

CHAPTER VI
RESULTS AND DISCUSSION OF POLY (METHYL METHACRYLATE)
COATED ON NATURAL RUBBER LATEX AND NANOMAGNETIC
PARTICLES BY ADMICELLAR POLYMERIZATION

6.1 Abstract

Thin poly(methyl methacrylate) (PMMA) film covers each natural rubber (NR) particles by using bilayers of cetyltrimethylammonium bromide (CTAB) as a reaction template for the admicellar polymerization of PMMA-NR by varying methyl methacrylate (20, 50, 100 mM). The confirmation of synthesizing admicelled PMMA-NR is investigated by FT-IR, TGA, SEM and OM. The natural rubber round particles about 0.5-1 μm were successfully coated by poly(methyl methacrylate) thin film of thickness about 0.3-0.5 μm as observed by SEM. Nanomagnetic particles are added to the admicellar polymerization to help viscous properties as observed by capillary rheometer.

Keywords : Admicellar polymerization/ Natural rubber/ Poly(methyl methacrylate)/ Magnetite particles

6.2 Introduction

Admicellar polymerization is an innovative method. It can be used to improve the compatibility at the interface between different materials. Admicellar polymerization generally consists of four main steps:

1. Surfactant adsorption
2. Monomer adsolubilization
3. Polymerization
4. Surfactant removal

The method makes use of the formation of surfactant bilayer or admicelle on a substrate at a surfactant concentration just below the critical micelle concentration (CMC). The polymeric film formation in this process is controlled by

several parameters including the characteristic of the substrate surface, the type of surfactant, the monomer molecule, the electrolyte, and the pH value. (Thirawudh *et.al.*, 2008)

This work aims to study polystyrene coated on natural rubber and magnetite particles by admicellar polymerization technique by varying condition of styrene concentrations.

6.3 Experimental

6.3.1 Materials

Natural rubber (Rubber Research Institute of Thailand), 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.

6.3.2 Equipments

The instruments is shown in Table 6.1.

Table 6.1 Parameters to be measured for admicelled PMMA-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

Parameters	Instrument / Technique
Functional group	Fourier Transform Infrared Spectroscopy (FTIR) (Nexus 670, HATR flat plate system with 45°C ZnSe crystal) PERKIN ELMER 1760X.

6.3.3 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.

6.3.4 Admicellar Polymerization of Styrene on Natural Rubber

Polymerization of methyl methacrylate on natural rubber latex particles were 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 methyl methacrylate 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 methyl methacrylate and initiator at 100:1 was added to initiate polymerization of styrene 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.

6.3.5 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 methyl methacrylate for 2 h. The initiator was added to start polymerization at 70 °C and the reaction was continued for 5 h. The obtained PMMA coated magnetite particles were washed by water several time. FTIR was used to detect the PMMA synthesized

6.4 Results and Discussion

6.4.1 Appearance of Admicelled PS-NR

The appearance of admicelled PMMA-NR with various methyl methacrylate concentrations were showed in figure 6.1. The colour of 20 PMMA-NR and 50PMMA-NR had light yellow. In higher methyl methacrylate concentrations had the phase seperated of poly(methyl methacrylate) and natural rubber.

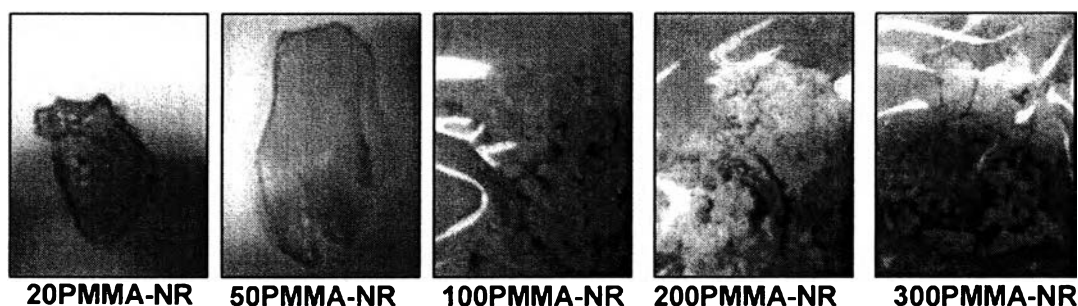


Figure 6.1 Appearance of admicelled PMMA-NR with 20 – 300 mM methyl methacrylate concentration.

6.4.2 Characgerizations of Admicelled PMMA-NR

6.4.2.1 *Fourier Transform Infrared Spectroscopy*

Figure 6.2 showed the spectra of modified surface of natural rubber with different methyl methacrylate monomer concentrations. FTIR spectra represented the carbonyl (C=O) group at 1733 cm^{-1} , methyl group at 1143 cm^{-1} . The absorption band of NR was also found in admicelled PMMA-NR at any methyl

methacrylate concentration especially at 837 cm^{-1} indicating the presence of C=CH wagging.

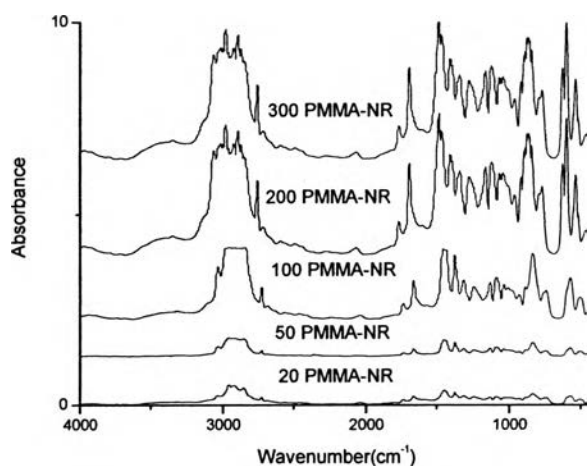


Figure 6.2 FTIR spectra of admicelled PMMA-NR at various methyl methacrylate monomer concentration.

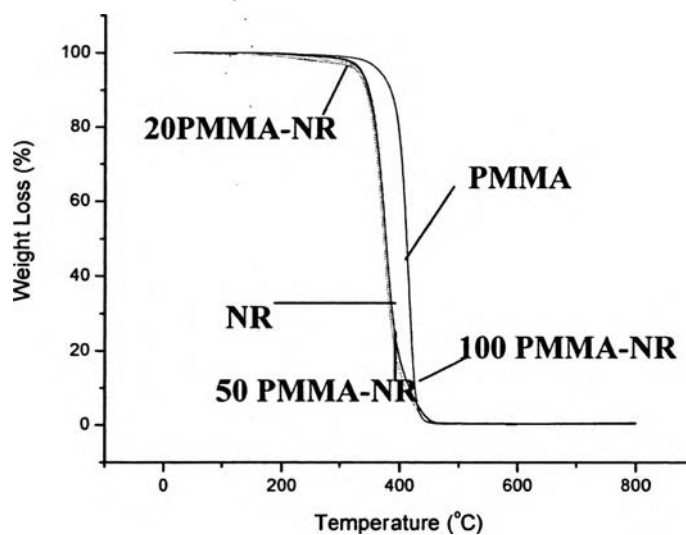
6.4.2.2 Thermogravimetric Analysis

The samples of admicelled PMMA-NR were heated up from ambient temperature to $800\text{ }^{\circ}\text{C}$ at heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$ to investigate their thermal stability. In Figure 6.3, it could be seen that the degradation temperature of admicelled PMMA-NR was increased as increase in methyl methacrylate monomer concentration. Due to this technique of admicellar polymerization, the decomposition for all cases of admicelled PMMA-NR products did not clearly show two transitions of natural rubber and poly(methyl methacrylate) like the blending method. A little changing in slope that reveals two compositions was observed only as shown in Figure 6.3. At higher methyl methacrylate concentration, it clearly showed that two decomposition temperatures of natural rubber and poly(methyl methacrylate) were about $376\text{ }^{\circ}\text{C}$ and $413\text{ }^{\circ}\text{C}$, respectively. It could be seen that, after natural rubber was completely decomposed at $400\text{ }^{\circ}\text{C}$ and then started the poly (methyl methacrylate) decomposition. Thus, the content of poly (methyl methacrylate) could be measured and confirmed by this technique.

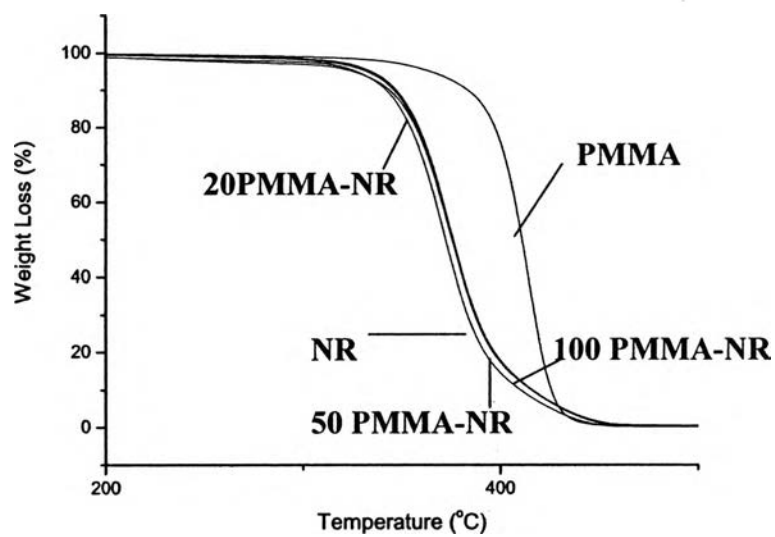
The DTG results in Figure 6.4 also exhibited two peaks of DTG in admicelled PMMA-NR. It showed that the admicellar modified natural rubber was composed of two components.

Table 6.2 Decomposition temperatures of admicelled PMMA-NR

Samples	Degradation Temperature (°C)			Residue (%)
	Onset	Peak	End point	
PMMA	393.17	413.74	429.28	1.04
NR	325.08	376.57	422.18	1.53
20 PMMA-NR	314.89	368.24	413.55	1.27
50 PMMA-NR	316.63	369.73	417.88	0.71
100 PMMA-NR	326.25	372.96	419.65	1.22



(a)



(b)

Figure 6.3 TGA results of admicelled PMMA-NR (a) 0 °C – 800 °C and (b) 200 °C – 500 °C

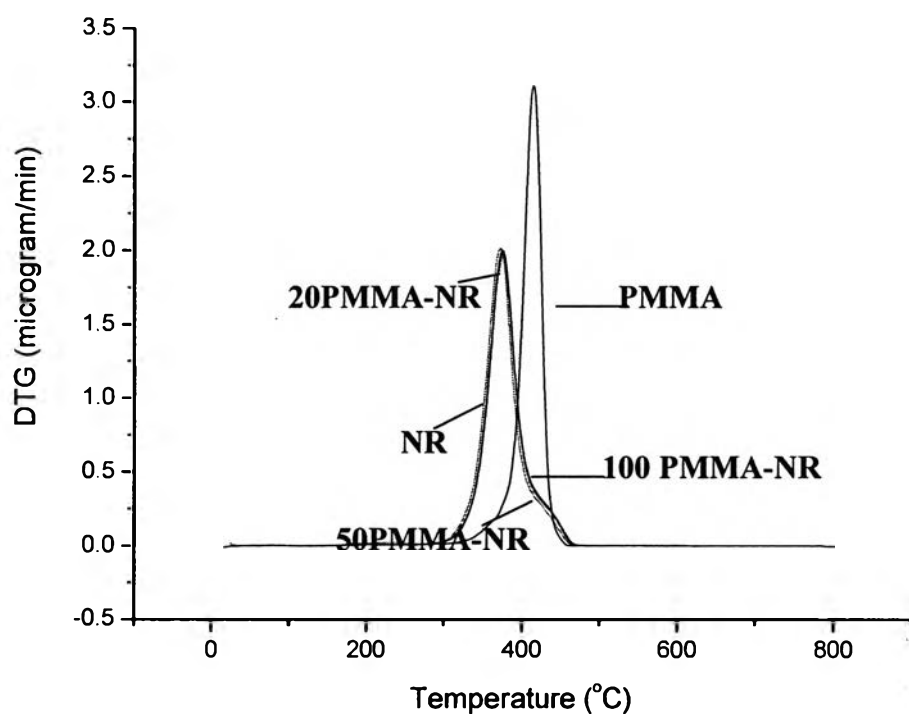


Figure 6.4 DTG results of admicelled PMMA-NR at various methyl methacrylate monomer concentration.

6.4.2.3 Phase Morphology of Admicelled PMMA-NR

Surface morphology of the modified natural rubber emulsion obtained after reaction was observed by optical microscope. The results exhibited core-shell structure which the core of natural rubber particles was coated with poly (methyl methacrylate) film as shell as shown in figure 6.5.

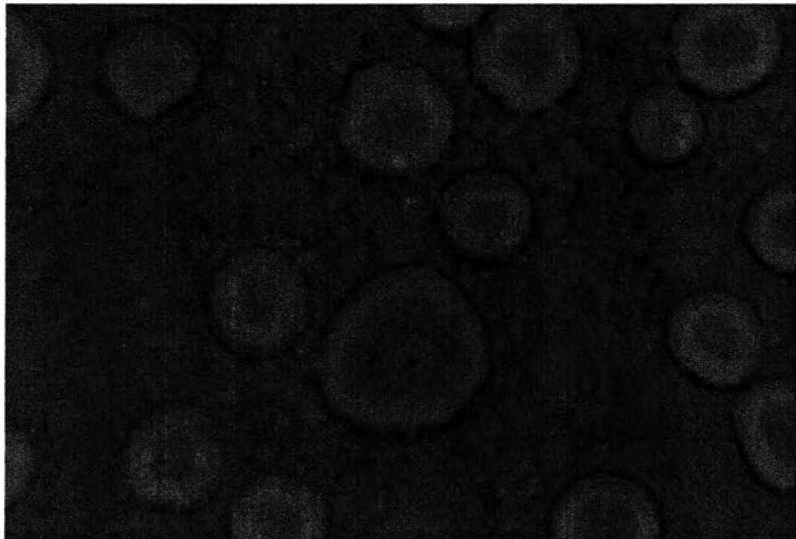


Figure 6.5 The phase morphology of 50 mM PMMA - 5 %wt. NR.

The phase morphologies of admicelled PMMA-NR by SEM after OSO_4 was showed in figure 6.6. In figures 6.6, natural rubber particles were coated with poly(methyl methacrylate) film. The poly(methyl methacrylate) film connected and held each natural rubber particles.

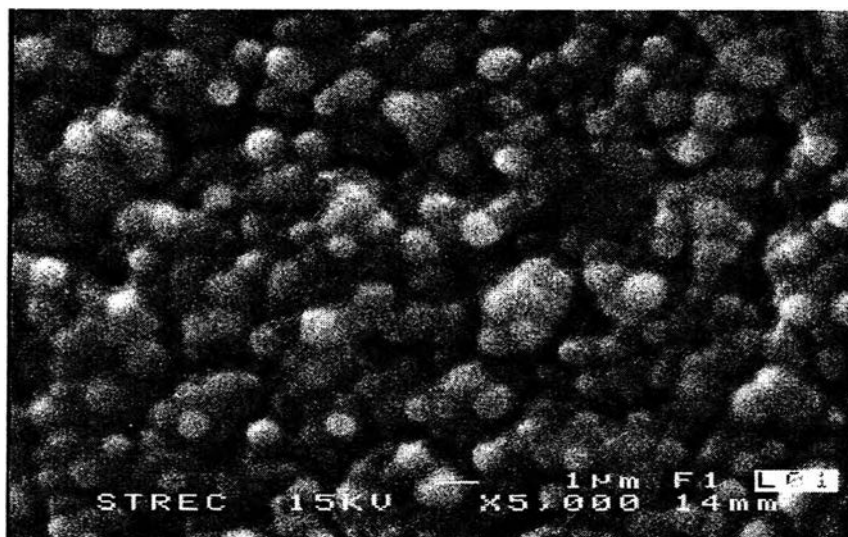


Figure 6.6 The SEM of of admicellar modified natural rubber with poly(methyl methacrylate).

6.4.3 Characterize of Admicelled Mag-NR

6.4.3.1 Fourier-Transform Infrared Spectroscopy

Figure 6.7 showed infrared spectra of PMMA-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 PMMA showed the absorption bands 1718 cm^{-1} .

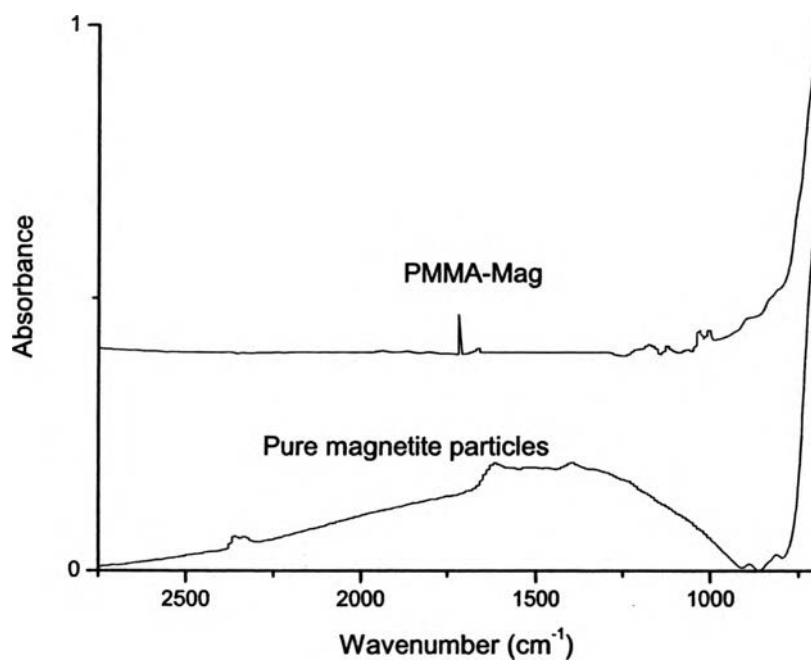


Figure 6.7 Infrared spectra of admicelled PMMA-Mag and pure magnetite particles $3000 - 500\text{ cm}^{-1}$.

6.4.3.2 Phase Morphology of Admicelled PMMA-Mag

Surface morphology of the modified magnetite particles with methyl methacrylate monomer obtained after reaction was observed by optical microscope. The results exhibited core-shell structure which the core of magnetite

particles was coated with poly(methyl methacrylate) film as shell as showed in figure 6.8.

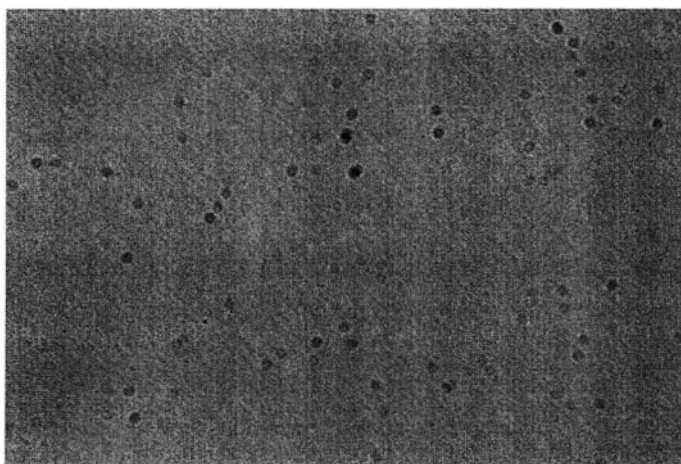


Figure 6.8 The phase morphology of admicellar modified magnetite particle with poly(methyl methacrylate).

6.4.4 Rheological Properties of Admicelled PMMA-NR and Admicelled PMMA-NR Blend with 0.5 % Admicelled PMMA-Mag

Figure 6.9 was showed the logarithmic plots of apparent shear stress versus apparent shear rate of PMMA-NR and PMMA-NR-0.5%Mag at 150 °C. In all of cases the apparent shear stress increased with increasing apparent shear rate.

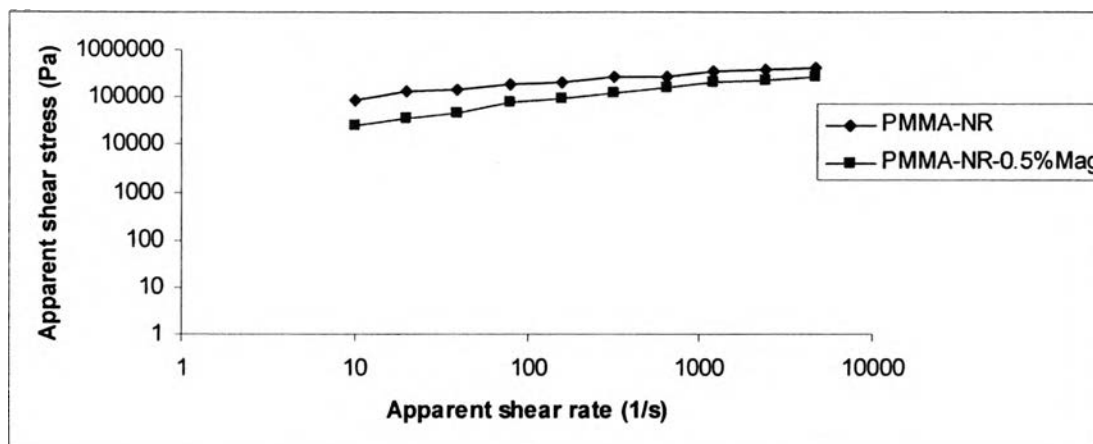


Figure 6.9 Logarithmic plots of apparent shear stress versus apparent shear rate of PMMA-NR and PMMA-NR-0.5%Mag at 150 °C.

The flow behavior of admicelled PMMA-NR and admicelled PMMA-NR blend with 0.5 % admicelled PMMA-Mag was shown in figure 6.10. It can be seen that the PMMA-NR-0.5%Mag exhibited lower the apparent shear viscosity than PMMA-NR. All of case, the apparent shear viscosity decreased as increase in shear rate.

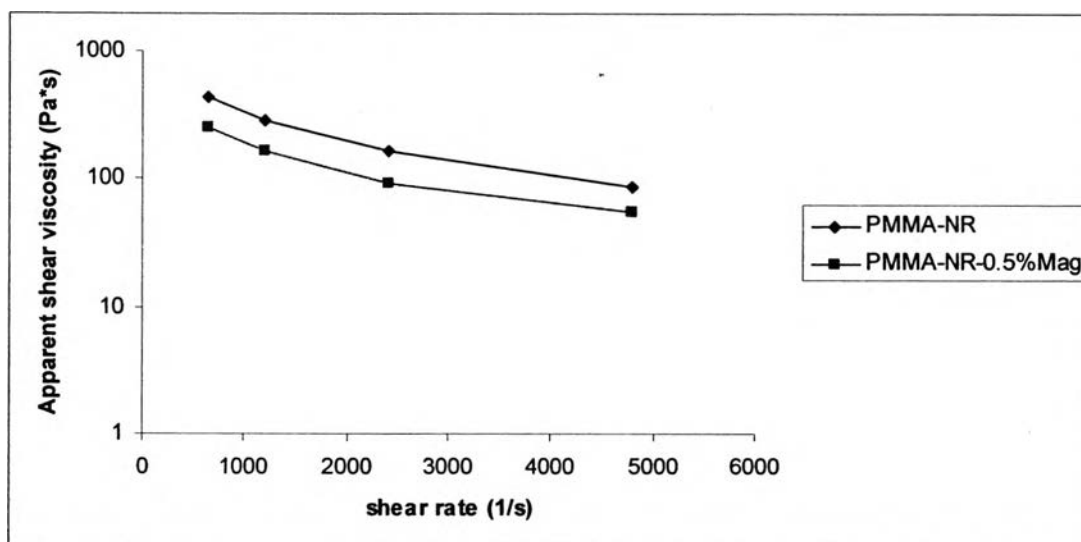


Figure 6.10 Logarithmic plots of apparent shear viscosity versus apparent shear rate of PMMA-NR and PMMA-NR-0.5%Mag at 150 °C.

Figure 6.11 showed the die swell ratio of admicelled PMMA-NR and admicelled PMMA-NR blend with 0.5% admicelled PMMA-Mag at various apparent shear rate. The die swell of admicelled PMMA-NR was higher than that of admicelled PMMA-NR blend with 0.5% admicelled PMMA-Mag.

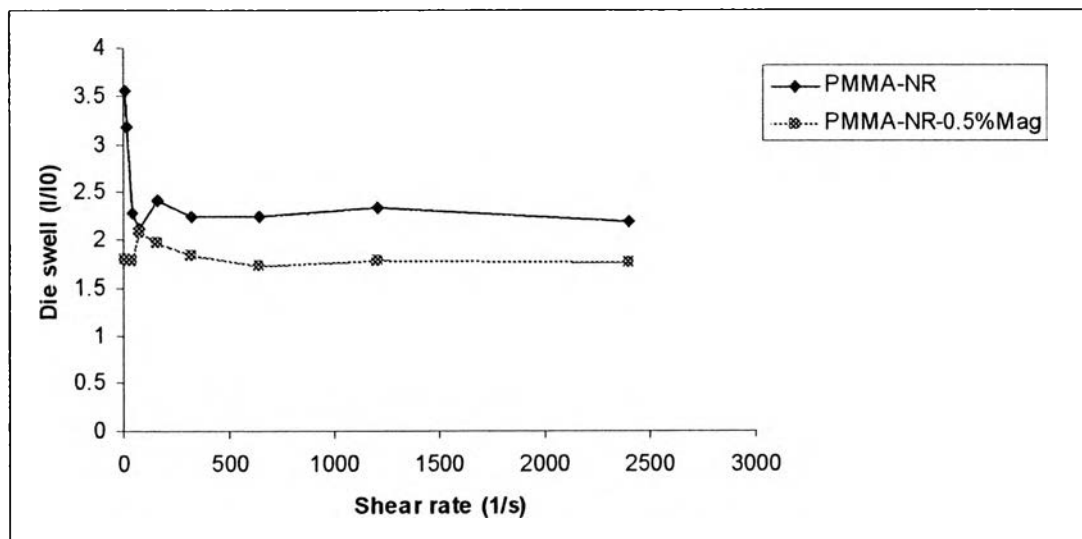


Figure 6.11 Plots of die swell versus apparent shear rate of PMMA-NR and PMMA-NR-0.5%Mag at 150 °C.

6.4.5 Molecular Weight Measurement

Table 6.3 and figure 6.12 were shown the Mw, Mn and molecular weight distribution of 50 PMMA-NR. The Mw of the 50 PMMA-NR was observed to be about 74,670. Figure 6.13 was shown the 50 PMMA-NR molecular weight chromatogram and suggested that 50 PMMA-NR was come out at elution time about 18.317 min.

Table 6.3 The molecular weight of 50 PMMA-NR

Retention time (min)	Mw (Daltons)	Mn (Daltons)	MP (Daltons)	Mz (Daltons)	MWD
18.317	74670	32220	48075	197031	2.317506

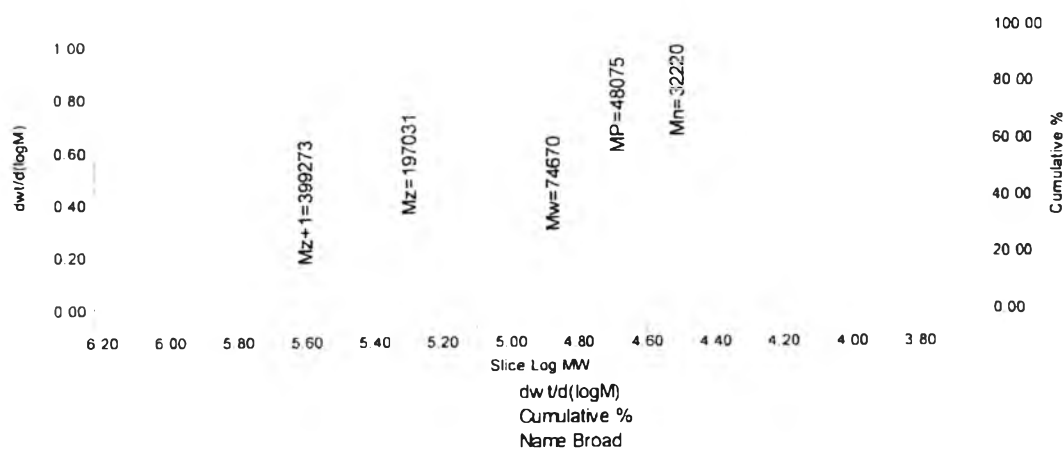


Figure 6.12 The molecular weight result of 50 PMMA-NR.

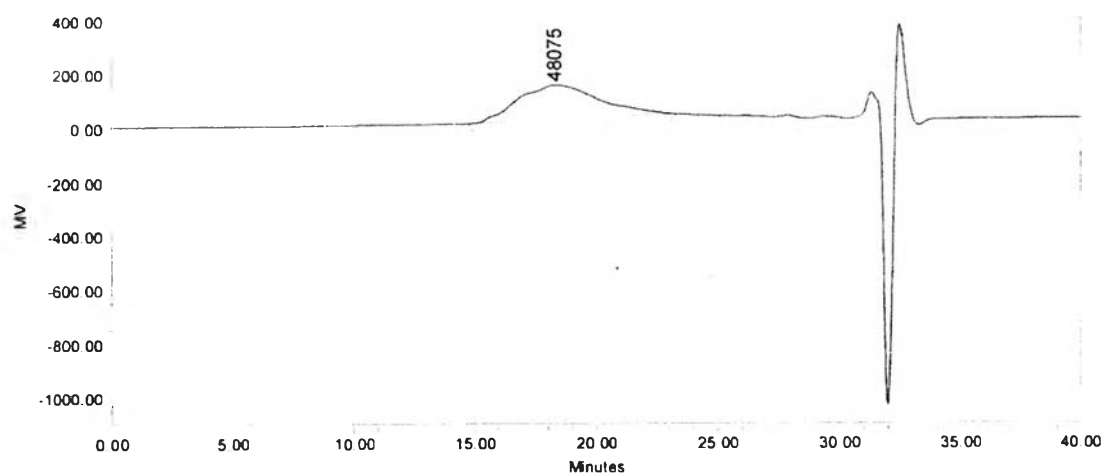


Figure 6.13 Chromatogram of 50 PMMA-NR.

6.5 Conclusion

The modified surface of natural rubber and magnetite particles with methyl methacrylate monomer was investigated by using FTIR, SEM, OM, and TGA. From the FTIR study, the admicelled rubbers showed the characteristic peaks of poly(methyl methacrylate), which confirmed the existence of PMMA after the polymerization. The OM and SEM micrographs revealed the even coating of PMMA

over latex particles and they showed the core-shell structure of PMMA and NR. 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 PMMA to higher temperature. The DTG curves also demonstrated an increase of char yields of the admicelled rubbers. As PMMA content increased, the residual content also increased. In rheological behaviors, the admicellar polymerization of magnetite particles have the effect to enhance viscous properties of admicelled PMMA-NR.

6.6 Acknowledgements

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