

CHAPTER III

EXPERIMENTAL

In the present study of LLDPE- Al_2O_3 nanocomposite synthesized via in situ polymerization with zirconocene/d-MMAO catalyst was investigated. The experiments were divided into four parts:

- (i) Preparation of d-MMAO
- (ii) Preparation of catalyst precursor
- (iii) Ethylene and 1-hexene copolymerization procedure
- (iv) Characterization of nano- Al_2O_3 , catalyst precursor nano- Al_2O_3 /d-MMAO and ethylene and hexene copolymer products

The details of the experiments are explained as follows.

3.1 Chemicals

The chemicals used in these experiments were analytical grade, but only major materials are specified as follows:

1. rac-Ethylenebis(indenyl)zirconium dichloride ($\text{Et}(\text{Ind})_2\text{ZrCl}_2$) was supplied from Aldrich Chemical Company, Inc. and used without further purification.
2. Ethylene gas (99.96%) was devolved from National Petrochemical Co., Ltd., Thailand and used as received.
3. 1-Hexene (99+%) was purchased from Aldrich Chemical Company, Inc. and purified by distilling over sodium under argon atmosphere before use.
4. Modified methylaluminoxane (MMAO) in hexane was donated by Tosoh (Akso, Japan). and used without further purification.
5. Trimethylaluminum [$\text{Al}(\text{CH}_3)_3$] 2.0 M in toluene was supplied from Nippon Aluminum Alkyls Ltd., Japan and used without further purification.
6. Triethyl ortho silicated (TEOS).

7. The Al_2O_3 nanofiller was obtained from Sigma-Aldrich having surface area of $35 \text{ m}^2/\text{g}$ and it was vacuum heated at $400 \text{ }^\circ\text{C}$ for 6 h prior to impregnation.

8. Hydrochloric acid (Fuming 36.7%) was supplied from Sigma.

9. Methanol (Commercial grade) was purchased from SR lab.

10. Toluene was devoted from EXXON Chemical Ltd., Thailand. This solvent was dried over dehydrated CaCl_2 and distilled over sodium/benzophenone under argon atmosphere before use.

11. Ultra high purity argon gas (99.999%) was purchased from Thai Industrial Gas Co., Ltd., and further purified by passing through columns packed with molecular sieve 3 A, BASF Catalyst R3-11G, sodium hydroxide (NaOH) and phosphorus pentaoxide (P_2O_5) to remove traces of oxygen and moisture.

3.2 Equipments

All types of equipments used in the catalyst precursor preparation and polymerization are listed below:

3.2.1 Cooling system

The cooling system was in the solvent distillation in order to condense the freshly evaporated solvent.

3.2.2 Inert gas supply

The inert gas (argon) was passed through columns of BASF catalyst R3-11G as oxygen scavenger, molecular sieve $3 \times 10^{-10} \text{ m}$ to remove moisture. The BASF catalyst was regenerated by treatment with hydrogen at $300 \text{ }^\circ\text{C}$ overnight before flowing the argon gas through all the above columns. The inert gas supply system is shown in Figure 3.1.

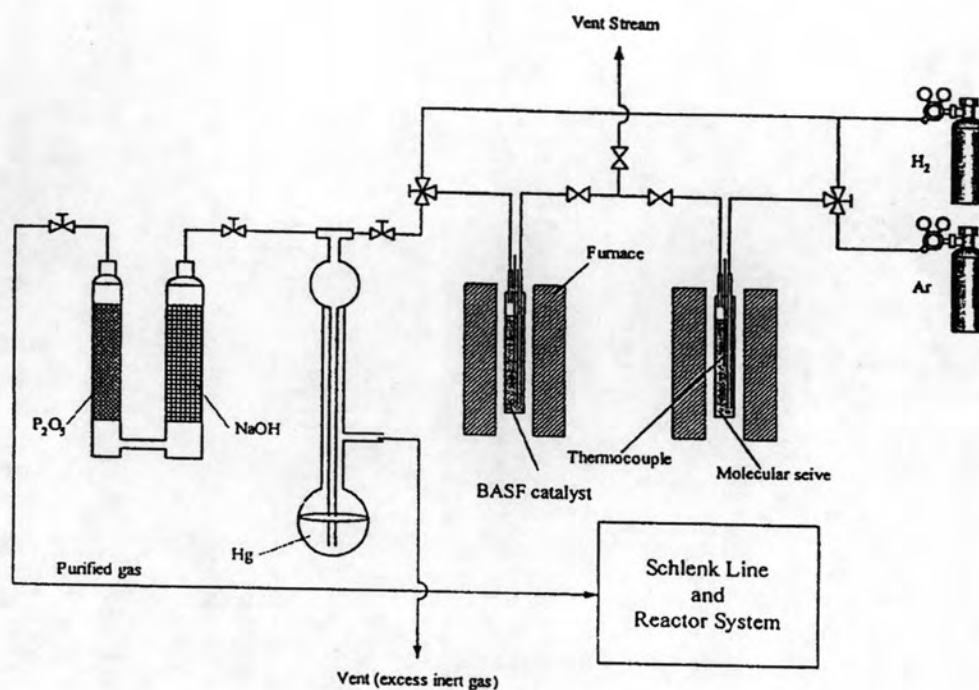


Figure 3.1 Inert gas supply system

3.2.3 Magnetic stirrer and heater

The magnetic stirrer and heater model RTC basis from IKA Labortechnik were used.

3.2.4 Reactor

A 100 ml stainless steel autoclave was used as the copolymerization reactor.

3.2.5 Schlenk line

Schlenk line consists of vacuum and argon lines. The vacuum line was equipped with the solvent trap and vacuum pump, respectively. The argon line was connected with the trap and the mercury bubbler that was a manometer tube and contain enough mercury to provide a seal from the atmosphere when argon line was evacuated. The Schlenk line was shown in Figure 3.2.

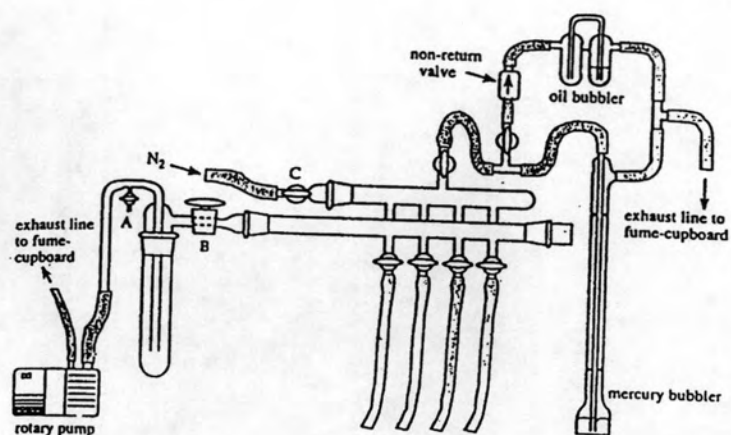


Figure 3.2 Schlenk line

3.2.6 Schlenk tube

A tube with a ground glass joint and side arm, which was three-way glass valve as shown in Figure 3.3. Sizes of Schlenk tubes were 50, 100 and 200 ml used to prepare catalyst and store materials which were sensitive to oxygen and moisture.

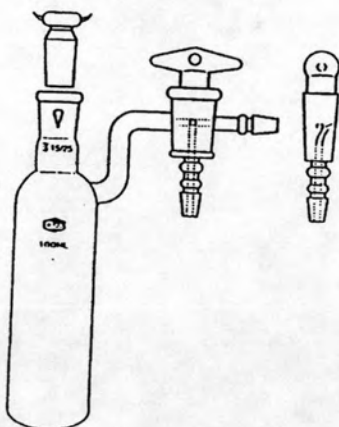


Figure 3.3 Schlenk tube

3.2.7 Vacuum pump

The vacuum pump model 195 from Labconco Corporation was used. A pressure of 10^{-1} to 10^{-3} mmHg was adequate for the vacuum supply to the vacuum line in the Schlenk line.

3.2.8 Polymerization line

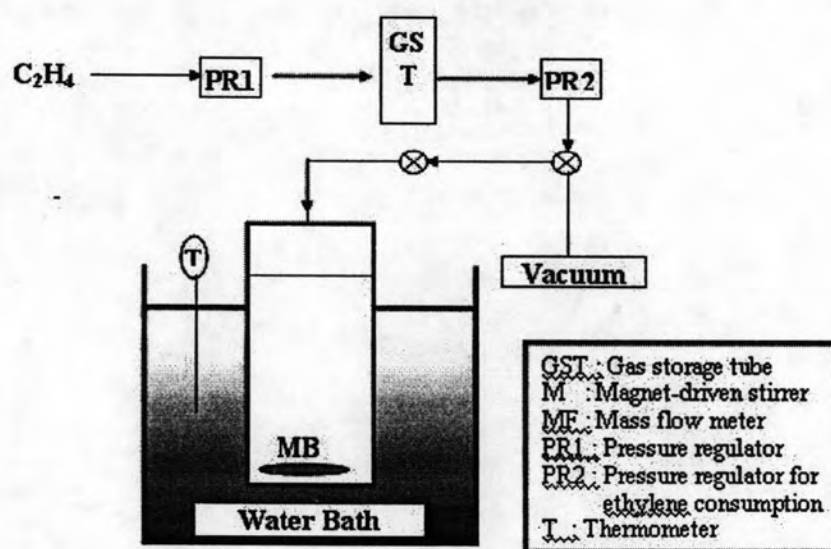


Figure 3.4 diagram of system in slurry phase polymerization

3.3 Characterizing instruments

The instruments used for characterizing catalysts and ethylene/ α -olefin copolymer products are specified below.

3.3.1 Differential scanning calorimetry (DSC)

The melting temperature of ethylene/ α -olefin copolymer products was determined with a Perkin-Elmer diamond DSC from MEKTEC, at the Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical

Engineering, Chulalongkorn University. The analyses were performed at the heating rate of 20 °C/ min in the temperature range of 50-150 °C. The heating cycle was run twice. In the first scan, samples were heated and the cooled to room temperature. In the second, samples were reheated at the same rate, but only the results of the second scan were reported because the first scan was influenced by the mechanical and thermal history of samples.

3.3.2 Nuclear magnetic resonance (NMR)

The ^{13}C -NMR spectra were recorded at 100°C using JEOL JNM-A500 operating at 125 MHz. Copolymer solutions were prepared using 1,2 - dichlorobenzene as solvent and benzene- d_6 for internal lock.

3.3.3 Scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX)

SEM observation with a JSM-5800 LV Scanning Microscope, Microspec EDX at Scientific Technological Research Equipment Center, Chulalongkorn University was employed to investigate the morphology of catalyst precursor and polymer. The polymer samples for SEM analysis were coated with gold particles by ion sputtering device to provide electrical contact to the specimen. EDX was performed using Link Isis series 300 program.

3.3.4 X-ray diffraction (XRD)

XRD was performed to determine the bulk crystalline phases of sample. It was conducted using a SIEMENS D-5000 X-ray diffractometer with $\text{CuK}\alpha$ ($\lambda = 1.54439 \times 10^{-10}$ m). The spectra were scanned at a rate 2.4 degree/min in the range $2\theta = 20$ -80 degrees.

3.3.5 Gel permeation chromatography (GPC)

The molecular weight and molecular weight distribution of polymer was determined using gel permeation chromatography (GPC, PL-GPC-220). Samples were prepared having approximately concentration of 1 to 2 mg/ml in trichlorobenzene (mobile phase) by using the sample preparation unit (PL-SP 260) with filtration system at a temperature of 423 K. The dissolved and filtered samples were transferred into the GPC instrument at 423 K. The calibration was conducted using the universal calibration curve based on narrow polystyrene standards.

3.3.6 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy (TEM) was used to determine the distribution of nano- Al_2O_3 within polymer matrix. The sample was dispersed in ethanol before using TEM (JEOL JEM-2010) for microstructural characterizations.

3.4 Preparation of fillers.

All reactions were conducted under argon atmosphere using Schlenk techniques and glove box

3.4.1 Preparation of nano- Al_2O_3

The Al_2O_3 nanofiller was obtained from Sigma-Aldrich having surface area of $35 \text{ m}^2/\text{g}$ and it was vacuum heated at 400°C for 6 h prior to impregnation

3.4.2 Preparation of dried-MMAO (d-MMAO)

100 ml of MMAO solution in hexane was evacuated and washed with toluene (100 ml x 2) to remove the impurities. Then, continue to wash with heptane for 6-8 times to remove TMA and TIBA in MMAO to obtain the d-MMAO as white solid.

3.4.3 Preparation of nano Al₂O₃-supported d-MMAO (d-MMAO/Al₂O₃)

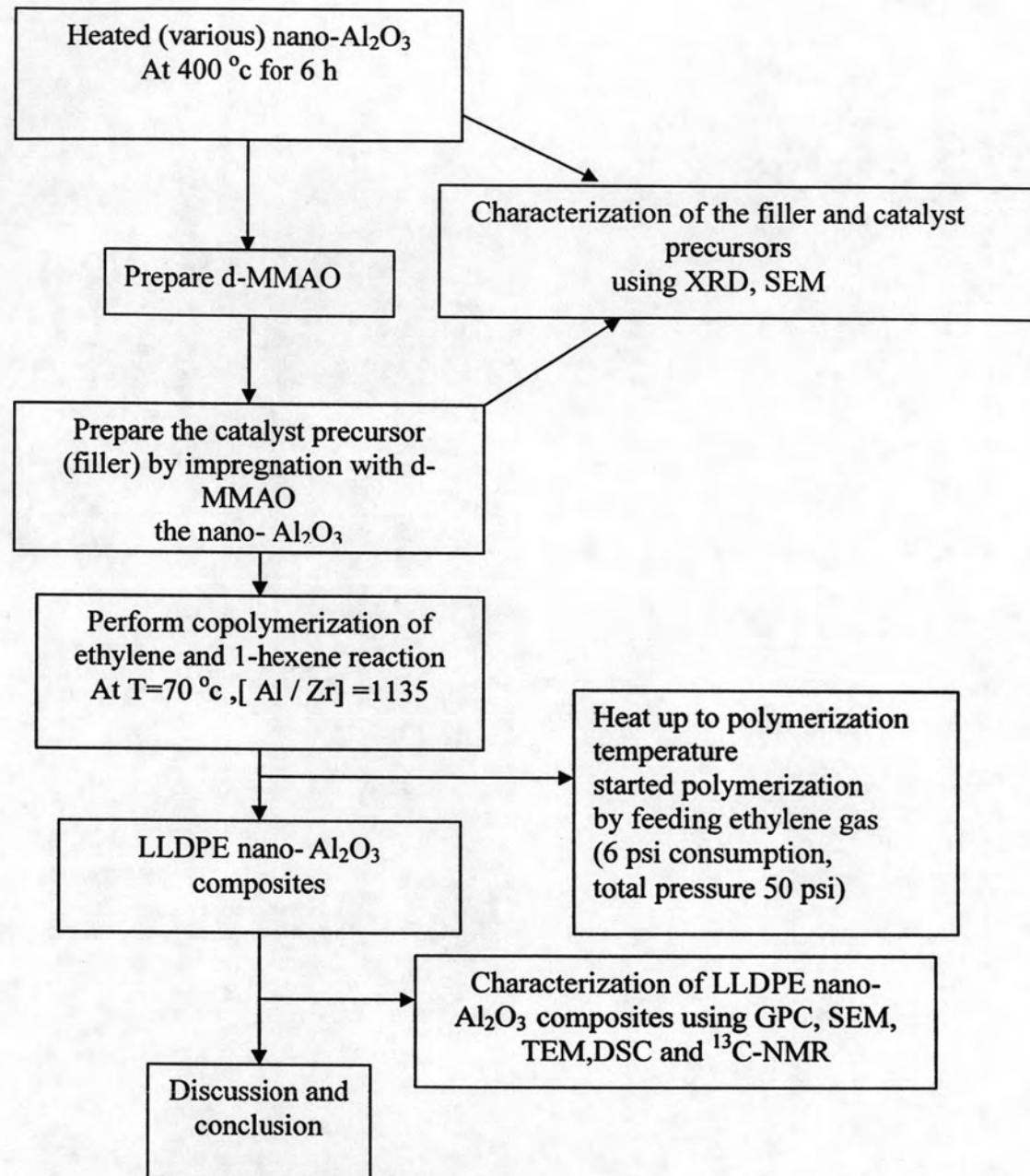
The primary particle size of Al₂O₃ was ca. 45 nm. First, the Al₂O₃ nanofiller was vacuum heated at 400 °C for 6 h. A toluene solution (50 mL) and d-MMAO (1.00 g) was added to the Al₂O₃ nanofiller (0.9 g), and the mixture was stirred for 30 min at room temperature. After the toluene was evaporated, the white powder obtained was further dried under vacuum, washed with hexane (20 mL × 7) and finally dried under vacuum to give d-MMAO/Al₂O₃ as white powder.

3.5 Ethylen and hexene Copolymerization Procedure

Polymerization was conducted upon the methods as follows. The ethylene /1-hexene copolymerization reaction was carried out in a 100 ml semi-batch stainless steel autoclave reactor equipped with a magnetic stirrer. At first, 0.1, 0.2, and 0.3 g of the nano-materials/d-MMAO ($[Al]_{MMAO}/[Zr] = 1135$) and 0.018 mole of 1-hexene along with toluene (to make the total volume of 30 ml) were put into the reactor. The desired amount of Et(Ind)₂ZrCl₂ (5×10^{-5} M) and TMA ($[Al]_{TMA}/[Zr] = 2500$) was mixed and stirred for 5-min aging at room temperature, separately, then was injected into the reactor. The reactor was frozen in liquid nitrogen to stop reaction for 15 min and then the reactor was evacuated to remove argon. The reactor was heated up to polymerization temperature (70°C). To start reaction, 0.018 mole of ethylene was fed into the reactor containing the comonomer and catalyst mixtures. After all ethylene was consumed, the reaction was terminated by addition of acidic methanol (10% HCl in methanol) and stirred over night. After filtration, the obtained copolymer (white powder) was washed with methanol and dried in vacuum oven.

The various effects on the ethylene/1-hexene copolymerization with silica-supported metallocene catalyst and optimized condition were investigated. The effects of copolymerization on production of ethylene/1-hexene copolymer were systematically varied as follow in the next page.

Research Methodology



3.6 Characterization

3.6.1 Nano- Al_2O_3

- Crystallinity

X-ray diffraction (XRD) was performed to determine the bulk crystalline phases of each nano- SiO_2 sample.

- The distribution of particle

Transmission electron microscope (TEM) was performed to determine the distribution and agglomeration of nano-material particle before they were impregnated with d-MMAO .

3.6.2 Catalyst precursor nano- Al_2O_3 /d-MMAO

- Morphology

Scanning electron microscopic (SEM) technique was the effective method to investigate catalyst precursor morphologies. The term of morphology was referred to shape, texture or form of catalyst precursor.

- The distribution of particle

Transmission electron microscope (TEM) was performed to determine the distribution and agglomeration of filler particle before they were in the polymer matrix after copolymerization procedure.

3.6.3 LLDPE-nanocomposites

- Morphology

The morphology of LLDPE-nanocomposites obtained was observed with scanning electron microscopy (SEM).

- Melting temperature (T_m)

Differential scanning calorimetry (DSC) was an instrument designed to measure the thermal properties especially melting temperature (T_m). The melting

temperature of LLDPE-nanocomposites were determined from the critical point of DSC curve.

- Microstructure

¹³C-NMR spectroscopy was widely used to determine comonomer incorporation and polymer structure. Comparison of the positions of peak in the ¹³C-NMR spectrum of polymer sample with characteristic led to identification of the sequence of the comonomer incorporation.

- The distribution of particle

Energy-dispersive X-ray Spectrometer (EDX) and Transmission Electron Microscopy (TEM) were used to determined the distribution and agglomeration of nano-SiO₂ within polymer matrix.

- The molecular weight and molecular weight distribution of polymer

Gel permeation chromatography (GPC, PL-GPC-220). Samples were prepared having approximately concentration of 1 to 2 mg/ml in trichlorobenzene (mobile phase) by using the sample preparation unit (PL-SP 260) with filtration system at a temperature of 423 K. The dissolved and filtered samples were transferred into the GPC instrument at 423 K. The calibration was conducted using the universal calibration curve based on narrow polystyrene standards.