

CHAPTER IV

EXPERIMENTAL

In the present study, the influence of synthesis graft copolymer between ethylene-propylene-diene terpolymer and polystyrene were investigated. Moreover, the polymer blend between polystyrene and the synthesized graft copolymer was examined.

The details of the experiments were explained as in the following.

4.1 Chemicals

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

1. Ultra high purity argon gas (99.999 %) was purchased from Thai Industrial Gas Co., Ltd. And further purified by passing through column packed with copper catalyst, NaOH, P₂O₅ and molecular sieve 4A to remove traces of oxygen and moisture.

2. Toluene was donated from EXSOL Chemical Ltd., Thailand. This solvent was dried over dehydrated CaCl₂ and distilled over sodium/benzophenone under argon atmosphere before use.

3. Sodium Hydroxide (NaOH) was purchased from Labscan Asia Co., Ltd and used as received.

4. EPDM 4640 was donated from S.K. polymer Co., Ltd. (Dupont) and used as received.

5. Benzoyl peroxide (C₁₄H₁₀O₄) (with 25% H₂O) was purchased from Merck-Schuchardt, Germany and recrystalline by Ethanol 99.8% before used.

6. Hexane (C₆H₁₄) was received from Esso Chemical (Thailand) Co., Ltd. It was dried over dehydrated CaCl₂ and was distilled over sodium/benzophenone under argon atmosphere before use.

7. Heptane (C_7H_{14} , 99.84%) was purchased from J.T., Baker and used as solvent for polymer extraction without further purified.
8. Benzophenone (purum 99.0%) was obtained from Fluka Chemie A.G. Switzerland.
9. Calcium chloride (Dehydrated) was manufactured from Fluka Chemie A.G. Switzerland.
10. Hydrochloric acid (Fuming 36.7%) was supplied from Sigma
11. Methanol (Commercial grade) was purchased from SR lab.
12. Sodium (lump in kerosene, 99.0%) was supplied from Aldrich chemical Company, Inc.
13. Ethyl Alcohol absolute (99.8%) was purchased from CARLO ERBA REAGENTI and used as received.
14. Styrene Monomer was purchased from Fluka Chemie A.G. Switzerland and purify by NaOH and distill by vacuum before used.

4.2 Equipments

All equipments used in the preparation and polymerization of the polymer are listed as below:

4.2.1 Cooling System

The cooling system was utilized in the solvent distillation in order to condense the freshly evaporated solvent and soxhlet polymer.

4.2.2 Magnetic Stirrer and Heater

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

4.2.3 Reactor

A 250 ml glass reactor was utilized as the free radical polymerization vessel.

4.2.4 Inert Gas Supply

The inert gas (argon) was passed through columns of BASF catalyst R3-11G as oxygen scavenger, molecular sieve 3A to remove moisture. The BASF catalyst was regenerated by treatment with hydrogen at 300 °C overnight before passing the argon gas through all the above mentioned columns. The inert gas supply system is shown in Figure 4.1.1

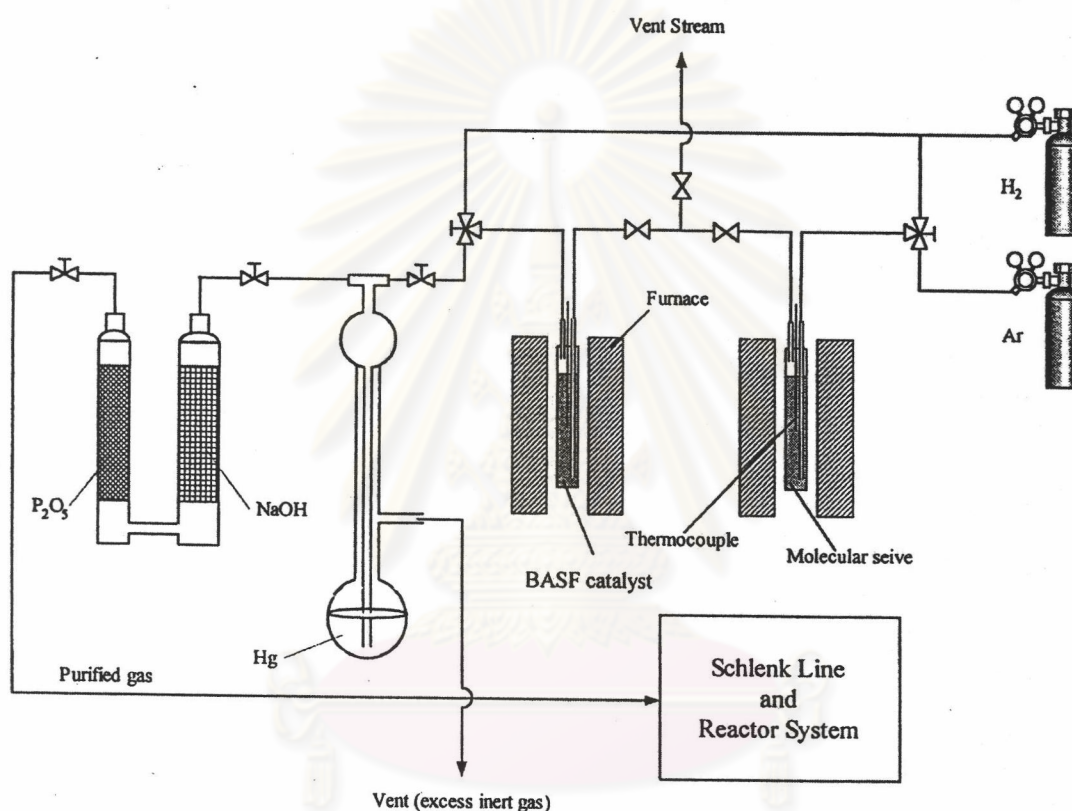


Figure 4.1.1 Inert gas supply system

4.2.5 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.

4.2.6 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 4.1.2

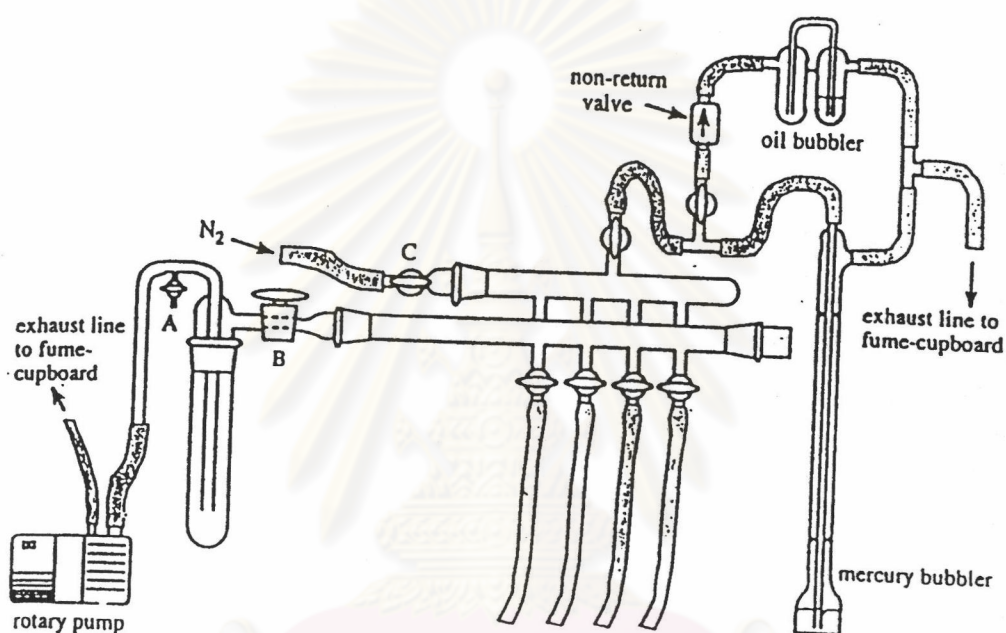


Figure 4.1.2 Schlenk line

4.2.7. Gas Distribution System

The system consists of an ultra high purity argon feeding lines made of stainless steel pipe with diameter of $\frac{1}{4}$ inch.

4.2.8. Digital Hot Plate Stirrer

The Cole-Palmer which is a programmable digital laboratory hot plate was used for preparing the phase diagram of the blends and samples by melted mixing between Polystyrene and Graft copolymer between Ethylene-Propylene-diene terpolymer (EPDM) and Styrene monomer. All functions can be set from digital panel and display their status on LCD. The plate temperature, stir speed and time are controllable.

4.2.9. Automatic Hydraulic Hot Press

The LAB TECH hydraulic hotpress LP-50 M/C 9701 was used for preparing the thin film form polymer blend between Polystyrene and Graft copolymer between Ethylene-Propylene diene terpolymer (EPDM) and Styrene monomer. It has both the automatic mode and manual mode. In automatic mode, it has four steps (preheat, vent, full press and cooling step), that can be controlled in one touch which times adjustment of each of step separately. The hotpress can be compressed up to maximum 50 ton (160 kg/cm^2).

4.2.10. Surface Temperature Probe and Digital Thermometer

The Cole-Palmer surface probe model E-08516-60 with 0.5 inch tip diameter, which has a temperature range from -250 to $649 \text{ }^\circ\text{C}$, was used for measuring the temperature during the mixing of sample and measuring the temperature of hot plate during the phase separation of miscible samples.

4.3 Polymer Characterization

The instruments used to characterize the EPDM graft copolymer products were specified as in the following paragraph.

4.3.1. Differential Scanning Calorimetry (DSC)

The melting temperature and glass transition temperature of the polymers were measured by a Perkin-Elmer DSC 7 at Mahidol University. The heating rate of 20° C/min in the temperature range -150 - 120 °C was employed. The heating cycle were twice operated. The first scan, samples were heated up and then cooled down to room temperature. In the second scan, samples were reheated at the same rate. Only the results of the second scan were reported because the DSC data of the first scan were influenced by the mechanical and thermal history of the samples during the polymerization.

4.3.2. Scanning Electron Microscopy (SEM)

All distribution polymer particles were investigated by Scanning Electron Microscopy (SEM), JSM-640 Scanning Microscope, Microspec WDX at Technological Research Equipment Center, Chulalongkorn Univeristy, with Energy Dispersive X-ray analysis (EDX).

4.3.3. Transmission Electron Microscopy (TEM)

All distribution polymer particles were investigated by Transmission Electron Microscopy (TEM), JEOL JEM 1220 Transmission Microscope at Equipment Center, Kasertsart Univeristy

4.3.4 Soxhlet-Type Extractor

Soxhlet-Type extractor was used to determine the graft copolymer content. The obtained polymer was weighed in cellulose timber then was extracted in Soxhlet-Type extractor using hexane as solvent for 12 hours. After the first extract the second extract using acetone 12 hours was performed. The fraction of insoluble polymers were defined as yield weight. This method can control the molecular weight distribution of polymer. However, its have low grafting polymer because the short chain graft copolymer can dissolve in the solvent.

4.3.5. ^{13}C -Nuclear Magnetic Resonance (^{13}C -NMR)

NMR is one of the most powerful tools available to the chemists and biochemist for elucidating the structure of both organic and inorganic species. NMR is based upon the measurement of absorption of electromagnetic radiation in the radio-frequency region of roughly 4 to 600 MHz. ^{13}C NMR spectra were recorded on JEOL JNM-A500 Nuclear Magnetic Resonance Spectrometer at Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University. Spectra were referenced to 0 ppm for trimethylsilane- d_6 and 7.26 ppm for deuteriochloroform. Chemical shifts were given in parts per million (ppm) and coupling constant (J) are in Hertz (Hz).

4.3.6. Tensile Testing Machine

Tensile tests were performed using LLOYD tensile testing machine model 2000R. Obtained results are the stress-strain behaviors of polymers and their blends. The test procedure is modified in accordance with ASTM D638 covering determination of basic tensile properties of plastics.

The force necessary to elongate and break that specimen was measured by load cell. The stress at the break was designated as the tensile stress at break. The average tensile value of 5 specimens was used. In this study, the cross head speed was set at constant rate of 50 mm/min. Load cell used is 10,000 N. The experiments are performed at Polymer Engineering Laboratory, the Department of Chemical Engineering, Chulalongkorn University.

4.4 Polymerization Procedure

4.4.1 Preparation of EPDM

EPDM approximately 5 g weights was dissolved in 50 ml toluene and heated at 80°C. The solution was stirred until the EPDM was completely dissolved. The solution was used as a substance for radical polymerization.

4.4.2 Preparation of Initiator (Benzoyl peroxide (BPO))

Initiator was Benzoyl Peroxide recrystalline by weight approximately 0.5 g of BPO in 2 ml of Ethanol and heat at 50 °C to remove the impurities. After heated, the solution was cool down to room temperature to crystallize pure crystal BPO. The crystal was further dry under vacuum for 30 mins to evaporate the ethanol remained.

4.4.3 Preparation of Styrene Monomer

Styrene monomer was extracted with NaOH solution (5 % w/w) in distilled water, then the styrene was further purified by distilled over sodium under vacuum atmosphere before use.

4.4.4 Graft-Copolymer Polymerization

The 250 ml glass reactor and magnetic bar were dried in oven at 110°C for 30 minutes. The reactor are vacuumed and purged with argon gases 5 times. The loading of EPDM solution (the total volume of mixture solution was 50 ml) in the reactor and heated at 90 °C. Next, loading the BPO initiator and styrene monomer were mixed and stirred in the reactor. After the polymerization reaction was stopped, the reaction solution was terminated by addition of acidic methanol. The precipitated polymer was washed with methanol several times and dried under vacuum.

4.4.5 Soxhlet Polymer

Measured the weight of polymer and Soxhlet polymer. Hexane solvent used for eliminate unreacted EPDM for 12 hrs and acetone solvent used for eliminate side product polystyrene for 12 hrs.

4.5 Polymer Blend between Polystyrene and Synthesis Graft copolymer

Polystyrene was heated over T_g about $50\text{ }^{\circ}\text{C}$ and blended with Synthesis Graft copolymer (5 % w/w). Blend polymer was heated at $200\text{ }^{\circ}\text{C}$ and hold for 15 minutes, then cooled at $120\text{ }^{\circ}\text{C}$ and hold for 10 minutes and finally cooled to room temperature.

4.6 Tensile Strength Tests of Polymer Blend

Polymer blend between polystyrene and synthesis graft copolymer (5 % w/w) are melts in the mold (breath 0.8 mm) at $200\text{ }^{\circ}\text{C}$ for 20 minutes and press at pressure 4250 psi for 10 minutes. Cool down the polymer to room temperature and cut polymer in size $4\text{ cm} \times 10\text{ cm}$ for tensile strength test.

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