrated with tritriplex III solution (Na-EDTA).

#### E. Chloride concentration

25 ml of the separated sample in the part of determination of magnesium was pipetted to a beaker. The chloride concentration was determined following the ASTM D 512-88. Chloride concentration in catalyst was analyzed by autometric titrator (Metrohm model 702 SM titrino, Ag/AgCl electrode model 6.0404.100PF).

#### F. Percentage of chloride content in catalyst

200-250 mg of dried catalyst was dissolved in 50 ml of deionization water. After adding 5 ml of 20% HNO<sub>3</sub>, chloride content in catalyst was analyzed by autometric titrator (Metrohm model 702 SM titrino, Ag/AgCl electrode model 6.0404.100PF).

### 3.3.3. Functional group of catalysts

FTIR-spectra of catalysts were recorded by using PERKIN-ELMER spectrometer (model 1760). The catalyst sample was well milled with KBr in nitrogen glove box and compressed in to a thin disc. The sample was placed in a sample holder under nitrogen atmosphere. FTIR-spectra were recorded at the wavelength of 400-4000 cm<sup>-1</sup>.

### 3.3.4. Determination of particle size of catalyst

Average particle size and particle size distribution were determined by using Sympatec particle sizer (HELOS/KF; Laser Diffraction, HELOS sensor R3 for size

range of 0.5-175 micron, focal length of 100 mm). The catalyst was filled into small volume unit, which was connected to SUCELL dispersion system under nitrogen gas. Concentration of injected catalysts was monitored via HELOS program. After that, average particle size at mean over volume ( $D [4, 3]$ ) and particle size distribution of samples was recorded.

### **3.3.5. Morphology**

The morphology of catalyst was determined by using scanning electron microscope (SEM). It has been known that the catalyst is highly sensitive to moisture. Therefore, precautions were taken to limit the particle exposure. Catalysts were prepared in the nitrogen glove box and then sealed in a plastic container. The container top was sealed with parafilm. The samples were then quickly transferred to the gold coating machine. This machine was operated in vacuum. After the layer of gold was applied, the sample was transferred to the SEM chamber, which was also under nitrogen or vacuum. SEM analyses were performed using JSM 6031 JEOL operating at 3 kV. The image magnification was varied from 750 to 5,000. The SEM pictures showed the shape and texture of the particles formed.

## **3.4. Ethylene polymerization and characterization of polymer**

### **3.4.1. Ethylene polymerization**

#### **A. High molecular weight polyethylene**

1000 ml of hexane and 1 mmol triethyl aluminium (TEA) were successively added to a 2-liter reactor filled with nitrogen gas. The catalyst (containing 0.02 mmol Ti) was added. Then, the reactor system was purged three times with 4 bar of nitrogen. The temperature of the reactor was raised to 85°C and 1 bar of hydrogen was fed into the reactor, followed by ethylene feeding for 2 h. The total pressure of the reactor was kept at 8 bar. After that the ethylene feeding was stopped and the reactor was cooled down to room temperature. The polymer powder was separated from hexane and dried in a drying oven at 85°C for 2 h.

### **3. Low molecular weight polyethylene**

1000 ml of hexane and 1 mmol triethyl aluminium (TEA) were successively added to a 2-liter reactor filled with nitrogen gas. The catalyst (containing 0.02 mmol Ti) was added. Then, the reactor system was purged three times with 4 bar of nitrogen. The temperature of the reactor was raised to 85°C and 3 bar of hydrogen was fed into the reactor, followed by ethylene feeding for 2 h. The total pressure of the reactor was kept at 8 bar. After that the ethylene feeding was stopped and the reactor was cooled down to room temperature. The polymer powder was separated from hexane and dried in a drying oven at 85°C for 2 h.

#### **3.4.2. Melt flow properties**

Melt flow index (MFI) properties were determined with a MPX 62.92 Gottfert Melt flow Indexer at 190°C according to the ASTM D1238 2.16/190°C, MFI 5/190°C, and MFI 21.6/190°C.

#### **3.4.3. Molecular weight and molecular weight distribution**

Molecular weight (MW) and molecular weight distribution (MWD) of polymer were measured using a PL-GPC high temperature chromatographer with differential refractive index detector and viscometric detector. The polymer samples were dissolved in *o*-dichlorobenzene (ODCB) at a concentration of 0.02 wt% and measured at 160°C with a flow rate of 1 ml/min. The GPC was equipped with two linear crosslinked polystyrene columns (PLgel: Mixed-B). The reaction times were calibrated at 160°C against known monodisperse TSK polystyrene standards.

#### **3.4.4. Determination of particle size of polymer powder**

Particle size and particle size distribution of powders were determined by Sympatec particle sizer. (HELOS/KF; Laser Diffraction, RODOS R4 for the size range of 0.5-350 micron and focal length of 200 mm). Powders were filled into small



volume unit which was connected to RODOS system under air pressure of 6 bars in HOLOS/KF. After that, average particle size at mean over volume ( $D [4, 3]$ ) and particle size distribution of samples was recorded.

#### **3.4.5. Morphology**

The morphology of polyethylene powder was determined by using scanning electron microscope (SEM). Powders were deposited on SEM stubs. The samples were transferred to the gold coating machine. After the layer of gold was applied by the sputtering technique to avoid electronic discharges during observations. SEM analyses were performed using JSM 6031, JEOL operating at 3 kV. The image magnification varied from 50 to 15,000. The SEM pictures presented the shape of the particles formed.

#### **3.4.6. Bulk density**

The bulk density of powder was determined by weight of polyethylene in 100 ml of cylinder following the ASTM D1895.