

CHAPTER III

EXPERIMENTAL

3.1 Materials

- Ethylene gas (polymerization grade)
- Nitrogen gas (ultra high purified grade)
- *n*-Hexane
- Toluene
- TiCl₄ supported on MgCl₂ in heptane (Ziegler-Natta catalyst)
- Cp₂ZrCl₂ (metallocene)
- Trimethylaluminum (TMA) in toluene
- Triethylaluminum (TEA) in heptane
- Tris(pentafluoro phenyl)borane (B(C₆F₅)₃)
- Sodium metal
- Benzophenone
- *o*-Dichlorobenzene
- Decalin
- Methanol

3.2 Methodology

3.2.1 Solvent Purification

n-Hexane and toluene used as the solvents for Ziegler-Natta and metallocene catalyst systems were purified by refluxing with sodium/benzophenone for one night to remove water and oxygen. When the

solution turned blue, it was carefully distilled out and kept under nitrogen atmosphere before used.

3.2.2 Catalyst and Cocatalyst Solution Preparation

The catalyst and cocatalyst solutions are prepared in a glove box purged constantly with nitrogen gas. To transfer the prepared solutions to the reactor without exposure to air, closed injectors were used.

3.2.3 The Polymerization of Polyethylene

The ethylene and nitrogen gases are purified by passing through the oxygen traps before injecting into the reactor. $\text{TiCl}_4/\text{MgCl}_2$ in heptane, Cp_2ZrCl_2 , triethylaluminum (TEA), trimethylaluminum (TMA) and tris(penta fluorophenyl)borane ($\text{B}(\text{C}_6\text{F}_5)_3$) were used without further purification.

Polymerization of ethylene was carried out in a 300-ml parr reactor under nitrogen atmosphere. The reactor was heated up to 120°C and purged with dry nitrogen several times. Solvent was then added followed by ethylene gas at a set pressure. TMA or TEA cocatalyst solution and Ziegler or metallocene catalyst solution were injected respectively. Finally in case B (C_6F_5)₃ was used in the system it would be injected last. The total volume of the polymerization mixture was 150 ml for every run. The consumption of ethylene was determined by mass flow meter.

After one-hour polymerization time, the reactor was degassed. The polymerization mixture was stirred with acidic methanol (a mixture of methanol and a small amount of concentrated hydrochloric acid) to quench the polymerization. The polymer was taken out and washed several times with methanol, filtered, and dried.

3.2.4 Characterization of Polyethylene Products

3.2.4.1 Gel Permeation Chromatography (GPC)

Molecular weights and molecular weight distributions of the polyethylene samples were determined using a Waters high-temperature 150-C plus GPC instrument equipped with three Waters Styragel (exclusion limits for polystyrene 10^4 , 10^5 and 10^6 Å pore size) columns in series at 140°C . The solvent, o-dichlorobenzene, was applied at a flow rate of $1.0 \text{ cm}^3/\text{min}$. The columns were calibrated with narrow molecular weight distribution polystyrene samples.

3.2.4.2 Differential Scanning Calorimetry (DSC)

The thermal behavior of polyethylene product was measured by Perkin-Elmer DSC 7. The analyzed samples were in powder form. A 4-5 mg of the sample was sealed in a clamped aluminium pan. Each sample was heated from 50 to 160°C at a heating rate of $10^\circ\text{C}/\text{min}$ and kept at this temperature for 1 min. It was then cooled to 50°C at a rate of $10^\circ\text{C}/\text{min}$ for recrystallization and reheated at the same rate. The values of melting point (T_m), crystallization temperature (T_c), heat of fusion (ΔH_f), and heat of crystallization were obtained in the second scan thermograms. Degree of crystallinity of the polymer was calculated from the equation:

$$X_c(\%) = (\Delta H_f / \Delta H_f^\circ) \times 100 \quad (\text{Eq. 3.1})$$

Where ΔH_f is the heat of fusion of the sample as determined from the DSC curves of the second heating process, and ΔH_f° is the heat of fusion of perfectly crystalline polyethylene, 290 J/g .

3.2.4.3 Fourier Transform Infrared Spectroscopy (FT-IR)

Polyethylene powder was dissolved in decalin at 140 °C, spread on a petri dish, and heated in an oven at 80-90°C until dry. The spectra of HDPE films were determined in the wavenumber range between 4000 and 400 cm^{-1} .

3.2.4.4 Wide Angle X-ray Diffraction (WAXD)

X-ray diffraction patterns were obtained from D/MAX-2000 series of Rigaku/X-ray Diffractometer system. The experiment was performed in the range of 2-40 degree with scan speed 10 deg./min and scan step 0.02 deg.

From polyethylene X-ray diffraction pattern, the two sharp crystalline peaks lie over the broad amorphous diffraction peak. It is then possible to calculate the degree of crystallinity by dividing the two crystal peak areas (A_1+A_2) by total peak area ($A_1+A_2+A_3$).

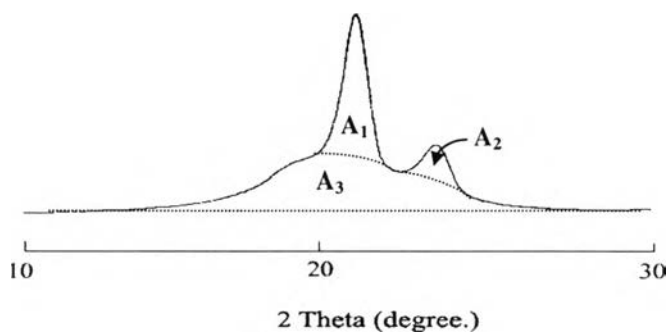


Figure 3.1 The X-ray diffraction pattern of polyethylene. The dashed line shows the estimated position of the amorphous scattering intensity (A_3).

3.2.4.5 Scanning Electron Microscope (SEM)

The morphology of polyethylene product was examined by using Scanning Electron Microscope model JOEL 520 at a voltage of 10 kV and 3500 \times magnification.