

CHAPTER V
RESULTS AND DISCUSSION OF MPS ADMICELLAR POLYMERIZATION
ON NATURAL RUBBER LATEX PARTICLES
USING CATIONIC SURFACTANT

5.1 Abstract

The new method is used to produce thin-film coating on solid substrate by using surfactant is called admicellar polymerization. According to this technique, the thin polymethacryloxypropyltrimethoxysilane (PMPS) film covered each natural rubber latex particles (NR) by using bilayer of hexadecylpyridinium chloride monohydrate (CPC) as a reaction template on the substrate surface (5 w/v% of NR). The concentrations of MPS monomer were varied from 50 to 200 mM and the ratio of MPS to initiator was 1:0.01. The confirmation of synthesized PMPS-ad-NR was characterized by Particle size analyzer, Fourier transform infrared spectroscopy (FT-IR), Thermogravimetric analysis (TGA), Field emission scanning electron microscope (FE-SEM), Energy-dispersive X-ray spectroscopy (EDX) and Transmission electron microscope (TEM). The results from particle size analyzer revealed that the size of PMPS-ad-NR was increased with MPS content. From the FT-IR study, the admicelled rubbers showed the characteristic peaks of PMPS which confirmed the existence of PMPS after polymerization. The TGA results showed that NR and PMPS combined like one single component and when PMPS content was increased, the shift of the tail of the transition to end at higher temperature was found together with significant residue content. From FE-SEM and EDX, the PMPS-ad-NR were definitely occurred as a full coverage and partial coverage of PMPS over NR particles yielding the core-shell particles (from the full coverage) embedded finely in the homogeneously fused PMPS-NR matrix (from partial coverage). From TEM revealed that the NR particle was coated by PMPS.

Keywords: Admicellar polymerization, Natural rubber, PMPS

5.2 Introduction

Thin-film coating on solid substrate has been a popular research topic because it has many applications in composite materials (Luna-Xavier *et al.*, 2002), health care products (Pongprayoon *et al.*, 2004) and microelectronic devices. The new method used to produce thin-film coating on solid substrate by using surfactant is called admicellar polymerization or the thin film via surfactant template (TFST). The film thickness is in a range of nanometers to tens of nanometers. The process has been characterized as occurring in four steps, 1) surfactant adsorption, 2) monomer adsorption, 3) polymerization and 4) surfactant removal. This method has been used to form a polymer film on various substrates such as aluminum (Karlsson *et al.*, 2009), calcium carbonate (Rungruang *et al.*, 2006), cotton (Tragoonwichian *et al.*, 2009), glass fiber (Sakhalkar *et al.*, 1995), natural rubber (NR) (Bunsomsit *et al.*, 2002), rice straw fiber (Zhao *et al.*, 2011) and silica (Luna-Xavier *et al.*, 2002). In previous studies, the adsorption isotherm of surfactant has been studied for admicellar polymerization. Cetyl trimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) were used to form surfactant bilayers on the NR surface and acted as a reaction template for admicellar polymerization (Bunsomsit *et al.*, 2002 and Magaraphan *et al.*, 2009). The purpose of this research is to study the adsorption isotherm of hexadecylpyridinium chloride monohydrate (CPC, cationic surfactant) on NR latex particles. A plot of the equilibrium concentration versus the amount of adsorbed surfactant was made to obtain the adsorption isotherm. After that, the admicellar polymerization of 3-(trimethoxysilyl)propylmethacrylate (MPS) on NR latex particles was carried out. The PMPS film coated on NR latex particles was characterized by using particle size analyzer, FT-IR, TGA, FE-SEM, EDX and TEM.

5.3 Experimental

5.3.1 Materials

Natural rubber (60 wt% dry rubber content) (Rubber Research Institute of Thailand), Hexadecylpyridinium chloride monohydrate (CPC) (99% purity) (Sigma), 3-(Trimethoxysilyl)propylmethacrylate monomer (MPS) (98%

purity) (Aldrich), Potassium persulfate (KPS) (97% purity) (Aldrich), Sodium hydroxide (NaOH) (MERCK), Hydrochloric acid (HCl) (37 wt%) (Carlo Erba Reagent Company). All materials were used without further purification.

5.3.2 Equipments

The instruments are shown in Table 5.1

Table 5.1 Parameters to be measured for admicellar polymerization

Parameters	Instrument/Technique
Prepared and purified natural rubber	- Centrifuge, Kubota 5922 (at 10,000 rpm/20 min) (ASTM 1076-02) - Hot plate and magnetic stirrer
Admicellar polymerization	- Shaking bath (Memmert) - pH meter, Eutech instruments pH 510 - Vacuum oven: Isotemp vacuum oven Model 2854
Particle size measurement	- Particle size analyzer, Malvern Mastersizer X Ver.2.18
Functional group	- Fourier transform infrared attenuated total reflectance spectroscopy (FTIR-ATR) (Nexus 670, HATR flat plate system with 45°C ZnSe crystal)
Thermal properties and amount of polymer formed	- Thermogravimetric Analyzer (Perkin Elmer, model Pyris diamond TG-DTA)
Surface morphology	- Field emission scanning electron microscopy (FE-SEM) and Energy-dispersive X-ray spectroscopy (EDX) (Hitachi, model S4800, 5 kV) - Transmission electron microscopy (TEM) (H-7650, Hitachi High-Technologies Co., Japan)

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. The resulting particles were considered to be clean.

5.3.4 Admicellar polymerization

Admicellar polymerization of PMPS on natural rubber was carried out at various MPS concentrations (50, 100 and 200 mM). The process started with adsorption of CPC surfactant bilayer on NR particles by agitating the mixture of NR and surfactant at 30°C in the shaking bath for 4 hrs. After that, MPS monomer at various concentrations was added into the system. The mixture was continuously agitated in the shaking bath for 2 hrs. Then KPS (with ratio of MPS and initiator at 1:0.01) was added into the system to start the polymerization reaction. Polymerization reaction of MPS was set at 70°C in the shaking bath for 3 hrs. At the end of the polymerization time, the reaction was stopped by immersing the reaction vials in an ice bath for 10 minutes. The NR particles were washed with water to remove the upper layer of surfactant and separated from the mixture by centrifuging at 3000 rpm. Finally, the products were dried in the vacuum oven at 70°C for 16 hrs.

5.4 **Results and discussion**

5.4.1 Particle size measurement

The measurement showed that particle diameter of NR covered a wide range. The diameter of NR was in the range of 0.28 - 1.75 μm , confirming that the particle size of NR was naturally polydisperse. The particles size analysis presented that the NR latex had a diameter of 0.80 μm by volume average. The size of PMPS-ad-NR was 2.83-42.75 μm advising that the size was increased with MPS content. Moreover, it is to be underlined that the large size could be the combined of several particles.

5.4.2 Fourier transform infrared spectroscopy (FT-IR)

FT-IR was used to confirm the formation of polymethacryloxypropyltrimethoxysilane (PMPS) on the natural rubber. Figure 5.1 shows the spectra of modified surface of natural rubber at different MPS monomer concentrations. FT-IR spectra represented the characteristic peaks of NR were at 1449 cm^{-1} and 1376 cm^{-1} which were assigned to CH_2 bending and CH_2 wagging (Srinarang *et al.*, 2004), respectively. The characteristic peaks of PMPS also found in PMPS-ad-NR were 1720 cm^{-1} and $1200 - 1100\text{ cm}^{-1}$ which referred to $\text{C}=\text{O}$ stretching and $\text{Si}-\text{O}_2$ stretching in siloxane group (Bourgeat-Lamai *et al.*, 2002), respectively. The adsorption band of NR was also found in PMPS-ad-NR at any MPS concentrations especially at 836 cm^{-1} indicating the presence of $\text{C}=\text{CH}$ deformation. The spectra confirmed the presence of both PMPS and NR. Furthermore, the intensities of peaks became stronger with increasing the concentration of MPS monomer.

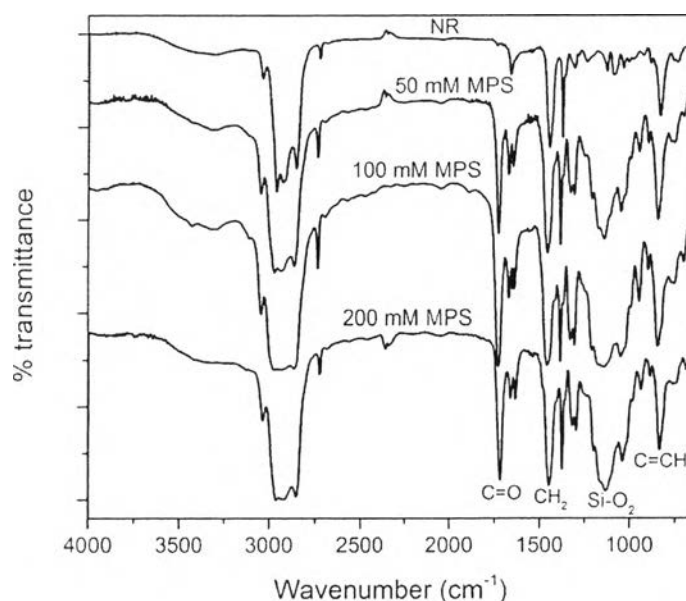


Figure 5.1 FT-IR spectra of NR and PMPS-ad-NR at different MPS concentration.

5.4.3 Thermogravimetric Analysis (TGA)

The samples of PMPS-ad-NR were heated up from ambient temperature to 600 °C with a heating rate of 10 °C/min to investigate their thermal stability. From the figure 5.2, it could be seen that the degradation temperature of NR sample was fully decomposed. The onset and the main decomposition temperature of NR located at 358.1 and 382.3 °C, respectively. While PMPS showed two stages of weight loss. The first weight loss was about 2.0 wt% at temperature up to 100 °C according to the loss of residual moisture in the PMPS. The second weight loss was about 53.7 wt% in the temperature range from 300 - 400 °C. The onset and main decomposition temperatures of PMPS were 368.4 and 414.7 °C. Moreover, PMPS showed a residual content of 44.3 wt% at 600 °C. It showed that at 50 mM of MPS, the onset and the main decomposition of PMPS-ad-NR were 357.4 and 382.2 °C, respectively. For 100 mM of MPS, the onset and the main decomposition of PMPS-ad-NR were 358.3 and 383.3 °C and 200 mM of MPS, the onset and the main decomposition of PMPS-ad-NR were 354.3 and 381.0 °C. Due to this technique of admicellar polymerization, the decomposition for all cases of PMPS-ad-NR products did not clearly show two transitions of natural rubber and PMPS like the blending method. The residual of PMPS-ad-NR, 50, 100 and 200 mM were about 4.5, 9.8 and 15.3 wt%, respectively. Generally, NR is decomposed completely when the temperature is high enough. Therefore, the residue obtained at above 500 °C could only be attributed to the inorganic component from PMPS (Li *et al.*, 2012) which coated on the NR particle.

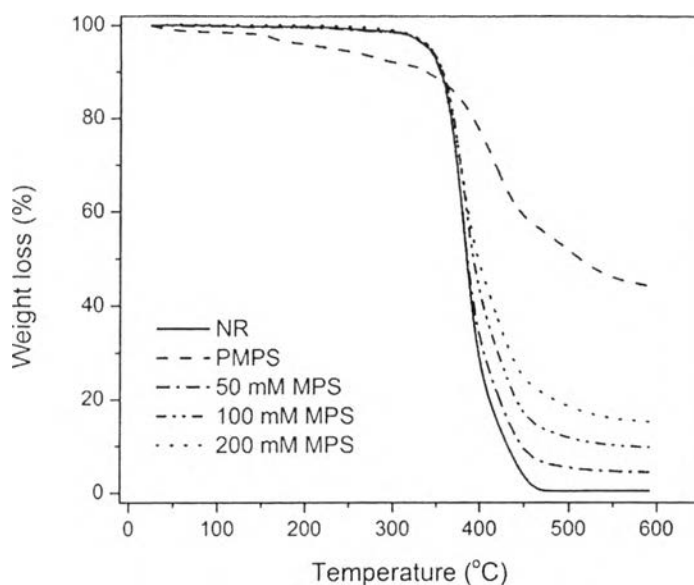


Figure 5.2 TGA results of NR, PMPS and PMPS-ad-NR at different MPS concentration.

5.4.4 Surface Morphology

5.4.4.1 Field emission scanning electron microscope (FE-SEM)

The modified surface rubber, after being washed and dried, was observed in FE-SEM micrographs. Figure 5.3 shows several preserved round shape particles instead of fused homogeneous matrix implying the presence of core-shell structure that the core NR was covered with rigid PMPS to obstruct the fusion of NR particles upon drying (Pojanavaraphan *et al.*, 2009). Due to the broad size distribution of original NR particles in the latex, a wide distribution of PMPS coated NR particles with the size distribution range of 0.2-1.0 μm is undoubtedly obtained and this suggests the thin PMPS film covering the NR particles. The core-shell particles were surrounded with smooth adhesion to the bulk matrix which was the fused NR-PMPS matrix as evident by EDX results in Figure 5.4 showing uniform distribution of Si (silicon) all over the samples. The homogeneous matrix not only recommends that it is from the fusion of incomplete covering of PMPS on NR particles but also exposed the good compatibility between PMPS and NR characteristic admicellar polymerization from the simple blending.



Figure 5.3 The SEM micrographs of (a) PMPS-ad-NR 50 mM, (b) PMPS-ad-NR 100 mM and (c) PMPS-ad-NR 200 mM.

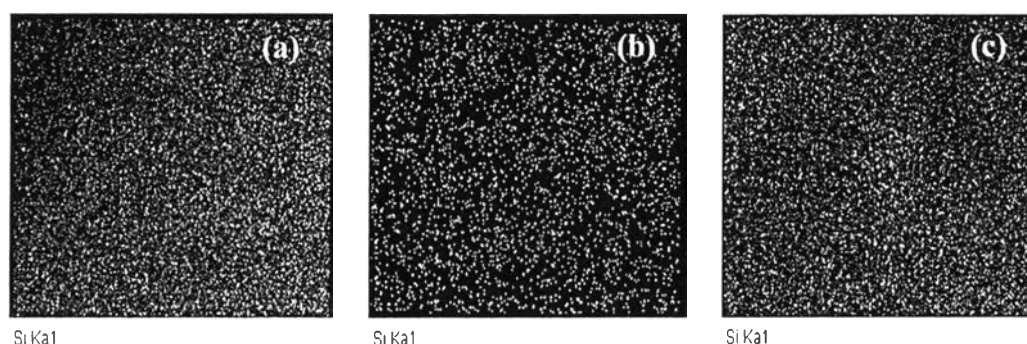


Figure 5.4 The EDX (Si) micrographs of (a) PMPS-ad-NR 50 mM, (b) PMPS-ad-NR 100 mM and (c) PMPS-ad-NR 200 mM.

5.4.4.2 Transmission electron microscope (TEM)

From the micrographs (Figure 5.5) showing the NR particle (the dark circle) was surrounded with the grey layer which refers to the PMPS layer. The size of NR was 0.2-0.8 μm . The thickness of PMPS was 100-300 nm. The NR particles had a smooth surface and round shape. The coated NR revealed the roughness surface, partial coverage and fully coverage of PMPS on the surface of NR according to the irregularly dispersion of MPS monomer in the bilayer of surfactant during the polymerization leading to non-finely coated NR. It is interesting to note that at 100 mM MPS is enough to form the thin PMPS shell covering the NR particle according to the regular forming of the shell around the NR core. The thickness of the PMPS film tended to be increased with MPS content.

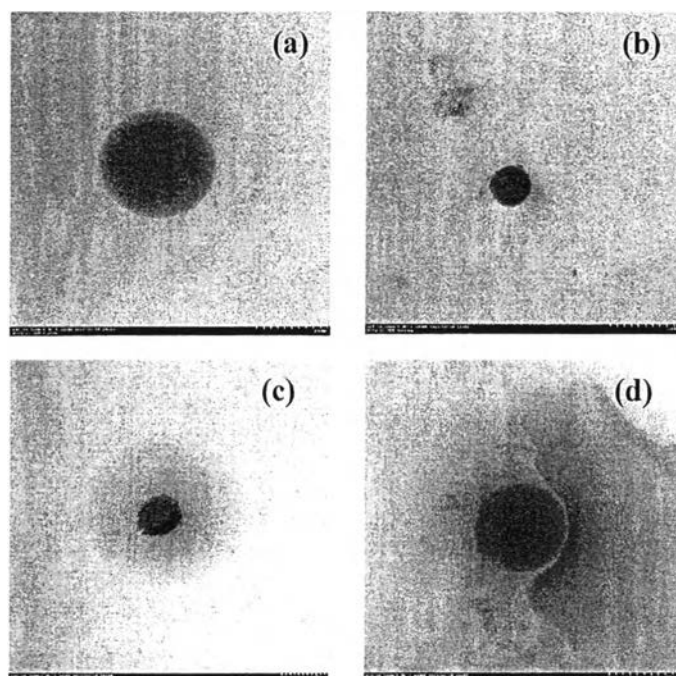


Figure 5.5 The TEM micrographs of (a) NR, (b) PMPS-ad-NR 50 mM, (b) PMPS-ad-NR 100 mM and (c) PMPS-ad-NR 200 mM.

5.5 Conclusions

The success of the admicellar polymerization of polymethacryloxypropyltrimethoxysilane (PMPS) coated natural rubber latex particles was investigated by using particle size analyzer, FT-IR, TGA, SEM, EDX and TEM. The results from particle size analyzer revealed that the size of PMPS-ad-NR was 2.83-42.75 μm and increased with MPS content. From the FT-IR study, the admicelled rubbers showed the characteristic peaks of PMPS which confirmed the existence of PMPS after polymerization. The TGA results showed that NR and PMPS combined like one single component and when PMPS content was increased, the shift of the tail of the transition to end at higher temperature was found together with a significant residue content. From FE-SEM and EDX, the PMPS-ad-NR were definitely occurred as a full coverage and partial coverage of PMPS over NR particles yielding the core-shell particles (from the full coverage) embedded finely in the

homogeneously fused PMPS-NR matrix (from partial coverage). From TEM exposed that the core NR was fully coated by PMPS.

5.6 Acknowledgements

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5.7 References

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