

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

EPDM (NORDEL IP 5565 containing 7.5 wt% of 5-ethylidene 2-norbornene) was purchased from The Dow Chemical Company (Midland, USA). The properties of EPDM are shown in Appendix A. The commercial grade ST monomer and the analytical grades of toluene and acetone were supplied by SR Lab Co., Ltd (Bangkok, Thailand). The commercial grade MMA and 2,4-dimethylvaleronitrile (ABVN) were obtained from Pan Asia Industrial Co., Ltd (Bangkok, Thailand). Benzoyl peroxide (BPO) (humidified with ~25% of H₂O) from PANREAC QUIMICA (Barcelona, Spain) was used as received. Sodium hydroxide (NaOH) and anhydrous sodium sulfate (Na₂SO₄) were purchased from Merck (Bangkok, Thailand). The analytical grades of light petroleum ether (LPE) and methyl ethyl ketone (MEK) were obtained from Fisher Scientific (Leicestershire, UK). The commercial grade of methanol was the product of Reagent Chemical Industry (Bangkok, Thailand). Nitrogen gas with 99.9% purity was manufactured by Linde Co., Ltd (Bangkok, Thailand).

3.2 Experiment apparatus

- Three-neck round bottle (500 ml) equipped with condenser, nitrogen inlet and outlet tubes, overhead stirrer and thermometer for graft copolymerization step (Figure 3.1)
- Soxhlet extraction apparatus
- Glass mould for casting process
- Other general laboratory glassware
- Water bath
- Hot air oven
- UV cure apparatus

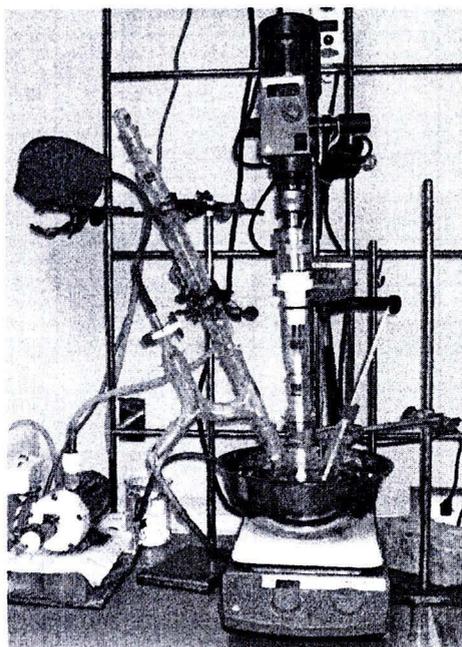


Figure 3.1 Experimental apparatus for graft copolymerization.

3.3 Analytical equipments

- Fourier- transform infrared spectrometer (FT-IR): Thermo 470 FT- IR spectroscopy
- Proton-nuclear magnetic resonance spectrometer ($^1\text{H-NMR}$): Bruker ACF 200 MHz
- Universal testing machine: LLOYD Instrument LR 10K Plus
- Hardness testing machine: Rockwell Hardness Tester 4150 AR
- Impact testing machine: Impact tester GOTECH GT 7045
- Color measurement: Gretagmacbeth Instrument color i5
- Scanning Electron Microscope: JEOL model JSM-5800 LV
- Differential Scanning Calorimeter: PerkinElmer Thermal analysis controller TAC 7/DX

3.4 Grafted ethylene propylene diene rubber preparation

3.4.1 Purification of monomer (Thawornwisit, 2006)

The ST monomer (b.p. 145.2°C/760 mmHg) contained a trace amount of hydroquinone as an inhibitor. The inhibitor was removed by washing with 10% NaOH solution and then followed by distilled water until neutral. The washed ST monomer was distilled under reduced pressure (50-60°C, 20 mmHg). The purified ST monomer was stored in the refrigerator.

For MMA purification, this monomer (b.p. 98°C/760 mmHg) also contained a small amount of hydroquinone as inhibitor. It was purified by following the above procedure similar to ST purification. The washed MMA monomer was distilled under reduced pressure at 20 mmHg and 40°C. The purified MMA monomer was also kept in the refrigerator.

3.4.2. Preparation of graft EPDM (GEPDM)

The graft copolymer of ST and MMA on EPDM was prepared by solution copolymerization performed in a three-necked round glass bottle (300 mL) equipped with a stirrer, thermometer and condenser. EPDM dissolved in toluene (8 wt%) was transferred into the glass bottle. The system was deoxygenated by purging nitrogen gas for at least 15 min. When the reaction temperature reached to 90°C, 0.1 wt% of BPO was charged into the reactor following the gradual addition of the monomer mixture (MMA/ST = 75/25 %w/w). The reaction was allowed to proceed for 4, 10 and 16 h under continuous stirring speed at 200 rpm. Then, the reaction was ceased by adding a small amount of phenol. The graft product was precipitated in the excess methanol, filtered and dried in vacuum oven at 80°C until constant weight was received. The standard recipe used for graft copolymerization is shown in Table 3.1.

Table 3.1 Recipe for preparation of GEPDM (Fu et al., 2008)

Condition	Description
Purified MMA/ST ratio (%w/w)	75/25
Rubber/monomer ratio (%w/w)	50/50
Rubber concentration (wt%)*	6, 8, 10
Initiator dosage (BPO) (wt%)**	1.0
Reaction temperature (°C)	80 - 90
Reaction time (h)	4 - 20

* The rubber concentration was based on total weight of monomer

** The initiator dosage was based on EPDM content.

3.5 Properties of GEPDM

3.5.1 Determination of monomer conversion and grafting efficiency

The gross graft EPDM (GEPDM) consisted of three parts: graft copolymer (EPDM-*g*-(MMA-*co*-ST)), free EPDM and free copolymer. The free EPDM and free copolymer were removed by using soxhlet extraction. The free rubber was extracted by light petroleum ether (60-80°C) for 24 h, while free copolymer was then extracted in MEK/ acetone at 50/50 %v/v for 24 h. The dried final product was the graft copolymer. The different weight of sample before and after soxhlet extraction in each step was defined as %free EPDM, %free copolymer and %graft copolymer, respectively (eq. 3.1-3.3) (Thawornwisit, 2006). The total conversion of monomer and percentage of grafting efficiency (%GE) were calculated from eq. 3.4 and 3.5, respectively.

$$\text{Free EPDM (\%)} = \frac{\text{weight of free rubber}}{\text{weight of gross polymer products}} \times 100 \quad (3.1)$$

$$\text{Free copolymer (\%)} = \frac{\text{weight of of free homopolymer}}{\text{weight of gross polymer products}} \times 100 \quad (3.2)$$

$$\text{Graft copolymer (\%)} = \frac{\text{weight of of graft copolymer}}{\text{weight of gross polymer products}} \times 100 \quad (3.3)$$

$$\text{Total conversion (\%)} = \frac{\text{weight of polymer formed} - \text{weight of GEPDM}}{\text{weight of monomer charged}} \times 100 \quad (3.4)$$

$$\text{Grafting efficiency (\%)} = \frac{\text{weight of of monomer grafted}}{\text{weight of monomer polymerized}} \times 100 \quad (3.5)$$

3.5.2 Structured characterization of GEPDM

The structures of EPDM and graft copolymer obtained after soxhlet extraction were characterized by using fourier-transform infrared spectroscopy (FT-IR) (Thermo 470 FT-IR spectroscopy). The graft product was dissolved in toluene (ca. 2 %w/v) and then casted as a film on a NaCl cell. To confirm the FT-IR results, the proton nuclear magnetic resonance spectroscopy (¹H-NMR) was also used analyse. ¹H-NMR spectra were obtained on the Bruker ACF 200 MHz. The 0.01 g of samples were dissolved in CDCl₃.

3.5.3 Preparation of modified acrylic sheet containing GEPDM

The modified acrylic sheets were prepared by dissolving EPDM (1.0 wt%) or GEPDM (1.0-4.0 wt%) in the mixture of MMA/ST solution (80/20 %w/w) in the vigorous agitation at 95°C for 0.5-3.0 h to obtain the homogeneous solution. In the pre-polymerization step, BPO (0.1 wt%) was added into the mixture as the first initiator and then heated up to 110°C for 25 min. When the mixture was viscous, it was cooled down to room temperature. Then, ABVN (0.03 wt%) was added into the mixture. The air bubble in the mixture was removed by using vacuum pump until the reaction mixture was cooled down to room temperature. The obtained syrup was filled into a glass mold and immerg in a water bath at 60°C to harden the acrylic sheet.

The acrylic sheet was further placed in an oven at 120°C for 2 h. The finished sheet was taken off from the glass mold after cooling at room temperature (Drive, 1979, Grulke, 1994 and Saechtling, 1995). The sheet was cut as a shape according to the ASTM test method. The standard recipe and conditions used for preparation of the modified acrylic sheet are shown in Table 3.2.

3.6. Testing of mechanical properties of modified acrylic sheet

The mechanical properties of the modified acrylic sheets containing various contents of EPDM or GEPDM were measured following the ASTM test methods.

3.6.1 Impact strength (ASTM D 256)

The dimension and geometry of specimens for impact strength testing are shown in Figure 3.2. The machine used to investigate the impact strength of the modified acrylic sheet was Izod Impact Tester (GOTECH GT 7045). The width of each specimen was measured in the notch with a micrometer caliper and recorded its average width.

Table 3.2 Recipe for preparation of modified acrylic sheets

Ingredient	Quantities
MMA/ST ratio (%w/w)	80/20
EPDM (wt%)	1.0
GEPDM (wt%)	1.0 - 4.0
BPO (wt%)	0.1
ABVN (wt%)	0.03
Water bath temperature (°C)	60
Oven temperature (°C)	120



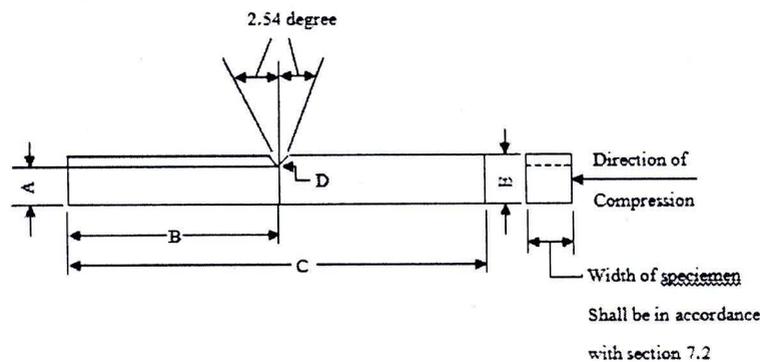
The breaking energy of specimen was estimated and the weight hammer with 2 J was applied for the specimens. The pendulum was released and an excess energy remaining in the pendulum was recorded after breaking the specimen.

3.6.2 Flexural strength (ASTM D 790)

The flexural strength of specimens was measured using a three point bending test in a universal testing machine (LLOYD Instrument LR 10K Plus) at a cross-head speed of 1 mm/min. Stress was applied until fracture by a centrally located rod connected to a 50 kgf load cell. The specimens were cut from a 3.0 mm thick sheet. The flexural strength was calculated using the eq. 3.6.

$$TS = \frac{3WL}{2bd^2} \quad (3.6)$$

where W is the maximum load before fracture, L is the distance between supports (50 mm), b is the width of specimens and d is the specimen thickness.



Unit: mm

A: 10.16 ± 0.05

D: 0.25 ± 0.05

B: 32.00 max, 31.50 min

E: 12.70 ± 0.05

C: 80 ± 0.2

Figure 3.2 Dimensions of specimens for impact strength testing (Izod type) (Shah, 2007).

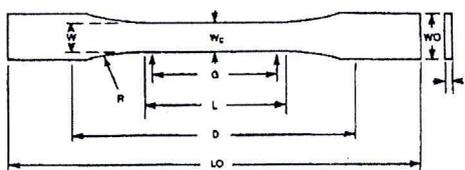
3.6.3 Tensile properties (ASTM D 638)

Tensile properties of dumbbell-shaped specimens (Type I) (Figure 3.3) were measured at 25°C and 60% of humidity. The specimens were cut from a 3.0 mm thick sheet. The testing was performed by using a universal testing machine (LLOYD Instrument LR 10K Plus) with a crosshead speed of 50 mm/min.

3.7 Properties retention after thermal and UV aging

The effect of thermal aging on the physical and mechanical properties of the modified acrylic sheets was carried out in a hot air oven at 165°C for 25 min according to Pan Asia Industrial Standard method. At the terminal of aging time interval, the specimens in the shape for each mechanical properties testing were removed from the oven and cooled down to room temperature on a flat surface for 24 h before mechanical properties determination. For the test of UV resistance, the specimens were placed in the Ultraviolet box (The Q.PANEL company model Q.U.V) with the UV wavelength at 280-320 nm and 60°C for 1 week according to Pan Asia Industrial Standard method. The impact strength, flexural strength, tensile properties and hardness of the modified acrylic sheets after thermal and UV aging were compared to untreated samples. The properties retention could be calculated following eq. 3.7.

$$\% \text{Retention} = \frac{\text{Pr operties after ageing}}{\text{Pr operties before ageing}} \times 100 \quad (3.7)$$



W : 13 mm WO : 19 mm G : 50 mm R : 76 mm
L : 57 mm LO : 165 mm D : 1155 mm T : 4 mm or under

Figure 3.3 Dimensions of specimens for tensile testing (Shah, 2007).

3.8. Thermal properties of the modified acrylic sheets

3.8.1 Differential scanning calorimetry (DSC)

The differential scanning calorimetry (DSC) was carried out on a Perkin Elmer JSM-5800 LV to evaluate the effect of the addition of EPDM or GEPDM on the glass transition temperature (T_g) of the modified acrylic sheets. The thermogram signal was obtained from the temperature difference between the sample and the reference.

The sample of 5-10 mg was placed in a crimped aluminium pan. The differential scanning calorimetry of the modified acrylic sheets was carried out under nitrogen atmosphere at a constant heating rate of $10^\circ\text{C}/\text{min}$ from -60 - 250°C . The T_g values were calculated from the midpoint of the base-line shift of the DSC thermogram.

3.8.2 Thermogravimetric analysis (TGA) (Kissinger, 1702)

The decomposition temperature and kinetics of thermal decomposition of the modified acrylic sheets were determined by using Thermogravimetric analysis (TGA). The thermogravimetric (TG) and its derivative (DTG) curves were performed on a Seiko SSC 5000 TG/DTA. Samples (10-20 mg) were heated from room temperature to 600°C at a heating rate of 2.5, 5 and $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere. The flow rate of nitrogen gas was controlled at $50\text{ mL}/\text{min}$. The initial (T_{id}) and final (T_f) decomposition temperatures was obtained from the intersection of two tangents at the initial and final stage of the decomposition, respectively. The temperature at the maximum weight-loss rate (T_p) was also recorded.

To study the overall kinetics of thermal decomposition, the Kissinger method (differential method) was applied to determine the activation energy (E_a) of the solid state reaction without a precise knowledge of any mechanism of thermal decomposition. The Kissinger method proposed employs in eq. 3.8:

$$\ln \frac{\beta}{T_p^2} = \ln \frac{AR}{E_a} + \ln [\ln(1 - \alpha_p)^{n-1}] + \frac{E_a}{RT_p} \quad (3.8)$$

where β is the heating rate, T_p and α_p are the absolute decomposition temperature and weight loss at the maximum weight-loss rate $(d\alpha/dt)_p$, respectively. R is the gas constant, A is the pre-exponential factor and n is the reaction order. E_a was calculated from the slope of the straight line obtained from a plot of $\ln(\beta/T_p^2)$ versus $1/T_p$.

3.9. Physical properties of the modified acrylic sheets

3.9.1 Change of color and transparent property

Transparent property was reported in term of opacity of specimens by using color measurement (Gretagmacbeth Instrument color i5). Thermal and UV resistance was reported in term yellow difference (ΔE) of the modified acrylic sheets after thermal and UV ageing were reported and compared to untreated sample.

3.9.2 Morphology investigation

The morphology of the fracture surface of the modified acrylic sheets was also investigated using a JEOL model JSM-6400 scanning electron microscope at 10 kV. The specimens were fractured under cryogenic condition by using liquid nitrogen. Then, the specimens were mounted on a SEM stub using a double-side tape and the fracture surface of specimens was sputtered with a thin gold layer.