CHAPTER III
EXPERIMENTAL

3.1 Materials

Natural rubber (60 % dry rubber content) was obtained from Rubber Research Institute of Thailand. Anionic surfactant sodium dodecyl sulfate (SDS) with a purity of 99 % was obtained from Aldrich. Cationic surfactant hexadecyltrimethylammonium bromide (CTAB) surfactant with a purity of 98 % and styrene monomer (99 %) were purchased from Fluka. A water insoluble 2,2'-Azobis-2 methypropionitrile (AIBN, 98 %) and 2,2'-Azobis (2-methylpropionamidine) dihydrochloride (V50, 97 %), an initiator were obtained from Aldrich. Sodium bromide (99.5 %) was obtained from Unilab. Tetra hydrofuran (THF, 99.8 %) was purchased from LAB-SCAN. Sodium hydroxide and hydrochloric acid were used for adjusted pH obtained from Carrlo Eba Reagent Company. All materials were used without further purification.

3.2 Equipment

3.2.1 Fourier Transform Infared Spectrometer (FTIR)

FTIR spectra were obtained from a Nexus 670 spectrometer (Nicolet) with 64 scans at a resolution of 4 cm^{-1} and a frequency range of 4000-400 cm^{-1}.

3.2.2 Thermogravimetric Analysis (TGA)

TGA was performed by High Resolution TG-DTA Pyris Diamond (Perkin Elmer) with a heating rate of 10°C/min using a nitrogen purge with a purge rate of 200 ml/min.

3.2.3 Scanning Electron Microscope (SEM)

Morphology of the fibers and the composite samples was studied by a Scanning Electron Microscope JEOL, model JSM 2590 (Joel Ltd., Tokyo, Japan).

3.2.4 Optical Microscope (OM)

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

3.2.5 Gel Permeation Chromatography (GPC)

Gel permeation chromatography Shimatzu was used a mobile phase at flow rate 0.8 ml/min and pressure was 1.0MPa. Polymer solutions were injected with a volume of 200 μL at temperature 30°C. The column size 7.8x300 mm used was a styragel columns. Polystyrene standards were used for calibration and calculation.

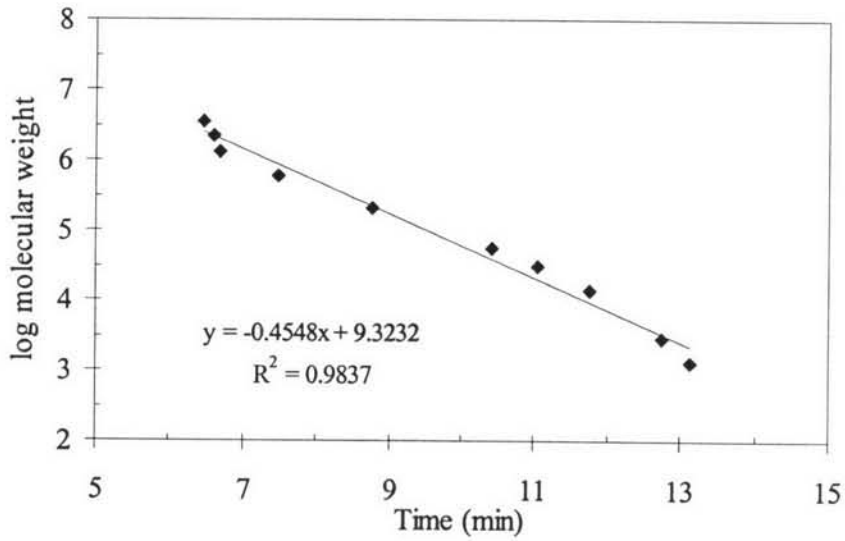

Figure 3.1 Calibration curve of styrene standard solution by Gel Permeation Chromatography (flow rate 0.8 ml/min, pressure 1 MPa and temperature 30°C).

3.2.6 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analyzer GABO model EPLEXOR QC 25 was used to analyze the effect of thermal change on the mechanical properties. It used compression mode in scan rate at 2 ° C/min, static strain at 1.0%, dynamic strain at 0.1%, Frequency at 1Hz, contact force at 0.5 N and using temperature between (-90)-100°C under liquid nitrogen.

3.2.7 Barblender Mixing

Barblender mixer OHG DUISBURG KULTURSTRASSE 51-55 model D-47055 DUISBURG TYPE 815602 and sample at 200°C, screw speed 70 rpm and fill capacity 30 g.

3.2.8 Compression Molding Machine

Blend samples are prepared by compression press, model V50H-18-CX (Wabash).

3.2.9 Lloyd Universal Testing Machine

Tensile tests of blend samples were carried out using Lloyd universal testing machine, LRX. The dumbell sample type IV followed ASTM D638-91. A gage length of 25 mm was employed with a crosshead speed of 10 mm/min.

3.3 Methodology

3.3.1 Natural Rubber Latex Preparation

Natural rubber latex particles were purified by centrifugation (at 20°C, 10000 rpm, 20 min) and were redispersed in distilled water 2 times to remove dissolved impurities and to reduce the particle size distribution. The resulting particles were considered to be clean. After washing, the particles were resuspended in water at suitable pH that depending on type of surfactant.

3.3.2 Admicellar Polymerization

Polymerization of styrene on natural rubber latex particles were carried out using two types of surfactant. Under acid condition, the anionic surfactant, sodium dodecyl sulfate (anionic surfactant) was used; on the other hand hexadecyltrimethylammonium bromide (CTAB, cationic surfactant) was used for basic condition. First, the natural rubber latex 4 g was added in bottle screw cap and was resuspended in the surfactants of 24,000 μM and 2,800 μM for SDS and CTAB respectively (See Table 3.1). The solution was adjusted to pH 3 and pH 8 for SDS and CTAB surfactant and make up volume by water to 80 ml total volume. Then the vial tubes were placed in a shaker bath set at 30°C for 4 h to allow the surfactant adsorption to reach equilibrium. After this period desired amount of styrene monomer was injected into each vial and the adsolubilization was allowed to reach

equilibrium in 2 h at 30°C. After that the initiator was added into a vial tube. The temperature was raised to 70°C for initiate the polymerization reaction and kept to 2 h. After 2 h, the natural rubber emulsions were pour into centrifugal tubes and washed with distilled water to remove the outer layer of surfactant for 2 times. Then, the admicellar polymerized natural rubber were filtered and dried in an oven at 70°C for 8 h. before taken for further examination.

3.3.3 Admicellar Polymerization Conditions

3.3.3.1 The Formation of Polystyrene Film

Based on 4 g of natural rubber (dry weight) in total volume of 80 ml, styrene and initiator mole ratios were used at 1:0.04 and 1:0.1 in CTAB or SDS surfactant with styrene concentration 100, 200, 300mM. After admicellar polymerization was completed, the obtained product was cleaned by water and dried in vacuum oven for 6 h before taken to characterize by FTIR, SEM and TGA.

3.3.3.2 The Effect of Initiator to The Molecular Weight of Polystyrene

Natural rubber 4 g was mixed with CTAB surfactant; styrene and initiator mole ratios were used at 1:0.04, 1:0.1 and 1:0.2 with styrene concentration at 100 and 200 mM (See Table 3.2). The molecular weight after reaction characterize by using GPC

3.3.3.3 The Effect of Salt to The Molecular Weigh of Polystyrene

Natural rubber 4 g in dry weight was solved with CTAB or SDS surfactant in total volume 80 ml. The mole ratio between styrene and initiator was set at 1:0.04 with styrene concentration 50-300 mM. NaBr salt of 0.3 mM was added to the solution together with styrene and initiator. The reaction was taken at 70°C for 2 h. Another reaction was also carried out but without salt. These obtained products were subjected to GPC analysis for molecular weight.

3.3.3.4 The Mechanical Thermal Properties in Unaged and Aged Conditions

Natural rubber 4 g in aqueous solution 80 ml with CTAB or SDS surfactant used styrene and initiator ratio at 1:0.04 with styrene concentration 100-300 mM and NaBr 0.3 mM. The modified natural rubber was aging at 100°C for 24 hour and testing the mechanical propertied with DMA.

3.3.3.5 The Mechanical Properties of Blended Sample in Unaged and Aged Conditions

Natural rubber 4 g in aqueous solution 80 ml with CTAB or SDS surfactant synthesized by using the mole ratio of styrene and initiator at 1:0.04 with styrene concentration 100-300 mM and NaBr 0.3 mM. The modified natural rubbers was blended with pure polystyrene and aged at 100°C for 24 h. Then the mechanical property of the blends was determined by using tensile testing.

Table 3.1 Experimental ratio between styrene and initiator designations used in this study (Total volume 80 ml).

Styrene : Initiator (mole:mole)	Natural rubber (g)	Styrene monomer (mM)	Surfactant (μM)
1:0.04	4	50,100,200,300	CTAB 2800 μM or SDS 24000 μM
1:0.1	4	50,100,200,300	

Table 3.2 Experimental designations for study the effect of initiator to the molecular weight.

Styrene : Initiator (mole:mole)	Natural rubber (g)	Styrene monomer (mM)	Surfactant (μM)
1:0.04	4	100,200	CTAB 2800 μM or SDS 24000 μM
1:0.1	4	100,200	
1:0.2	4	100,200	

Table 3.3 Experimental different concentration of styrene designation used in mechanical properties testing (Total volume 80 ml).

Surfactant (μM)	Styrene (mM)	Natural rubber (g)	SR : IN (mole)	NaBr (mM)
SDS 24000	100,200,300	4	1:0.04	0.3
CTAB 2800	100,200,300	4	1:0.04	0.3

3.3.4 Specimen Preparation for DMA and Tensile Testing

Test specimens were prepared by using a Wabash V 50 H 50-ton compression-molding machine. The dry admicelled polystyrene on natural rubber were placed in a circle frame mold and the mold was preheated at 140°C for 5 minutes in the press without any applied pressure for complete melting. The mold was then compressed under a force of 10 tons for another 5 minutes after which the mold is cooled to 35°C under pressure. Test specimens were completed for DMA and tensile testing.

3.3.5 Modified Natural Rubber Characterization

3.3.5.1 Fourier Transform Infrared Spectroscopy

FTIR spectra used to determine the formation of polystyrene films coated on surface of natural rubber. The absorption spectra were obtained from a Vector 3.0 Bruker Spectrophotometer with a resolution of 4 cm^{-1} in the frequency ranged from 4000 to 400 cm^{-1}. The absorbance were detected by using a deuterated triglycinesulfate detector (DTGS) with a specific detectivity, D^* of $1x10^9$ $cmHz^{1/2}w^{-1}$ with a repetition of 64 scans.

3.3.5.2 Molecular Weight Measurement

Gel permeation chromatography Shimatzu was used for determination of the molecular weight and polydispersion index of polystyrene as well as natural rubber. Tetrahydrofuran (HPLC grade) was used as a mobile phase at flow rate 0.8 ml/min and pressure was 1.0 MPa. Polymer solutions were injected with a volume of 200 μl at temperature 30°C. The column size 7.8x300 mm used was a styragel columns. Polystyrene standards were used for calibration and calculation.

3.3.5.3 Phase Morphology

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

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 N_2 the sample at temperature about -70^{0}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 750 and 1500 times at 15 kV.

3.3.5.4 Thermal Properties

Thermal analysis of the product was carried out under nitrogen atmosphere flow rate of 200 ml/min by using TG-DTA (Perkin Elmer, model Pyris dimond TG-DTA) to observe thermal stability and degradation temperatures of the products. Samples were put into the Pt pan and heated from 30-800^{0}C at a heating rate of 10^{0}C/minute.

Dynamic mechanical analysis was used to analyze the effect of thermal change on the mechanical properties. Sample shape is cylinder, size 2 cm of diameter and 0.5 cm thick. Strain sweep was used at 0.1% and using temperature between (-90)-100^{0}C in compression mode.

3.3.5.5 Mechanical Properties

Tensile properties of the blended samples were determined from the compressed specimens following the test conditions suggested by ASTM standards.

Lloyd universal testing machine, LRX was used to measure the tensile strength and tensile modulus of the sample. The tests were conducted according to ASTM D638-91 test procedure, using a crosshead speed of 10 mm/min.