

Introduction

Natural rubber (NR) is an interesting biomaterial which widely used in the industry with some good properties such as high strength, high resilience, sticky and flexible. However, NR is very sensitive to heat, solvent and oxidation reaction because of the present of the double bond in its chain (Oliveira *et al.*, 2005). This led to the limitations to use NR in many industrial applications. To extend its use, various modification methods have been used such as epoxidization and graft copolymerization. Many types of monomers have been used to grafted NR such as methyl methacrylate (MMA), styrene, vinyl monomer and silane coupling agent (Kochthongrasamee *et al.*, 2006). Silane grafted NR can improve the compatibility to the polymer matrix. The silane coupling agent contains hydrolysable alkoxy groups which can react with inorganic materials. When these groups are hydrolyzed, silanol groups are formed which can adhere and bond to hydroxyl groups on the surface of the inorganic material such as fiber or silica (Shin-Etsu Chemical Co., Ltd, 2012). The hydrolysable alkoxy groups include methoxy and ethoxy groups.

This research studied the preparation of grafting vinyltrimethoxysilane (VTMS) onto natural rubber (NR) in a latex system using cumene hydroperoxide (CHP) and tetraethylene pentamine (TEPA) as redox couple (Kochthongrasamee *et al.*, 2006). Effects of monomer content and grafting temperature on grafting efficiency and percentages of grafting (%GP) were investigated. The grafted NR was characterized by Fourier transform infrared spectrophotometry (FT-IR). Morphology of

copolymer was observed by transmission electron microscopy (TEM).

Objective

To synthesize and study properties of natural rubber grafted with vinyltrimethoxysilane (NR-g-VTMS).

Experimental

Materials

NR latex containing 60.05% dried rubber was purchased from Thaihua Latex Co. , Ltd. Vinyltrimethoxysilane (VTMS), cumenehydro peroxide (CHP, 80%) and tetraethylene-pentamine (TEPA) were obtained from Aldrich. Sodium dodecyl sulfate (SDS) were purchased from Fluka.

Synthesis of NR-g-VTMS

NR latex was stirred for 15 min in 500 mL flask reactor under nitrogen atmosphere, using distilled water as continuous phase. The distilled water, surfactant CHP and TEPA was added, respectively (Juntuek *et al.*, 2011). After that VTMS monomer was added with various monomer contents (5, 10 and 15 phr). Oxygen was released into the reactor to stop reaction and then the emulsion samples were poured on petidish and dried in an oven at 70°C for 48 h to remove water and unreacted monomers. After that, the obtained film samples were washed several times by water, and finally dried in oven to remove water before being extracted by acetone in a soxhlet setup for 24 h.

After extraction, the film sample was dried in a vacuum oven at 60°C for 24 h and characterized by FTIR. Weight of VTMS grafted NR was obtained

from the difference between weight of extracted sample and weight of NR. Weight of VTMS homopolymer was obtained from the difference between weight of initial sample and extracted sample. Grafting efficiency, %grafting and %conversion of VTMS monomer are defined and calculated as follow; (Juntuek *et al.*, 2011)

$$\% \text{Grafting efficiency} = \left(\frac{\text{Weight of VTMS grafted}}{\text{Weight of VTMS grafted} + \text{Weight of homo VTMS}} \right) \times 100$$

$$\% \text{Grafting} = \left(\frac{\text{Weight of VTMS grafted}}{\text{Weight of NR}} \right) \times 100$$

$$\% \text{Grafting efficiency} = \left(\frac{\text{Weight of VTMS grafted} + \text{Weight of homo VTMS}}{\text{Weight of VTMS monomer}} \right) \times 100$$

FTIR analysis

The structural characterization of NR and NR-g-VTMS was conducted by using Attenuated total reflection Fourier Transform Infrared Spectrophotometer : ATR - FTIR. The spectra were obtained at 4 cm⁻¹ in wave number from 550 to 4000 cm⁻¹.

Morphology of copolymer was observed by Transmission electron microscopy: TEM. The particle of the graft copolymer in latex form were stained by Osmium tetroxide, (OsO₄) (Kawahara *et al.*, 2003) . Scanning electron microscope: SEM (SNE-4500M) was used to observe morphology of graft copolymer. The sample was obtained from the tensile fractured surface and coated with gold.

Tensile Test

Tensile strength and elongation at break of vulcanized rubber and graft copolymer was analyzed by universal testing machine (INSTRON) according to ASTM D412. The test was performed at crosshead

speed of 500 mm/min at room temperature (Juntuek *et al.*, 2011).

Results and Discussion

Chemical structure of NR and NR-g-VTMS was characterized by FTIR. The spectra of NR and NR-g-VTMS were showed in Figure 1. Spectrum of NR showed the absorption peaks at 1661 cm⁻¹, 1446 cm⁻¹ and 842 cm⁻¹. These bands can be assigned to C=C stretching, -CH₂ rocking vibration and =CH bending vibration, respectively. Spectrum of NR-g-VTMS showed absorbent peaks of -Si-O-C- at 1126 cm⁻¹ and -Si-O-Si- at 1040 cm⁻¹. These peaks indicated the siloxane linkage of copolymer obtained from the grafting reaction between NR and vinyl trimethoxy silane (Changjie *et al.*, 2011).

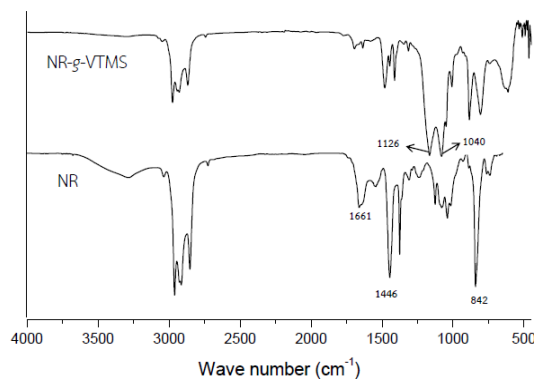


Figure 1 ATR-FTIR spectra of NR and NR-g-VTMS

Morphology of NR and NR-g-VTMS

The TEM micrographs in Figure 2 demonstrated that NR particle was spherical with the size around 630 nm. However, particle of VTMS grafted NR was about 730 nm in size. Figure 3 shows TEM micrographs of NR and NR-g-VTMS at various VTMS contents. The result showed the surface of copolymer particle was rougher than NR.

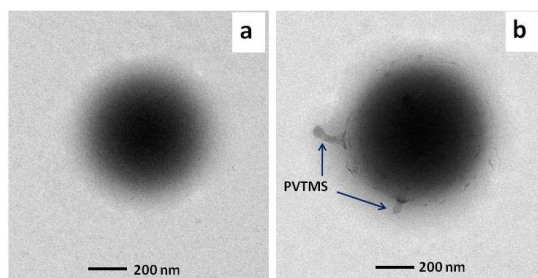


Figure 2 TEM micrographs of (a) NR and
 (b) NR-g-VTMS

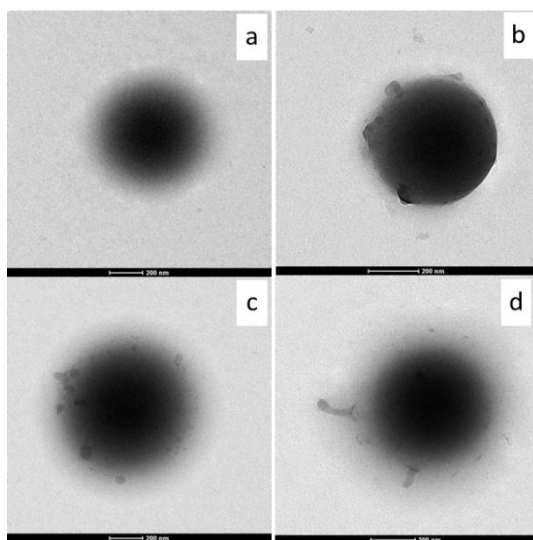


Figure 3 TEM micrographs of (a) NR (b) NR-g-VTMS5 (c) NR-g-VTMS10 and (d) NR-g-VTMS15

Effect of reaction temperature on grafting efficiency and %grafting (%GP)

To study the effect of reaction temperature on grafting efficiency, %grafting of the graft copolymerization was carried out at 30, 40, and 50°C using VTMS content at 5phr and the reaction time for 8 h. The effect of reaction temperature on grafting efficiency and %grafting is shown in Table 1. %Grafting increased from 13.76 to 16.76% with increasing temperature from 30 to 40°C. After that, grafting efficiency and %grafting decreased above this temperature. Because of at higher temperature

the amount of the macro-radicals increase and the termination reaction occurs led to the decrease of silane grafting reactions on NR main chain. The highest grafting efficiency was 72.13% at reaction temperature of 40°C (Juntuek *et al.*, 2011).

Effect of monomer content on grafting efficiency and %grafting (%GP)

To study the effect of monomer content varied was 5, 10 and 15phr, the grafting efficiency and %grafting (%GP) shown in Table 2. The copolymer was prepared at 40 °C for 8 h. The result shown highest grafting efficiency and %grafting with 10phr was 68.64 % and 8.99 %, respectively. Whereas, above 10 phr of VTMS, grafting efficiency and %grafting decreased. This might be attributed to the chain transfer reaction of radicals to monomer leading to the formation of homopolymer during the grafting reaction (Juntuek *et al.*, 2011).

Table 1 Grafting efficiency and %GP of VTMS at various grafting temperatures

Temperature	%GP	Grafting efficiency
30	13.76	63.59
40	16.76	72.13
50	1.79	13.19

Table 2 Grafting efficiency and %GP of VTMS with various monomer content

VTMS content	%GP	Grafting efficiency
5 phr	7.03	67.61
10 phr	8.99	68.64
15 phr	7.25	48.72

Mechanical properties by Tensile test

Figure 4 and Figure 5 shown effect of monomer content on tensile strength and elongation at break of NR-g-VTMS at various VTMS was 5, 10 and 15phr. The result shown tensile strength and elongation at break increased with increasing monomer content from 0 to 5phr and decreased with 10phr of VTMS loading, due to the higher crosslinking density of NR-g-VTMS than that of NR caused by the formation of siloxane linkage on NR chain (Juntuek *et al.*, 2011).

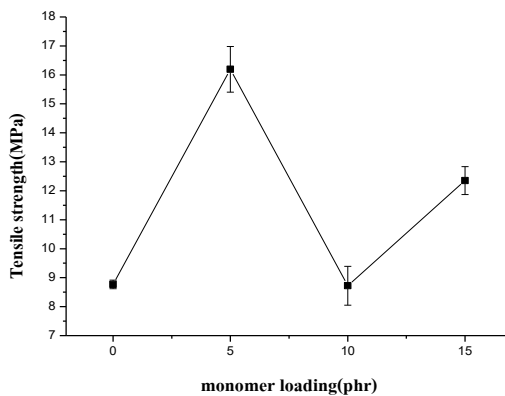


Figure 4 Effect of VTMS content on tensile strength of NR-g-VTMS.

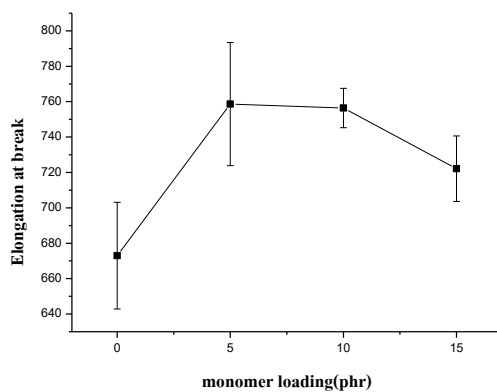


Figure 5 Effect of VTMS content on elongation at break of NR-g-VTMS.

SEM micrographs of the tensile-fractured surface of NR and copolymer with various monomer content from 5, 10 and 15phr were shown in Figure 6. The surface of the vulcanizates of NR and NR-g-VTMS10 was smooth, suggests that the interfacial adhesion between copolymer and rubber was relatively weak. In figure 6(b), 6(d) with 5 and 15phr of VTMS, the surface was very rough, suggest that the interfacial strength was improved with present of VTMS (Wu *et al.*, 2006).

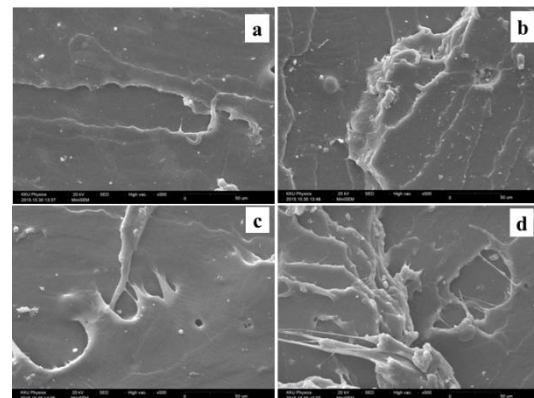


Figure 6 SEM micrographs of the tensile fractured surface of a) NR, b) NR-g-VTMS5 c) NR-g-VTMS10 and d) NR-g-VTMS15

Conclusions

Experimental result showed that the appropriate monomer content was 5phr at reaction time of 8 h and reaction temperature of 40°C. Moreover, tensile strength and elongation at break of the graft copolymer increased with increasing monomer content. The good interfacial adhesion between copolymer and rubber improved with present of VTMS.



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