

**CHAPTER VI**  
**RESULTS AND DISCUSSION OF MPS ADMICELLAR POLYMERIZATION**  
**ON NATURAL RUBBER LATEX PARTICLES**  
**USING ANIONIC SURFACTANT**

**6.1 Abstract**

Admicellar polymerization is a versatile method for forming ultrathin polymeric film on a substrate surface. According to this technique, the thin polymethacryloxypropyltrimethoxysilane (PMPS) film covers each natural rubber latex particles (NR) by using bilayers of DBSA as a reaction template on the substrate surface (5 % w/v of NR). The concentrations of MPS monomer was varying from 50 to 200 mM and the ratio of MPS to initiator was 1 : 0.01. The confirmation of synthesizing PMPS-ad-NR is characterized by 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 exposed that the size of PMPS-ad-NR was increased with MPS content. FT-IR spectrum of PMPS-ad-NR showed the combination of characteristic peaks of NR and PMPS. Furthermore, the peak intensities tended to be stronger when the MPS concentration increased. The PMPS-ad-NR decomposition curves presented the single transition like one single component of NR. When PMPS content was increased, the tail of the transition was shifted to end at higher temperature together with significant residue content. From FE-SEM and EDX, the synthesized products demonstrated the full coverage of PMPS over NR particles and exhibited the uniform dispersion of Si all over the samples. From TEM revealed that the NR particle was covered by PMPS.

**Keywords:** Admicellar polymerization, Natural rubber, PMPS

## 6.2 Introduction

The use of natural rubber in an industrial has been an interest of researchers and practitioners for many years. With the increasing awareness of environmental protection and sustainable development, more and more researchers have been studied to create the products that have a portion of natural substance. Decreasing the use of silicones (polysiloxanes) and inorganic silicon compounds in medicine and the food industry by modifying the surface of rubber with silane monomer via new method that used for producing thin-film coating on solid substrate by using surfactant is called admicellar polymerization or the thin-film via surfactant template (TFST). This technique has been developed over last several years. 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 adsolubilize 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 dodecylbenzenesulfonic acid sodium salt (DBSA, anionic 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.

## 6.3 Experimental

### 6.3.1 Materials

Natural rubber (60 wt% dry rubber content) (Rubber Research Institute of Thailand), Dodecylbenzenesulfonic acid sodium salt (DBSA) (Fluka), 3-(Trimethoxysilyl)propylmethacrylate monomer (MPS) (98% purity) (Aldrich), Potassium persulfate (KPS) (97% purity) (Aldrich), Sodium hydroxide (NaOH) (MERCK), Hydrochloric acid (HCl) (37%) (Carlo Erba Reagent Company). All materials were used without further purification.

### 6.3.2 Equipments

The instruments are shown in Table 6.1

**Table 6.1** 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)

### 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. The resulting particles were considered to be clean.

### 6.3.4 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 DBSA 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.

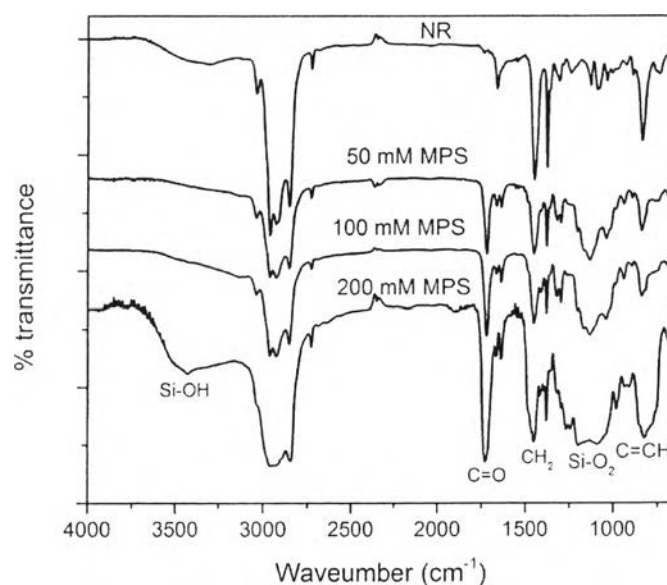
## 6.4 **Results and discussion**

### 6.4.1 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  $\mu\text{m}$ , 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  $\mu\text{m}$  by volume average. The size of PMPS-ad-NR was 3.49-52.68  $\mu\text{m}$  advising that the size was increased with MPS content. Moreover, it also suggests that the large size could be the combined of several particles.

#### 6.4.2 Fourier transform infrared spectroscopy (FT-IR)

FT-IR was used to confirm the formation of PMPS on NR. Figure 6.1 showed the spectra of modified surface of NR at different MPS monomer initial concentrations. FT-IR spectra represented the characteristic peaks of NR were at  $1448\text{ cm}^{-1}$ ,  $1375\text{ cm}^{-1}$  and  $834\text{ cm}^{-1}$  which were assigned to  $\text{CH}_2$  bending,  $\text{CH}_2$  wagging and  $\text{C}=\text{CH}$  deformation (Srinarang *et al.*, 2004). The characteristic peaks of PMPS also obtained in PMPS-ad-NR were  $1720\text{ cm}^{-1}$  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). The spectra demonstrated the presence of both PMPS and NR. Furthermore, the peak intensities tended to be stronger with increasing concentration of MPS monomer. It is noticed that for 200 mM MPS, the peak at  $3500\text{ cm}^{-1}$  assigned to hydroxyl group which could be contributed from silanol groups that were not easily undergone condensation, possibly due to steric effect (Mittal *et al.*, 1992).

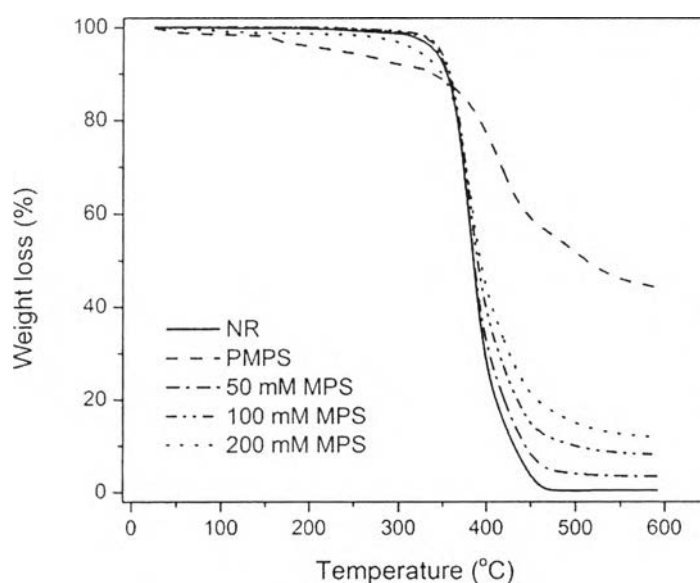


**Figure 6.1** FT-IR spectra of NR and PMPS-ad-NR at different MPS concentration.

#### 6.4.2 Thermogravimetric Analysis (TGA)

The samples of PMPS-ad-NR were heated up from ambient temperature to  $600\text{ }^{\circ}\text{C}$  at heating rate of  $10\text{ }^{\circ}\text{C}/\text{min}$  to investigate their thermal stability. In figure 6.2, it could be seen that the degradation temperature of NR

sample was fully decomposed. The onset and the main decomposition temperature of NR were 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 are 368.4 and 414.7 °C. Moreover, PMPS showed a residual content of 44.3 wt% at 600 °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 and the residual of PMPS-ad-NR, 50, 100 and 200 mM were about 3.5, 8.1 and 11.9 wt%, respectively. At the addition of 200 mM MPS, the onset of decomposition temperature is slightly lower than 50 and 100 mM MPS, resulting from excess amount of MPS at which oligomer is formed in the system leading to early decompose similar to the slope of pure PMPS. 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.

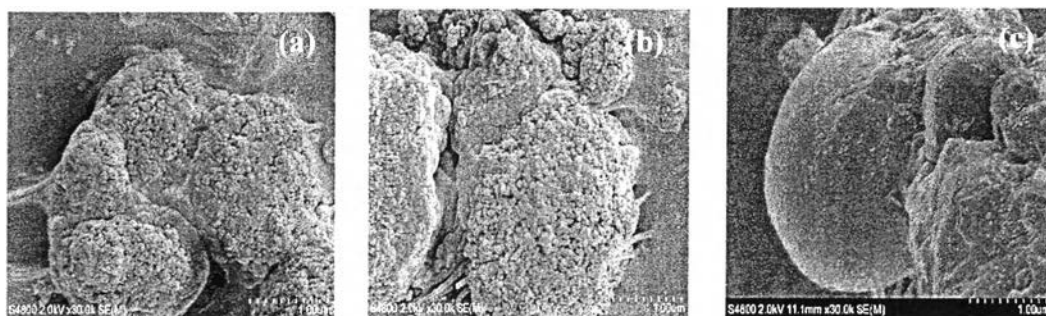


**Figure 6.2** TGA results of NR, PMPS and PMPS-ad-NR at different MPS concentration.

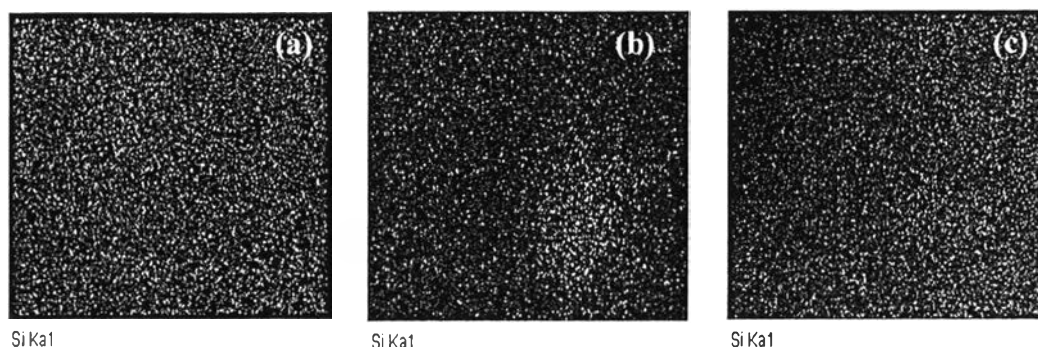
### 6.4.3 Surface Morphology

#### 6.4.3.1 Field emission scanning electron microscope (FE-SEM)

The modified surface rubber, after being washed and dried, was observed in FE-SEM micrographs. These micrographs in Figure 6.3 exposed round shape particles of PMPS-ad-NR, the presence of core-shell structure that the core NR was coated with rigid PMPS to obstruct the fusion of NR particles upon drying (Pojanavaraphan *et al.*, 2009). According to the broad size distribution of NR particles, a wide distribution of PMPS coated NR particles with the size distribution range of 1.5-3.0  $\mu\text{m}$  is undoubtedly achieved. The PMPS shell appears as the combination of tiny rigid particles of condensed silanol groups or rigid silica covering the NR particles. For 200 mM MPS, due to less condensation of silanol groups, the rigid particles are less observed. The PMPS shell appears as the combination of tiny rigid particles of condensed silanol groups or rigid silica covering the NR particles as evident by EDX results from Figure 6.4 presenting uniform dispersion of Si (silicon) all over the samples.



**Figure 6.3** The SEM micrographs of (a) PMPS-ad-NR 50 mM, (b) PMPS-ad-NR 100 mM and (c) PMPS-ad-NR 200 mM.

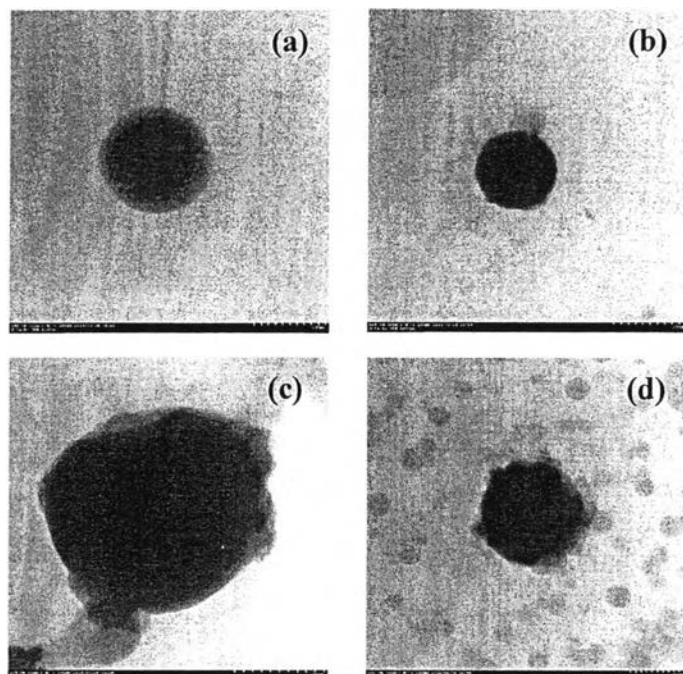


**Figure 6.4** The EDX (Si) micrographs of (a) PMPS-ad-NR 50 mM, (b) PMPS-ad-NR 100 mM and (c) PMPS-ad-NR 200 mM.

#### 6.4.3.2 Transmission electron microscope (TEM)

From the micrographs (Figure 6.5) showing the NR particle (the dark circle) was surrounded with the grey layer which referred to the PMPS layer. The size of NR was 0.2-0.8  $\mu\text{m}$ . The thickness of PMPS was 50-200 nm. The NR particle had a smooth surface and round shape. The coated NR revealed the roughness surface 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 50 mM MPS is enough to form the thin PMPS shell covering the NR particle. The thickness of the PMPS film tended to be increased with MPS content. Moreover, at 200 mM MPS showed the forming of the small grey particle on the surface of coated NR and in the system resulting from excess amount of MPS at which oligomer is formed which was agreeable with the TGA results.





**Figure 6.5** 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.

## 6.5 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 3.49-52.68  $\mu\text{m}$  and increased with MPS content. FT-IR spectrum of PMPS-ad-NR exposed the combination of characteristic peaks of NR and PMPS. Furthermore, the peak intensities disposed to be stronger when the MPS concentration increased. The PMPS-ad-NR decomposition curves presented the single transition like one single component of NR. When PMPS content was increased, the tail of the transition was shifted to end at higher temperature together with significant residue content. From FE-SEM and EDX, the synthesized products demonstrated the full coverage of PMPS over NR particles and exhibited the uniform

dispersion of Si all over the samples. From TEM exposed that the core NR was fully coated by PMPS.

## 6.6 Acknowledgements

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