



CHAPTER IV

RESULTS AND DISCUSSION OF SURFACTANT AID IN ADMICELLAR POLYMERIZATION OF STYRENE ON NATURAL RUBBER LATEX

4.1 Abstract

Admicellar polymerization is a fine-coating technique to form ultrathin polymer films on the charged surface of another polymer. According to this technique, the thin polystyrene (PS) film covers each natural rubber (NR) particles by using bilayers of cetyltrimethylammonium bromide (CTAB) as a reaction template for the admicellar polymerization of PS-NR by varying natural rubber, styrene monomer and CTAB concentrations. The confirmation of synthesizing admicelled PS-NR is investigated by Transform Infrared Spectroscopy (FTIR) which showed the peak at 1600, 1500 and 1450 cm^{-1} of C=C stretching and C-H deformation (out-of-plane) at 840 cm^{-1} . The surfactant (CTAB) improved the admicellar polymerization of styrene on natural rubber latex.

Keywords : Admicellar polymerization/ Natural rubber/ Polystyrene

4.2 Introduction

Thin-film coating on solid substrate has been a popular research topic because they have many applications in composite materials, health care products 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 range of nanometers to tens of nanometers. The process has been characterized as occurring in four step, 1) surfactant adsorption, 2) monomer adsolubilize, 3) polymerization and 4) surfactant removal. In previous studies, 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 work aims to study polystyrene coated on natural rubber by admicellar polymerization technique by varying condition of

reaction such as the effect of natural rubber, styrene monomer and CTAB concentration.

4.3 Experimental

4.3.1 Materials

Natural rubber (60 % dry rubber content) was obtained from Rubber Research Institute of Thailand. Styrene monomer (99%) was purchased from Fluka. Cationic surfactant Cetyltrimethylammonium bromide (CTAB) surfactant with a purity of 98% was purchased from Acros Organics. An initiator 2,2'-Azobis (2-methylpropionamide) dihydrochloride (V50) was obtained from Aldrich.

4.3.2 Equipments

The instruments is shown in Table 4.1

Table 4.1 Parameters to be measured for admicelled rubber 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.

4.3.3 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.

4.3.4 Admicellar Polymerization

Polymerization of styrene on natural rubber latex particles was carried out using two condition of surfactant (added and not added CTAB). Dilute natural rubber latex (5%wt, 10%wt and 20%wt) was suspended in the CTAB surfactant to obtain equilibrium concentration of 800 μM under basic condition. The reaction of admicellar polymerization was started by stirring at 30 °C for 4 h. After this period, the styrene monomer with required concentration (50, 100, 200 and 300 mM) was added into polymerization reactor and kept the monomer adsolubilization reaching to equilibrium in 12 h at 30 °C. After that, the V50 initiator with ratio of styrene and initiator at 25:1 was added into polymerization reactor 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

Table 4.2 Experimental condition of the natural rubber, styrene monomer and CTAB concentration

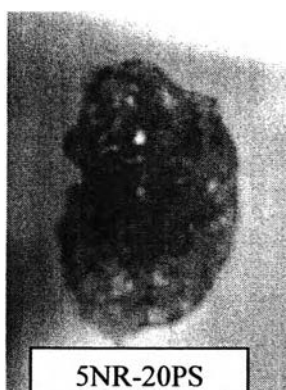
Natural rubber (%wt)	Styrene monomer (mM)	Surfactant (μM)
5	20	2800
5	20	-
5	100	2800
5	100	-
10	20	2800
10	20	-
10	100	2800
10	100	-
20	20	2800

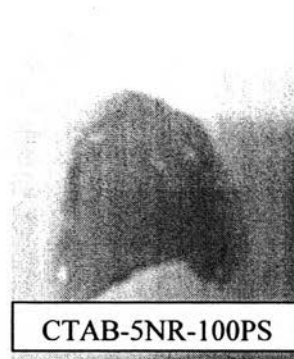
Natural rubber (%wt)	Styrene monomer (mM)	Surfactant (μM)
20	20	-
20	100	-

4.4 Results and Discussion

4.4.1 Appearance of Admicelled PS-NR with and without CTAB

The appearance of the dry admicellar polystyrene modified natural rubbers at various %wt. of natural rubber, styrene monomer, and surfactant showed in Figure 4.1. When the %wt. of natural rubber was increased the rigidity of products were increased too. The color of products was varied from light yellow to dark yellow as increase in concentration of styrene monomer. When the surfactant was added the color of the product was very light yellow and homogeneous indicating better compatibility between polystyrene and natural rubber phase. In other words, the product that did not contain surfactant had the big aggregates of polystyrene suggesting that polystyrene was formed freely in the mixture and its phase separation.





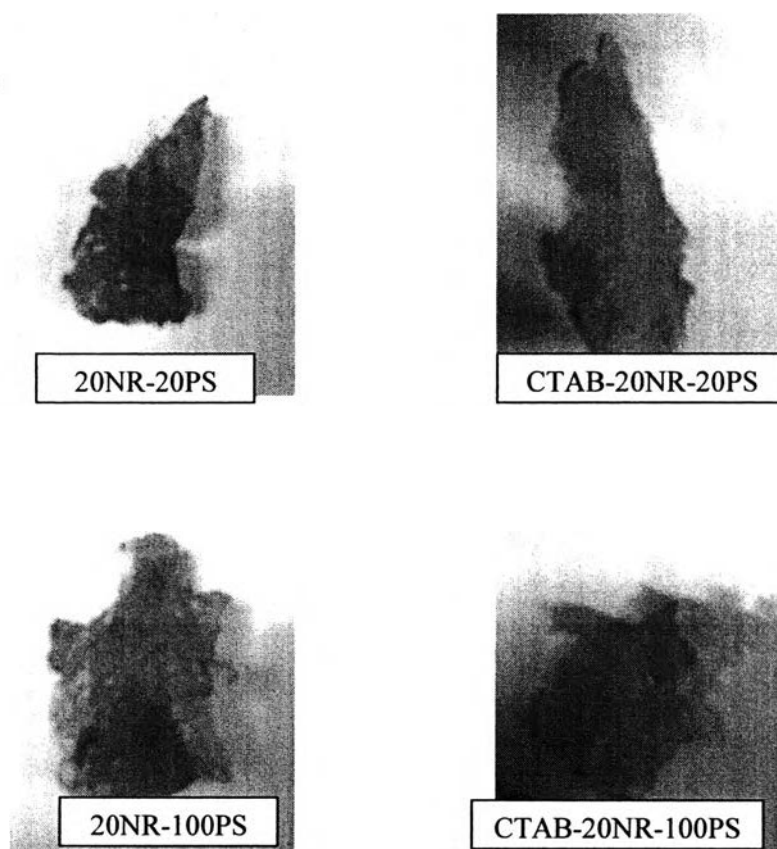


Figure 4.1 The appearance of modified natural rubber at different %wt of natural rubber, styrene monomer, and surfactant.

4.4.2 Characterize of Admicelled PS-NR

4.4.2.1 *Fourier-Transform Infrared Spectroscopy*

FTIR was used to confirm the formation of polystyrene on the natural rubber. Figure 4.2 showed the spectra of modified surface of natural rubber with and without CTAB at different styrene monomer concentrations. FTIR spectra represented the benzene ring which are aromatic C-H stretching at $3100\text{-}3000\text{ cm}^{-1}$, 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. This result showed the same peak of PS-NR in previous work (Preechasup *et al.*, 2006).

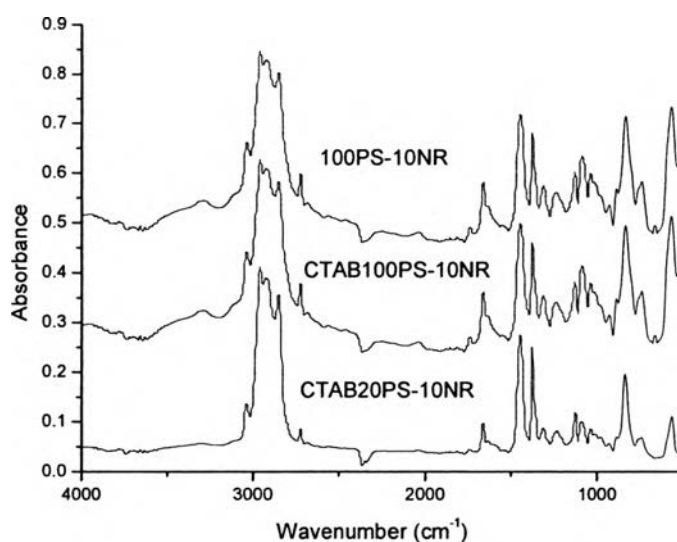
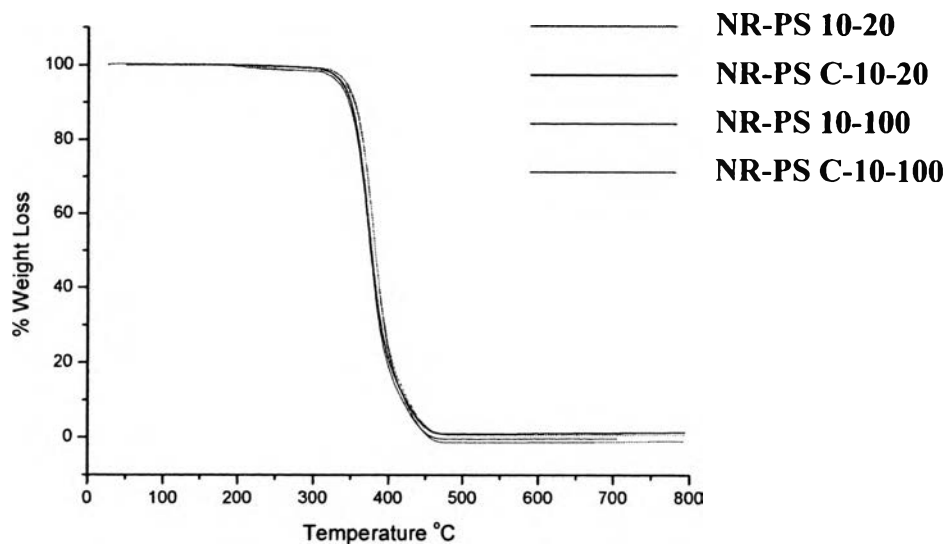


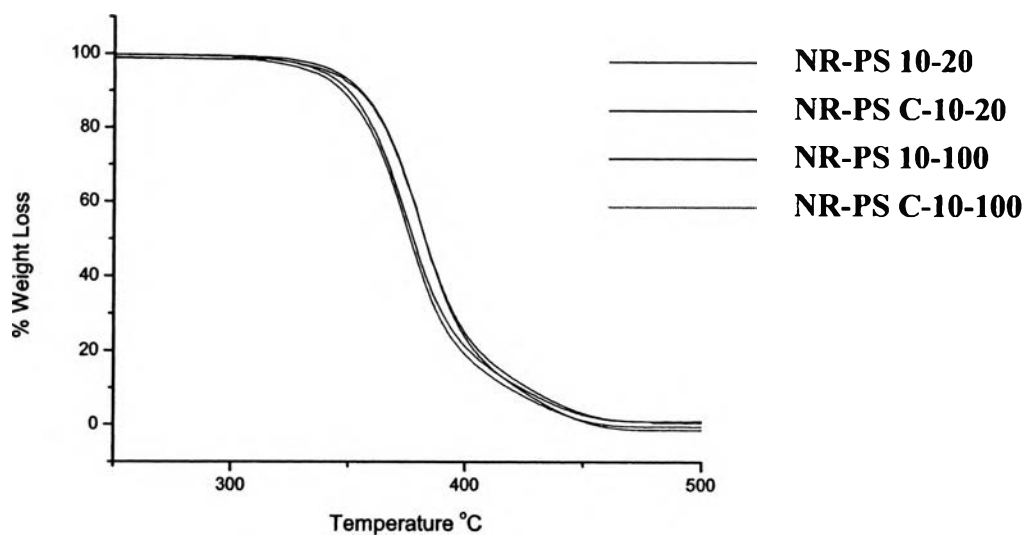
Figure 4.2 FTIR spectra of admicelled PS-NR with and without CTAB at different styrene concentration.

4.4.2.2 Thermogravimetric Analysis

The samples of admicelled PS-NR with and without CTAB were heated up from ambient temperature to 800 °C at heating rate of 10 °C/min to investigate their thermal stability. In Figure 4.3, it could be seen that the degradation temperature of admicelled PS-NR was increased with increasing 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. 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. The DTG results in Figure 4.4 also exhibited two peaks of DTG in admicelled PS-NR with CTAB. It showed that the admicellar modified natural rubber was composed of two components. In admicelled PS-NR without CTAB showed one peaks.



(a)



(b)

Figure 4.3 TGA results of admicelled PS-NR with and without CTAB at different styrene concentration (a) 0 °C – 800 °C and (b) 300 °C – 500 °C.

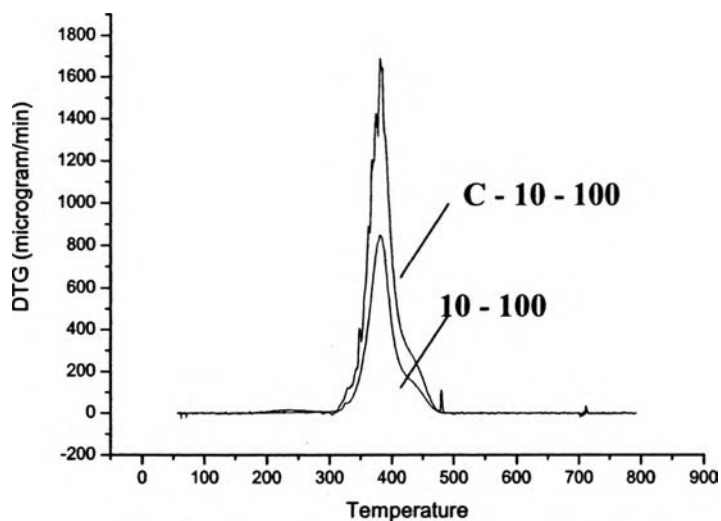


Figure 4.4 DTG results of admicelled PS-NR with and without CTAB.

4.4.3 Phase Morphology of Admicelled PS-NR

The phase morphologies of admicelled PS-NR with and without CTAB by SEM after OsO_4 was showed in figure 4.5 and figure 4.6. Figures 4.5 showed the polystyrene film were coated on natural rubber particles in circular shape about 0.5-1 μm size. The round shape of the natural rubber particles is preserved by the polystyrene film surrounded each particle. Figures 4.6, the polystyrene was agglomerated and saperated form natural rubber phase.

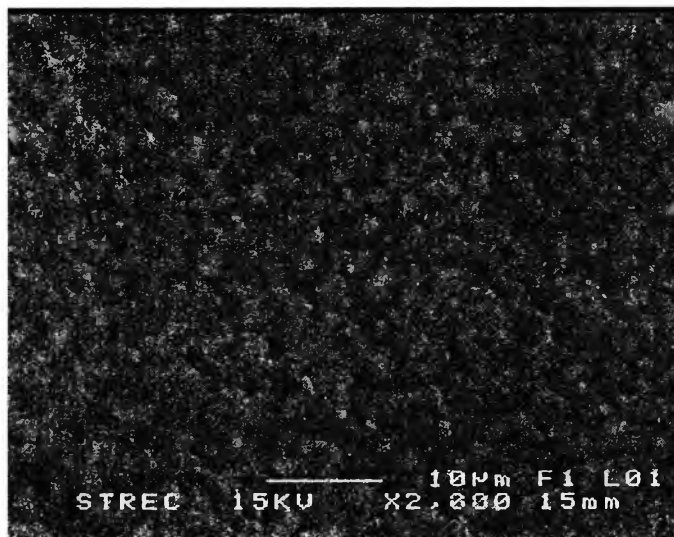
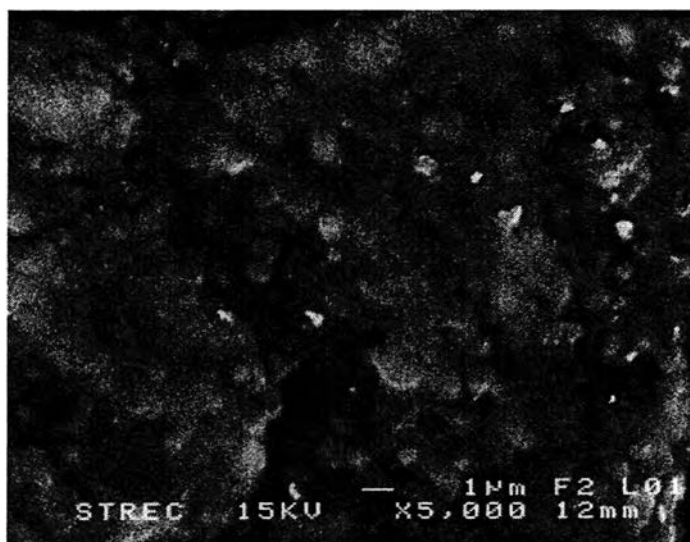
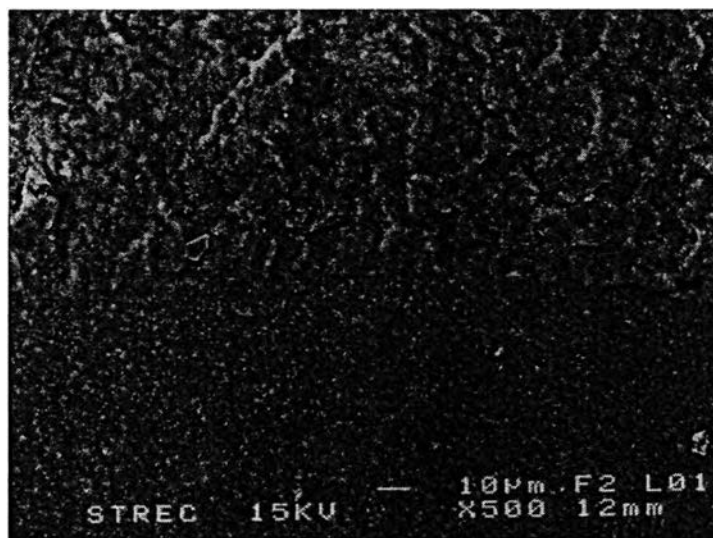


Figure 4.5 The SEM of admicelled 100PS-5NR with CTAB.



(a)



(b)

Figure 4.6 The SEM of admicelled 100PS-5NR without CTAB (a) 5000X (b) 500X.

4.5 Conclusion

The success of the admicellar polymerization of polystyrene-coated natural rubber latex particles with and without CTAB was investigated using FTIR, SEM, 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 SEM micrographs of PS admicelled polymerization covering NR with CTAB revealed the even coating of PS over latex particles and they showed the core-shell structure of PS and NR. In without CTAB, the SEM micrographs showed the phase separation between the NR and PS. 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.

4.6 Acknowledgements

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