



CHAPTER V

RESULTS AND DISCUSSION OF POLYSTYRENE COATED ON NATURAL RUBBER LATEX AND NANOMAGNETIC PARTICLES BY ADMICELLAR POLYMERIZATION

5.1 Abstract

The new method used to produce thin-film coating on solid substrate by using surfactant is called admicellar polymerization. According to this technique, the thin polystyrene (PS) film covers each natural rubber (NR) particles and magnetite (Mag) particles by using bilayers of cetyltrimethylammonium bromide (CTAB) as a reaction template. The concentrations of styrene monomer was varying from 20 to 300 mM., and the ratio of styrene to initiator was 25:1. The confirmation of synthesizing admicelled PS-NR and PS-Mag are investigated by FTIR, TGA, SEM and OM.

Keywords : Admicellar polymerization/ Natural rubber/ Polystyrene/ Magnetite particles

5.2 Introduction

The admicellar polymerization has been used to improve the adhesion between a filler substrate and polymer matrix by modifying the substrate surface with an ultra-thin polymer film. This admicellar process has been widely investigated on many types of substrates such as precipitated silica, alumina, glass fiber, cotton, natural rubber and with a variety monomers such as styrene, isoprene, tetrafluoroethylene and pyrrole. The admicellar polymerization is the one of technique that used to modified surface of substrate for improve adhesion in composite materials, increase water resistance, decrease friction in some part of machine, and prevent corrosion. The advantages of this process are quick and easy, no organic solvents involved and small amount of chemical are needed which makes

the process economical and free waste volume, the process can be applied on several substrates and many different monomers can be used.

5.3 Experimental

5.3.1 Materials

Natural rubber (Rubber Research Institute of Thailand), styrene monomer (Fluka), 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.

5.3.2 Equipments

The instruments is shown in Table 5.1.

Table 5.1 Parameters to be measured for admicelled PS-NR properties

| Parameters | Instrument / Technique |
|---|---|
| Prepared and purified natural rubber | -Hot plate and magnetic stirrer -Centrifugator, Hermle Z383K (at 10000 rpm/20 min) (ASTM 1076-02) |
| Thermal properties and amount of polymer formed | Thermogravimetric Analyzer (Perkin Elmer, Pyris Diamond) Thailand co.,ltd |
| Surface morphology | Scanning electron microscope (SEM) (JEOL JSM-5200) with magnification range between 1000-5000 times using voltage 15 kv |
| Functional group | Fourier Transform Infrared Spectroscopy (FTIR) (Nexus 670, HATR flat plate system with 45°C ZnSe crystal) PERKIN ELMER 1760X. |

5.3.3 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.

5.3.4 Admicellar Polymerization of Styrene on Natural Rubber

Polymerization of styrene on natural rubber latex particles was carried out using condition with 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 styrene monomer with required concentration (20, 50, 100, 200 and 300 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.

5.3.5 Preparation of Magnetite Particles Coated with Bilayer Surfactants (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. 100 ml ammonium hydroxide solution 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 5 h. The obtained PS coated magnetite particles were washed by water several time. FTIR was used to detect the PS synthesized.

5.4 Results and Discussion

5.4.1 Appearance of Admicelled PS-NR

The appearance of admicelled PS-NR with various styrene concentrations were showed in figure 5.1. The colour of products was varied from light yellow to opaque white with high styrene concentration. In addition, the rigidity of admicelled PS-NR was also increased due to the increment of styrene monomer concentration.

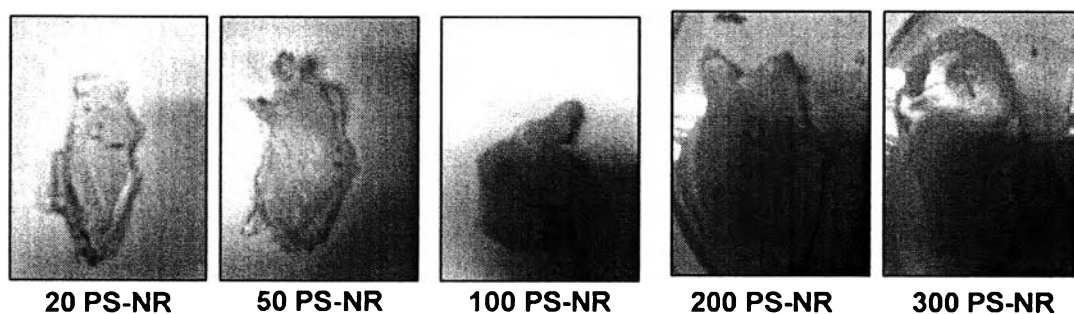


Figure 5.1 Appearance of admicelled PS-NR with 20 – 300 mM styrene concentration.

5.4.2 Characgterize of Admicelled PS-NR

5.4.2.1 *Fourier Transform Infrared Spectroscopy*

Figure 5.2 showed the spectra of modified surface of natural rubber with different styrene monomer concentrations. FTIR spectra represented the benzene ring which are aromatic C-H stretching at $3100-300\text{ cm}^{-1}$, aromatic C=C stretching at 1600 cm^{-1} , 1500 cm^{-1} , 1450 cm^{-1} and C-H deformation (out-of-plane) at 700 cm^{-1} . The absorption band of NR was also found in admicelled PS-NR at any styrene concentration especially at 837 cm^{-1} indicating the presence of C=CH wagging. The admicelled PS-NR with any different concentrations of styrene showed the same peaks as presented in standard styrene.(Preechasup et al., 2006)

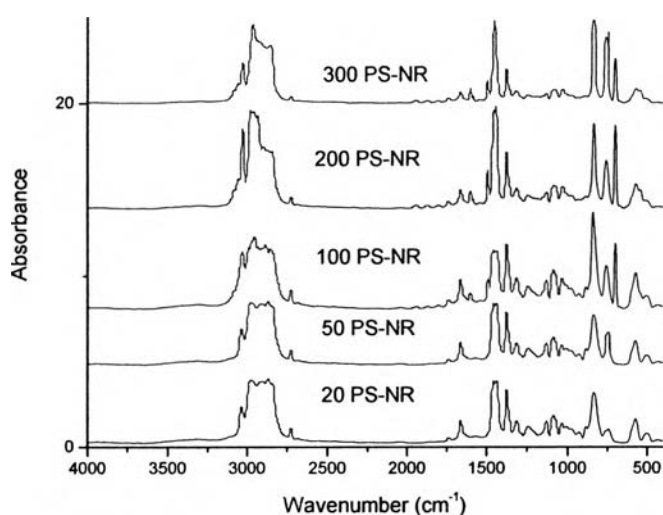


Figure 5.2 FTIR spectra of admicelled PS-NR at various styrene monomer concentration.

5.4.2.2 Thermogravimetric Analysis

The samples of admicelled PS-NR were heated up from ambient temperature to 800 °C at heating rate of 10 °C/min to investigate their thermal stability. In Figure 5.3, it could be seen that the degradation temperature of admicelled PS-NR was increased as increase in styrene monomer concentration. Due to this technique of admicellar polymerization, the decomposition for all cases of admicelled PS-NR products did not clearly show two transitions of natural rubber and polystyrene like the blending method. A little changing in slope that reveals two compositions was observed only as shown in Figure 5.3. At higher styrene concentration, especially the admicelled PS-NR with 200 mM-styrene and 300 mM-styrene, it clearly showed that two decomposition temperatures of natural rubber and polystyrene were about 380 °C and 420 °C, respectively (Preechasup, 2006). It could be seen that, after natural rubber was completely decomposed at 400 °C and then started the polystyrene decomposition. Thus, the content of polystyrene could be measured and confirmed by this technique.

The DTG results in Figure 5.4 also exhibited two peaks of DTG in admicelled PS-NR. It showed that the admicellar modified natural rubber was composed of two components.

Table 5.2 Decomposition temperatures of admicelled PS-NR

| Samples | Degradation Temperature (°C) | | | Residue (%) |
|-----------|------------------------------|--------|-----------|-------------|
| | Onset | Peak | End point | |
| PS | 389.56 | 412.48 | 422.13 | 0.73 |
| 20 PS-NR | 325.08 | 376.57 | 422.18 | 0.53 |
| 50 PS-NR | 316.13 | 369.73 | 417.88 | 0.71 |
| 100 PS-NR | 345.17 | 375.36 | 416.32 | 0.95 |
| 200 PS-NR | 327.76 | 375.09 | 444.40 | 1.24 |
| 300 PS-NR | 328.72 | 360.42 | 453.34 | 3.44 |
| NR | 324.72 | 373.67 | 429.18 | 0.44 |

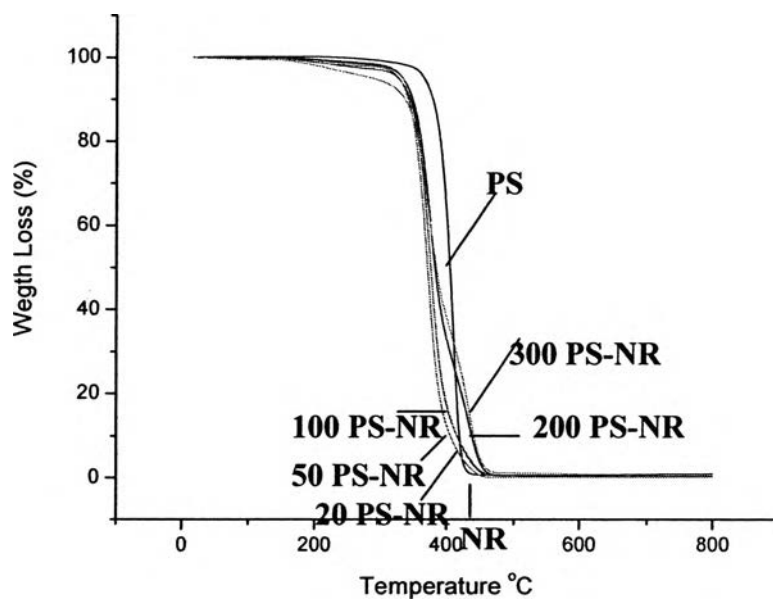


Figure 5.3 TGA results of admicelled PS-NR at various styrene monomer concentration.

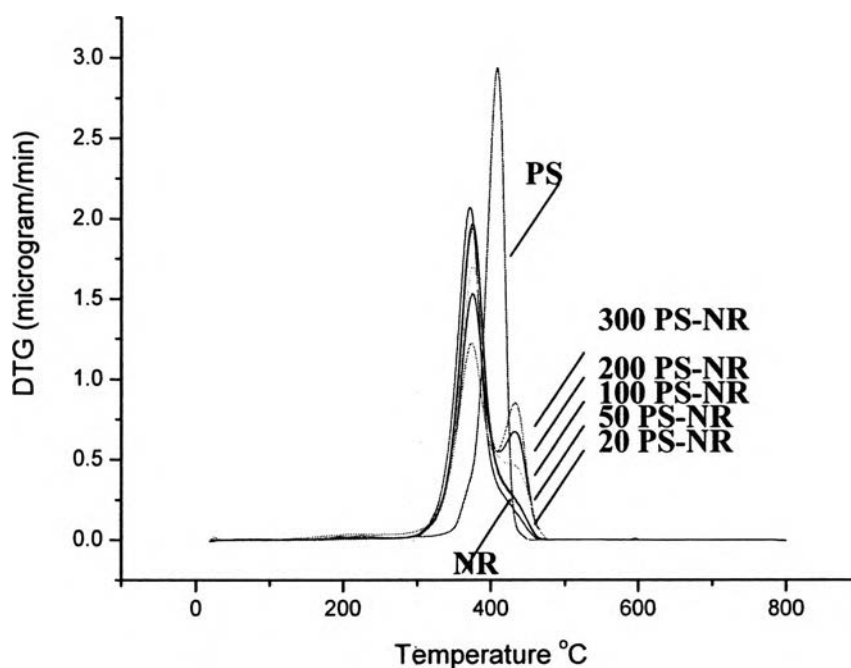


Figure 5.4 DTG results of admicelled PS-NR at various styrene monomer concentration.

5.4.2.3 Phase Morphology of Admicelled PS-NR

Surface morphology of the modified natural rubber emulsion obtained after reaction was observed by optical microscope. Figure 5.5 was showed the rough surface of pure natural rubber particles. The results exhibited core-shell structure which the core of natural rubber particles was coated with polystyrene film as shell as shown in figure 5.6. Figure 5.7 was showed admicellar modified natural rubber with polystyrene after heating to 300 °C. They have multilayer of polystyrene coated on natural rubber particles.



Figure 5.5 The phase morphology of pure natural rubber.

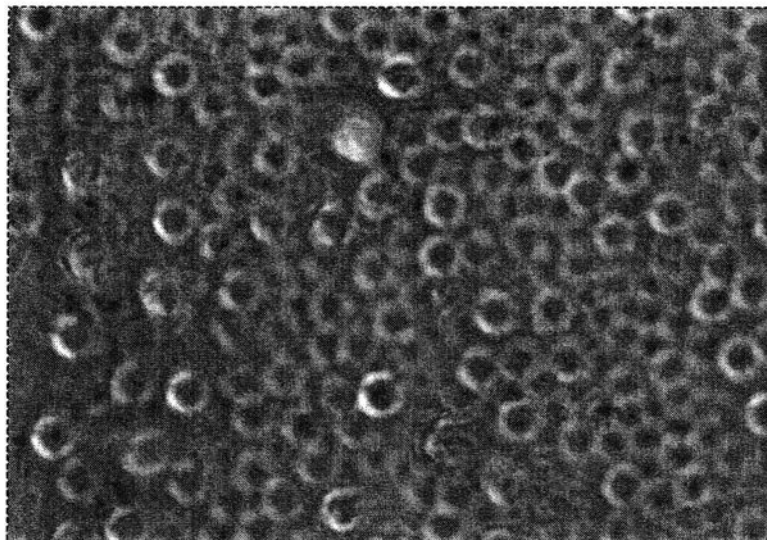


Figure 5.6 The phase morphology of admicellar modified natural rubber with polystyrene.

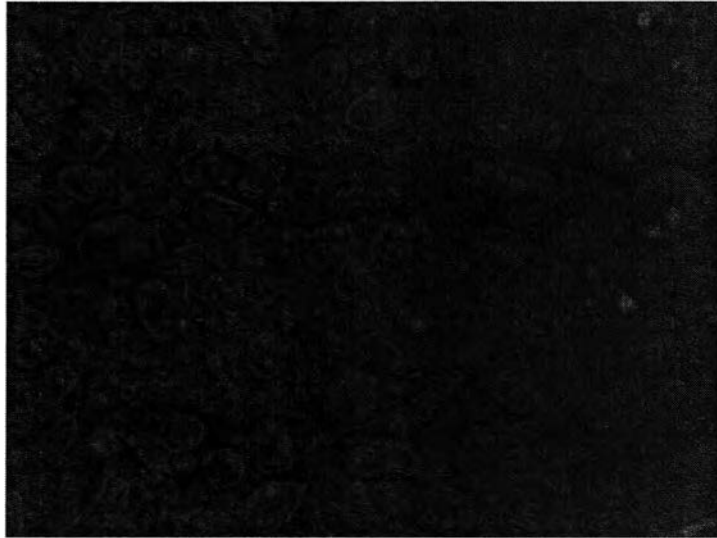


Figure 5.7 The phase morphology of admicellar modified natural rubber with polystyrene after heating to 300 °C.

Figure 5.8 shows the phase morphologies of admicelled PS-NR by SEM. It showed natural rubber particles round about 0.5-1 μm were coated with polystyrene film (Kawahara, 2003). The polystyrene film connected and held each natural rubber particles with about 0.3-0.5 μm thick.

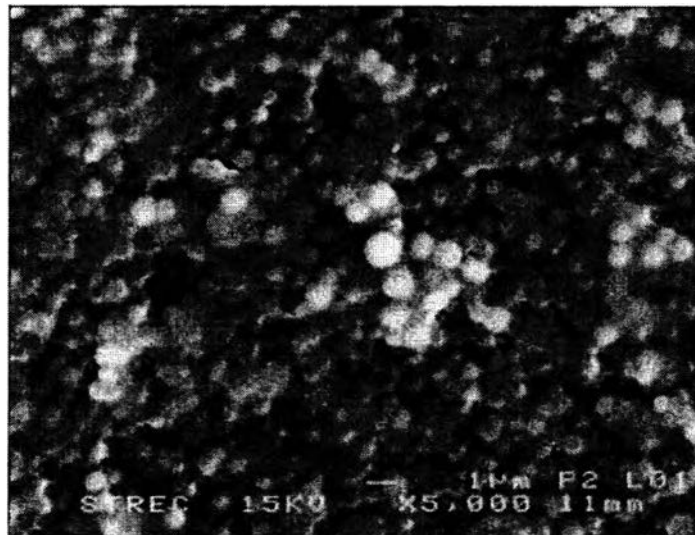


Figure 5.8 The SEM of admicellar modified natural rubber with polystyrene.

5.4.2 Characterize of Admicelled PS-Mag

5.4.2.1 Fourier-Transform Infrared Spectroscopy

Figure 5.9 was showed infrared spectra of PS-Mag and pure magnetite particles. The strong absorption band 580 cm^{-1} was the stretching vibration due to the interactions produced between the oxygen and the cations occupying the octahedral sites. IR spectra of the magnetite particles coated with SO showed the absorption bands of symmetric and asymmetric methylene($-\text{CH}_2-$) and methyl ($-\text{CH}_3-$) vibrations and C=O at 2853, 2924, 1446 and 1600 cm^{-1} . IR spectra of admicelled PS-NR represented the benzene ring which are aromatic C-H stretching at $3100-3000\text{ cm}^{-1}$, aromatic C=C stretching at 1600 cm^{-1} , 1500 cm^{-1} , 1450 cm^{-1} , C-H deformation (out-of-plane) at 700 cm^{-1} and the bands at 1185 cm^{-1} was attributed to the vibration of S=O of SDBS molecule.

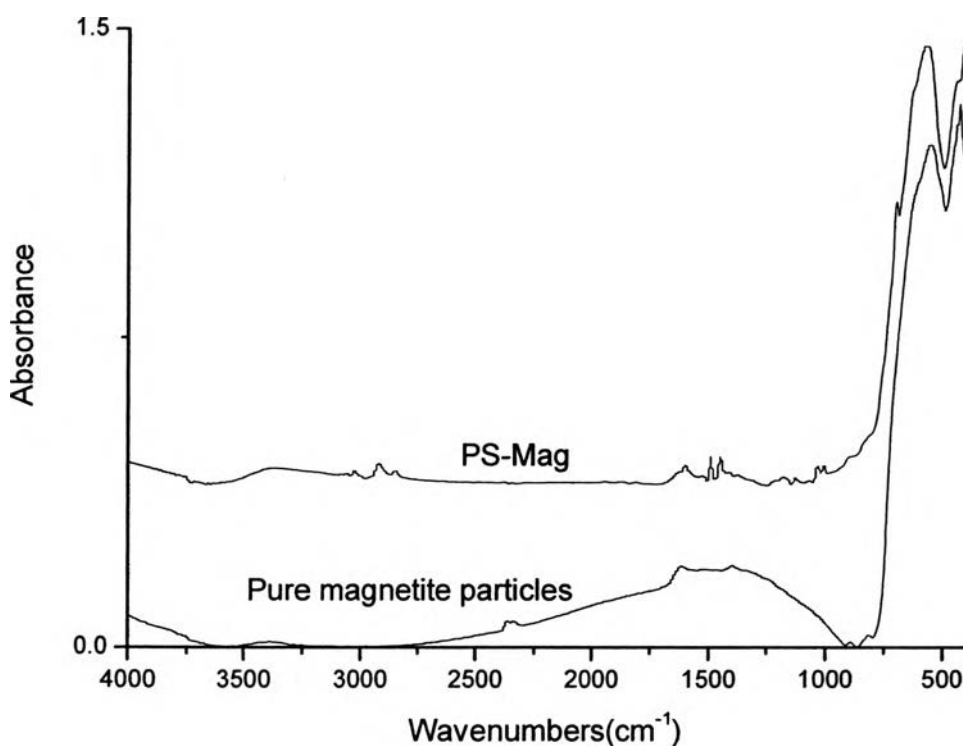


Figure 5.9 Infrared spectra of admicelled PS-Mag and pure magnetite particles.

5.4.2.2 Phase Morphology of Admicelled PS-Mag

Surface morphology of the modified magnetite particles with styrene monomer obtained after reaction was observed by optical microscope (see figure 5.10 and 5.11). Figure 5.10 was showed the agglomerate of pure magnetite particles. The results exhibited core-shell structure which the core of magnetite particles was coated with polystyrene film as shell as showed in figure 5.11.

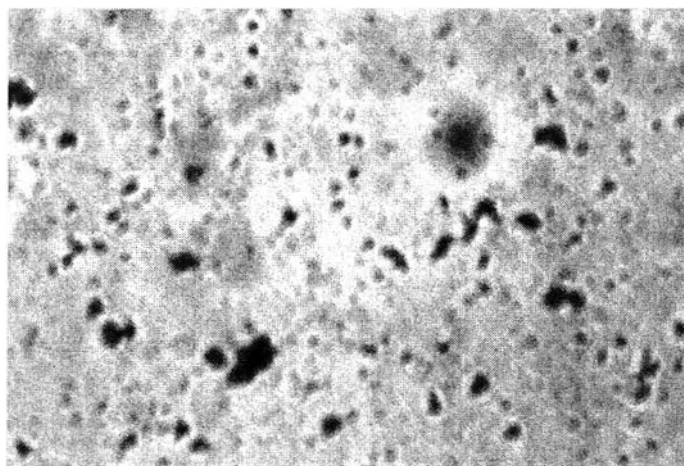


Figure 5.10 The phase morphology of pure magnetite particles.



Figure 5.11 The phase morphology of admicellar modified magnetite particle with polystyrene.

5.4.3 Rheological Properties of NR Blended with PS-NR, PS-Mag and PS

The rheological behaviors of 47.7/3/1.6/47.7 NR/PS-NR/PS-Mag/PS blends were shown in figures 5.12. It can be seen that the apparent shear viscosity of all cases was increased as the apparent shear rate was decreased. The 47.7/3/1.6/47.7 NR/PS-NR/PS-Mag/PS blends showed lower apparent shear rate than 50/50 NR/PS blends at apparent shear rate below 80. Figure 5.13 shows the die swell results of 47.7/3/1.6/47.7 NR/PS-NR/PS-Mag/PS blends. It could be seen that 50/50 NR/PS blends had the maximum die swell at apparent shear rate 160 s^{-1} and 47.7/3/1.6/47.7 NR/PS-NR/PS-Mag/PS blends had delay maximum die swell to apparent shear rate 640 s^{-1} . The magnetite particles helped viscous properties at low apparent shear rate e.g. below 160 s^{-1} .

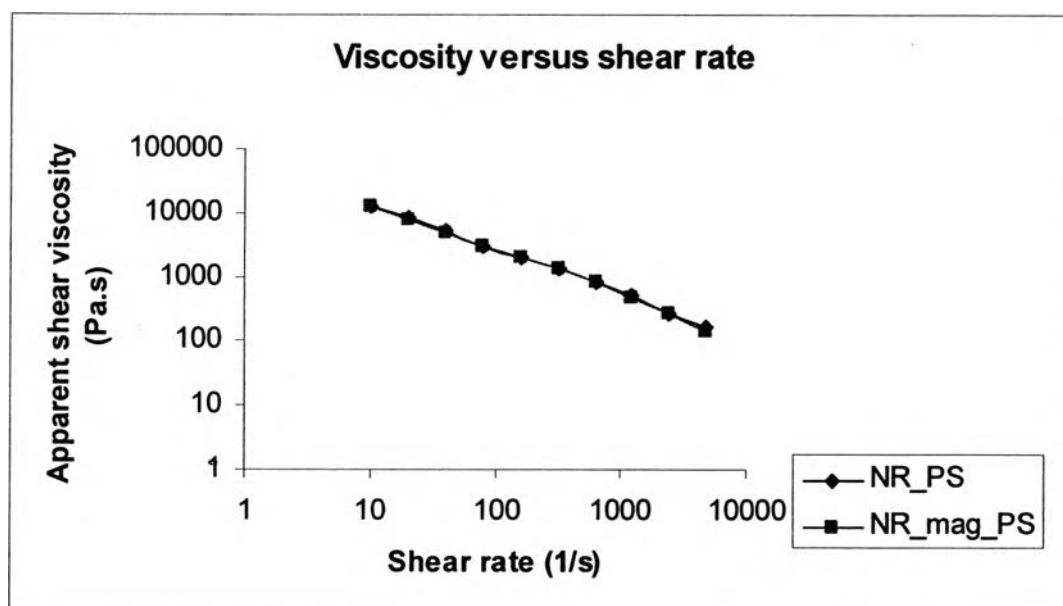


Figure 5.12 Logarithmic plots of apparent shear viscosity versus apparent shear rate of NR blend PS and NR blend Magnetic and PS at $150 \text{ }^\circ\text{C}$.

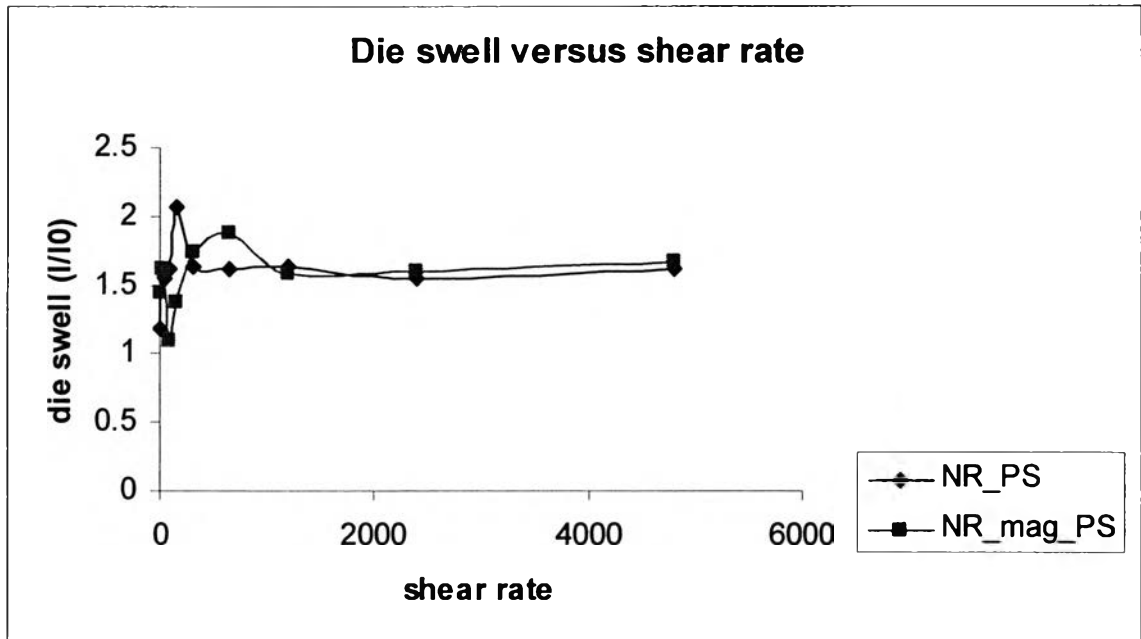
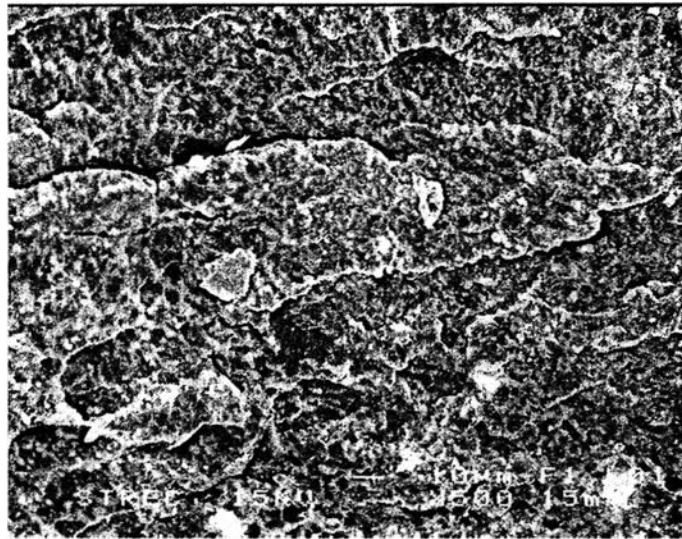


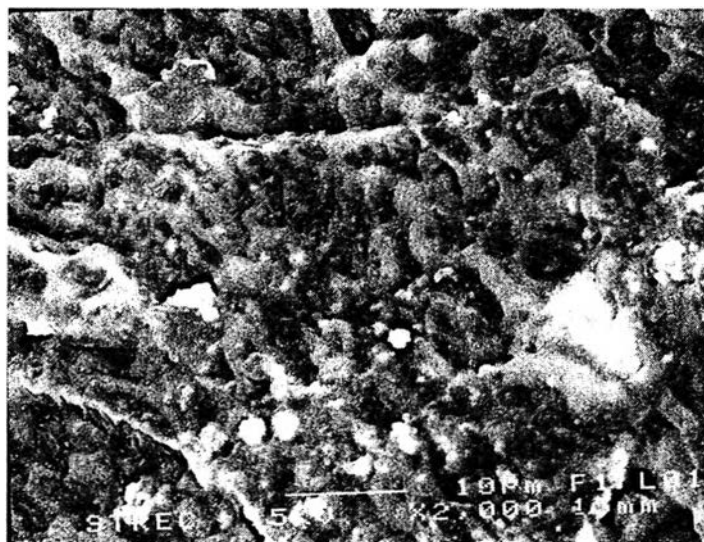
Figure 5.13 Plots of die swell versus apparent shear rate of NR blend PS and NR blend Mag and PS at 150 °C.

5.4.4 Phase Morphology of NR Blended with PS-NR, PS-Mag and PS

Surface morphology of the natural rubber blended with PS-NR, PS-Mag and PS observed by scanning electron microscope at magnification 500X and 2000X (see Figure 5.14). The results shows the dispersion of PS-Mag particles on natural rubber blend with polystyrene.



(a)



(b)

Figure 5.14 The phase morphology of natural rubber blended with PS-NR, PS-Mag and PS by using scanning electron microscope at magnification (a) 500X and (b) 2000X.

5.4.5 Rheological Properties of Admicelled PS-NR and Admicelled PS-NR Blend with 0.5 % Admicelled PS-Mag

The logarithmic plots of apparent shear stress versus apparent shear rate of PS-NR and PS-NR-0.5%Mag at 150 °C was showed in figure 5.15. In all of cases the apparent shear stress increased with increasing apparent shear rate. This is due to the applied force disturbed the long chain polymer from its equilibrium position and the molecules got disentangled (higher orientation) in the direction of applied force causing to increase in pressure and apparent shear stress (Thomas *et al.*, 1997).

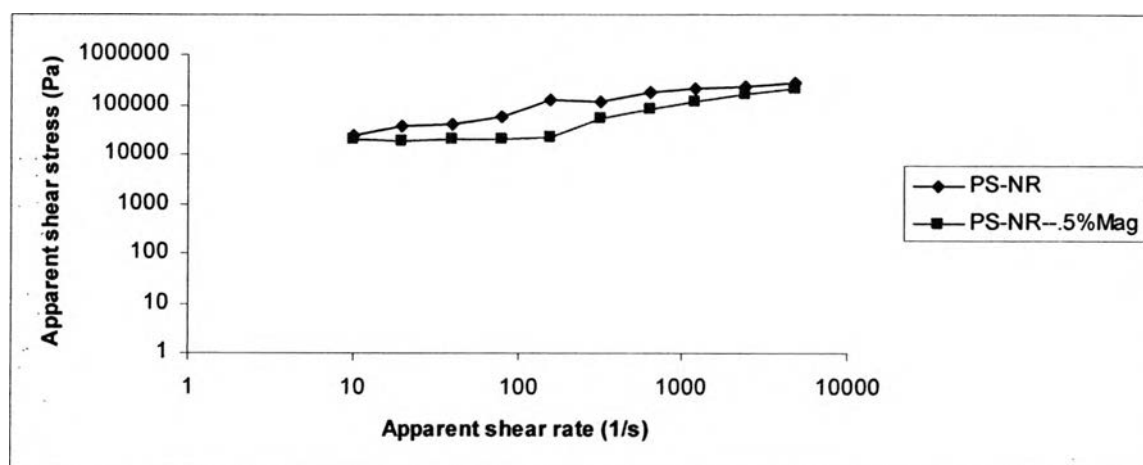


Figure 5.15 Logarithmic plots of apparent shear stress versus apparent shear rate of PS-NR and PS-NR-0.5%Mag at 150 °C.

The effect of shear rate on the apparent shear viscosity of admicelled PS-NR and admicelled PS-NR blend with 0.5% admicelled PS-Mag was shown in Figure 5.16. The result showed that the apparent shear viscosity of all case decreased as increase in shear rate. The admicelled PS-NR exhibited higher shear viscosity admicelled PS-NR blend with 0.5% admicelled PS-Mag.

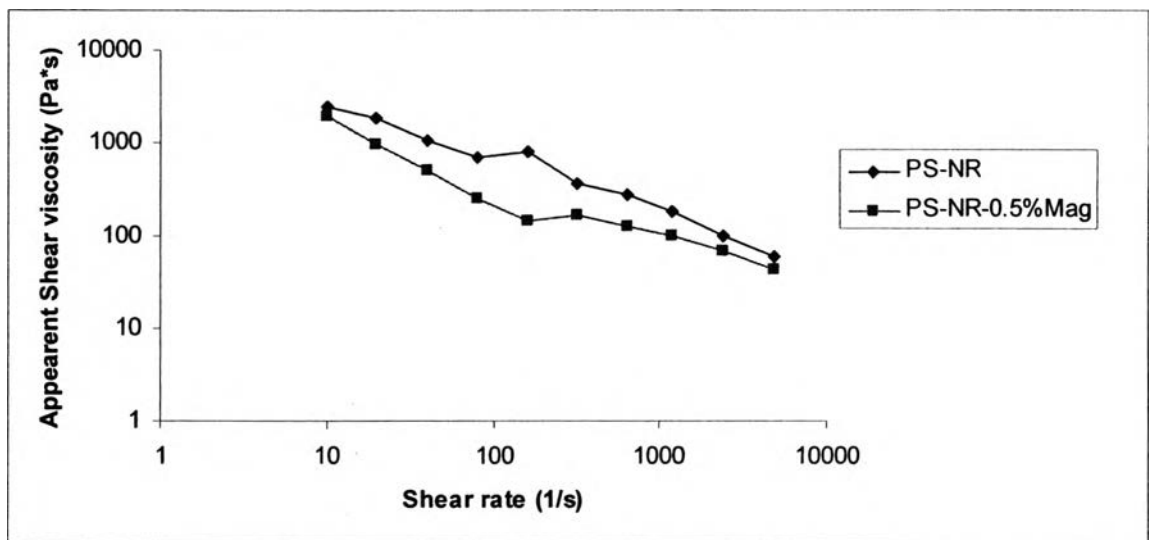


Figure 5.16 Logarithmic plots of apparent shear rate versus apparent shear rate of PS-NR and PS-NR-0.5%Mag at 150 °C.

The extrudates of admicelled PS-NR and of admicelled PS-NR blend with 0.5% admicelled PS-Mag were also measured for die swell. Figure 5.17 showed the die swell ratio of admicelled PS-NR and admicelled PS-NR blend with 0.5% admicelled PS-Mag at various apparent shear rate. The die swell of admicelled PS-NR was higher than that of admicelled PS-NR blend with 0.5% admicelled PS-Mag.

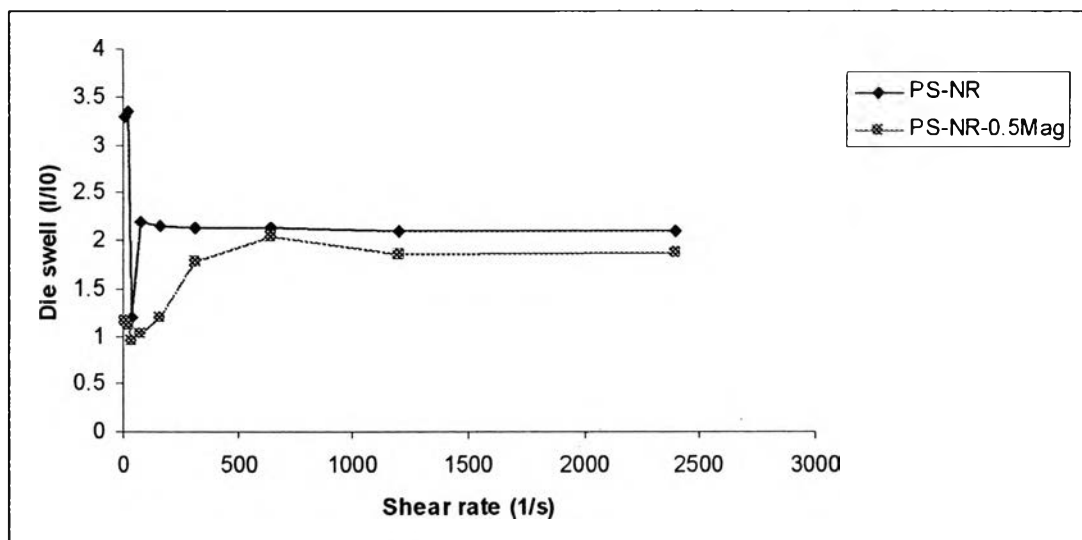


Figure 5.17 Plots of die swell versus apparent shear rate of PS-NR and PS-NR-0.5%Mag at 150 °C.

5.4.6 Molecular Weight Measurement

Molecular weight and molecular weight distribution of the 50 PS-NR was measured by using the GPC. GPC was carried out in THF (HPCL grade) using a THF column with refractometer index detector. Mw, Mn and molecular weight distribution are shown in table 5.3, figure 5.18 and figure 5.19.

Table 5.3 The molecular weight of 50 PS-NR

| Retention time (min) | Mw (Daltons) | Mn (Daltons) | MP (Daltons) | Mz (Daltons) | MWD |
|----------------------|--------------|--------------|--------------|--------------|----------|
| 15.998 | 293521 | 117717 | 329231 | 543046 | 2.493442 |

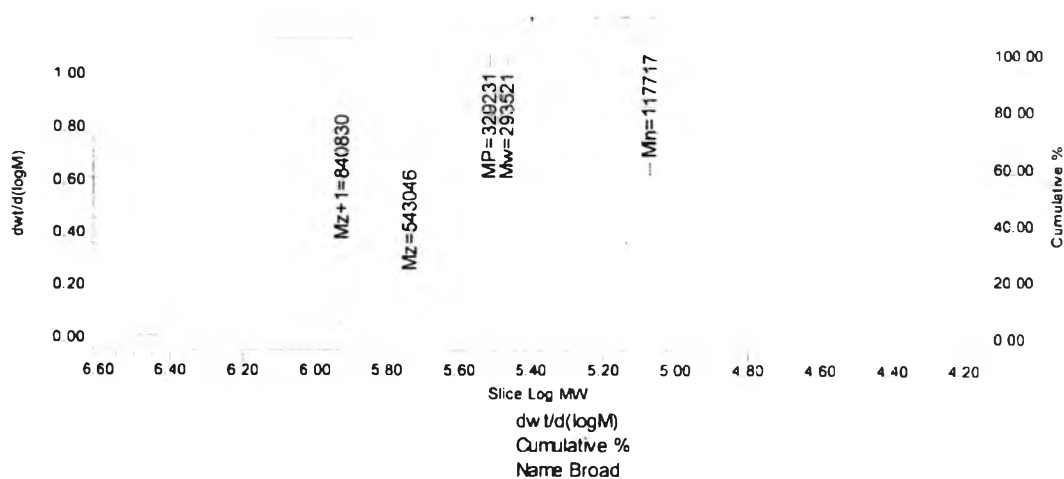


Figure 5.18 The molecular weight result of 50 PS-NR.

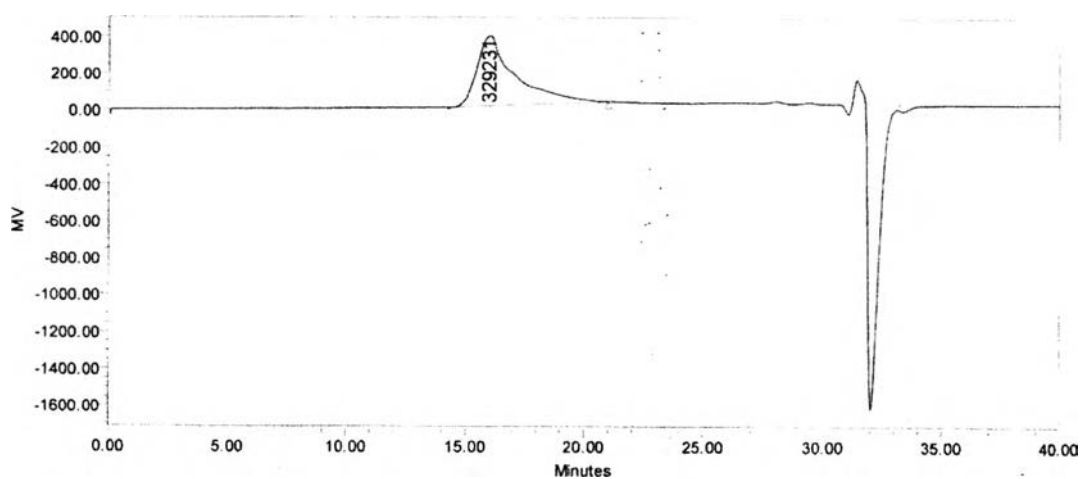


Figure 5.19 Chromatogram of 50 PS-NR.

5.5 Conclusion

The admicellar polymerization of polystyrene-coated natural rubber latex particles and polystyrene-coated magnetite particles was investigated using FTIR, SEM, OM, and TGA. From the FTIR study, the admicelled rubbers showed the characteristic peaks of polystyrene, which confirmed the existence of PS after the polymerization. The OM and SEM micrographs revealed the even coating of PS over latex particles and magnetite particles. They showed the core-shell structure of PS,

NR, and Mag. As seen in the result of TGA, the admicelled rubbers began to lose weight at higher temperature, compared to that of NR, and they also showed the shift of major decomposition of pure PS to higher temperature. The DTG curves also demonstrated an increase of char yields of the admicelled rubbers. As PS content increased, the residual content also increased. This resulted in slowing down the degradation of admicelled rubber at 194 to 378.7°C. These indicated that the admicelled rubbers were more thermostable than natural rubber. In rheological behaviors, the admicellar polymerization of magnetite particles have the effect to enhance viscous properties of admicelled PS-NR.

5.6 Acknowledgements

The author would like to acknowledge the Petroleum and Petrochemical College; the National Excellence Center for Petroleum, Petrochemicals, and Advanced Materials, Thailand; the National Research Council of Thailand, the Polymer Processing and Polymer Nanomaterials Research Unit, and Rachadapisek Sompoch Endevelopment (RU) for the financial support of this project.

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