



CHAPTER III METHODOLOGY

3.1 Materials and Equipment

3.1.1 Materials

Natural rubber (Rubber Research Institute of Thailand), styrene monomer (Fluka), methyl methacrylate monomer (Merk), Ferrous chloride (Fluka), Ferric chloride (Fluka), Ammonium hydroxide (Panreac), Sodium oleic (SO) (Fluka), Sodium dodecyl benzene sulfonate (SDBS) (Fluka), 2,2'-Azobis (2-methylpropionamide) dihydrochloride (V50) (Aldrich), Cetyltrimethylammonium bromide (CTAB) (Acros Organics). All materials were used without further purification.

3.1.2 Equipment

3.1.2.1 *Fourier Transform Infrared Spectrometer (FTIR)*

FTIR spectra were obtained from a Nexus 670 spectrometer (Nicolet) with 32 scans at a resolution of 4 cm^{-1} and a frequency range of $4000\text{-}400\text{ cm}^{-1}$.

3.2.2.2 *Thermogravimetric Analysis (TGA)*

TGA was performed by High Resolution TG-DTA Pyris Diamond (Perkin Elmer) with a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$ using a nitrogen purge with a purge rate of $200\text{ ml}/\text{min}$. Samples were put into the Pt pan and heated from $30\text{-}800\text{ }^{\circ}\text{C}$.

3.2.2.3 *Scanning Electron Microscope (SEM)*

Scanning electron microscope (SEM), JEOL 5200-2AE (MP152001) was used to study phase morphologies of the product after admicellar polymerization. The samples were prepared by dipping the dry specimens into liquid nitrogen and were broken in liquid nitrogen at temperature about $-70\text{ }^{\circ}\text{C}$. The cross section area was stained with osmium tetroxide, coated with gold under vacuum and observed by SEM.

3.2.2.4 *Optical Microscope (OM)*

Optical microscope was used for illustration of the dry emulsion after admicellar polymerization. The samples were prepared by dropping the product emulsion onto a glass slide and drying by hot air.

3.2.2.5 *Brablender Mixier*

Barblender mixer Plasti-corder PL2100 and sample at 150 °C, screw speed 50 rpm and fill capacity 50 g. First of all, mixing PS-NR or PMMA-NR for 3 min after that added PS-Mag or PMMA-Mag and mixing together until 5 min.

3.2.2.6 *Compression Molding Machine*

Film samples are prepared by compression press, model V50H-18-CX (Wabash) at 150 °C for 5 min after that cooled to room temperature.

3.2.2.7 *Lloyd Universal Testing Machine*

Tensile tests of PLA-PS-NR-PLA and PLA-PMMA-NR-PLA samples were carried out using Lloyd universal testing machine, LRX. The film sample followed ASTM D882-91. A gage length of 50 mm was employed with a crosshead speed of 10 mm/min.

3.2.2.8 *Capillary Rheometer*

The capillary rheometer was used to investigate the rheological behavior of PS-Mag/PS-NR blends and PMMA-Mag/PMMA-NR blends with different phr. of PS-Mag and PMMA-Mag. The dimensions of die is 1 mm diameter and 20 mm length ($L/D = 20$). The measurement was carried out at 150 °C over wide range of shear rates at 10 - 5,000 s^{-1} .

3.2.2.9 *Gel Permeation Chromatography (GPC)*

Gel permeation chromatograms of 50 PS-NR and 50 PMMA-NR were obtained from Waters 600 controller chromatograph equipped with water Styragel columne packed with high cross-links styrene divinylbenzene copolymerparticle connected 3 columes (MW resolving range 100 – 500,000).

3.2 Methodology

3.2.1 Natural Rubber Latex Preparation

Natural rubber latex particles were purified by centrifugation (at 20 °C, 10,000 rpm, 20 min) and were redispersed in distilled water 2 times to remove dissolved impurities and to reduce the particle size distribution.

3.2.2 Admicellar Polymerization of Styrene on Natural Rubber at Various with and without CTAB

Polymerization of styrene on natural rubber latex particles was carried out using two conditions with and without CTAB (2800 μ M). Dilute natural rubber latex (5%wt, 10%wt and 20%wt) was suspended in the CTAB surfactant to obtain equilibrium concentration of 800 μ M under basic condition. The mixture was started by stirring at 30 °C for 4 h. After this period, the styrene monomer with required concentration (20 and 100 mM) was added into the mixture and stirred to equilibrium at 30 °C. After that, the V50 initiator with ratio of styrene and initiator at 25:1 was added to initiate polymerization of styrene at 70 °C for 5 h. Then the product was washed by distilled water to remove the CTAB surfactant. The modified natural rubber was dried in vacuum oven at 70 °C.

3.2.3 Admicellar Polymerization of Styrene at Various Conditions on Natural Rubber

Polymerization of styrene on natural rubber latex particles was carried out using two conditions with and without CTAB (2800 μ M). Dilute natural rubber latex (5%wt) was suspended in the CTAB surfactant to obtain equilibrium concentration of 800 μ M under basic condition. The mixture was started by stirring at 30 °C for 4 h. After this period, the styrene monomer with required concentration (20, 50, 100, 200 and 300 mM) was added into the mixture and stir to equilibrium at 30 °C. After that, the V50 initiator with ratio of styrene and initiator at 25:1 was added to initiate polymerization of styrene at 70 °C for 5 h. Then the product was washed by distilled water to remove the CTAB surfactant. The modified natural rubber was dried in vacuum oven at 70 °C.

3.2.4 Admicellar Polymerization of Methyl Methacrylate on Natural Rubber

Polymerization of methyl methacrylate on natural rubber latex particles was carried out using two condition with and without CTAB (2800 μM). Dilute natural rubber latex (5%wt) was suspended in the CTAB surfactant to obtain equilibrium concentration of 800 μM under basic condition. The mixture was started by stirring at 30 °C for 4 h. After this period, the methyl methacrylate monomer with required concentration (20 ,50, 100, 200 and 300 mM) was added into the mixture and stir to equilibrium at 30 °C. After that, the V50 initiator with ratio of methyl methacrylate and initiator at 100:1 was added to initiate polymerization of methyl methacrylate at 80 °C for 5 h. Then the product was washed by distilled water to remove the CTAB surfactant. The modified natural rubber was dried in vacuum oven at 70 °C

3.2.5 Preparation of Magnetite Particles Coated with Polystyrene(Procedure adopted from Xunan Wang *et al.*, 2007)

For preparation of magnetite particles, 10 g ferrous chloride and 16 g ferric chloride were dissolved in 200 ml doubly distilled water, under vigorous stirring. Ammonium hydroxide solution (100 ml) was added into the mixture, and the magnetite was immediately precipitated. The reaction was continued 1 h at elevated temperature. The precipitate was washed 5-6 times with water. The precipitate was mixed with deionized water and SO at elevated temperature for 2 h. Then the particles were isolated from water by magnetic decantation. One gram of the fresh precipitate obtained in the above process was mixed with 30 ml doubly distilled water under vigorous stirring. Then a solution of 15% (w/w) SDBS was added to the mixture dropwise until stable suspension was formed. The magnetic precipitate – redispersed with no phase separation-was observed. Thus, the magnetite particles coated by an inner surfactant SO and an outer surfactant SDBS were equilibrated with styrene for 2 h. The initiator was added to start polymerization at 70 °C and the reaction was continued for 2 h. The obtained PS coated magnetite particles were washed by water several time. FTIR was used to detect the PS synthesized.

3.2.6 Preparation of Magnetite Particles Coated with Poly(Methyl Methacrylate) (Procedure adopted from Xunan Wang *et al.*, 2007)

For preparation of magnetite particles, 10 g ferrous chloride and 16 g ferric chloride were dissolved in 200 ml doubly distilled water, under vigorous stirring. Ammonium hydroxide solution (100 ml) was added into the mixture, and the magnetite was immediately precipitated. The reaction was continued 1 h at elevated temperature. The precipitate was washed 5-6 times with water. The precipitate was mixed with deionized water and SO at elevated temperature for 2 h. Then the particles were isolated from water by magnetic decantation. One gram of the fresh precipitate obtained in the above process was mixed with 30 ml doubly distilled water under vigorous stirring. Then a solution of 15% (w/w) SDBS was added to the mixture dropwise until stable suspension was formed. The magnetic precipitate – redispersed with no phase separation – was observed. Thus, the magnetite particles coated by an inner surfactant SO and an outer surfactant SDBS were equilibrated with methyl methacrylate for 2 h at monomer : initiator ratio 100:1. The initiator was added to start polymerization at 80 °C and the reaction was continued for 5 h. The obtained PMMA coated magnetite particles were washed by water several times. FTIR was used to detect the PMMA synthesized.

3.3 Characterization

3.3.1 Fourier Transform Infrared Spectroscopy

The IR absorption of the admicelled rubber films with a thickness of 0.3–0.8 mm obtained by compression at 150°C under pressure 30 tons for 15 min were determined using the horizontal attenuated total reflection accessories for the FTIR (Nexus 670, HATR flat plate system with 45 °C ZnSe crystal) to measure the spectra of materials. The spectra were recorded in the absorbance mode in a wavenumber range of 400–4000 cm^{-1} . The sample spectra were recorded by using air as a background.

The KBr technique was used to prepare the powder sample of PS-Mag and PMMA-Mag. They were prepared by grinding the powdered PS-Mag/PMMA-Mag with the KBr powder. The mixture was molded in special dies under a pressure

of 10 tons. The disc sample obtained with diameter 6 mm placed on the sample holder and the FTIR transmission mode was employed to obtain IR spectra of the samples.

3.3.2 Thermogravimetric Analysis (TGA)

Thermal stability, moisture content, and degradation process of the admicelled rubbers were studied by a thermogravimetric-differential thermal analyzer (Perkin Elmer, Pyris Diamond), TG-DTA. The samples weighed 10-18 mg and were put in a platinum pan. The instrument was set to operate at temperatures from 30 to 800°C at a heating rate of 10°C/min under nitrogen atmosphere, 100 ml/min.

3.3.3 Phase Morphology

Optical microscope was used for illustration of the dry emulsion after admicellar polymerization. The samples were prepared by dropping the product emulsion onto a glass slide and drying by hot air.

Scanning electron microscope (SEM), JEPL 5200-2AE (MP152001) was used to study phase morphologies of the product after admicellar polymerization. The samples were prepared by dipping the dry specimens into liquid nitrogen and were broken in liquid N₂ the sample at temperature about -70 °C. The cross section area was stained with osmium tetroxide, coated with gold under vacuum and observed by SEM. All SEM results were obtained for the magnification of 500 to 5000 times at 15 kV.

3.3.4 Gel Permeation Chromatography (GPC)

Gel permeation chromatograms of 50 PS-NR and 50 PMMA-NR were obtained from Waters 600 controller chromatograph equipped with three HR (Waters) columns (HR1, HR3, and HR4) (M.W. resolving range = 100 – 500,000) at 35 °C and a refractive index detector (Water 2414). Tetrahydrofuran (HPLC grade) were used as an eluent with the flow rate of 1.0 ml/min. Sample injection volume was 50 µl. Polystyrenes (996 – 188,000 Da) were used as standards for calibration.