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Graft Copolymerization of Vinyltriethoxysilane Onto Deproteinized Natural Rubber

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Abstract

In this work, graft copolymerization of vinyltriethoxysilane (VTES) onto deproteinized natural rubber (DPNR) was carried out to prepare in situ nanosilica reinforced natural rubber. Graft copolymerization of VTES onto DPNR was performed in latex stage with TBHP/TEPA as initiators with initiator concentrations of 0.033, 0.066 mol/kg-rubber and monomer concentrations of 1.05, 1.5 and 2.0 mol/kg-rubber. VTES conversion is derived from silica content which is determined by buring method. The graft copolymers were characterized by FT-IR and TEM. It was found that VTES conversion was about 80% and it is independent on initiator concentration. The high conversion is believed to be due to auto hydrolysis of ethoxy groups in aqueous solution and subsequent condensation to form in situ silica. Reinforcement effect of the in situ silica on DPNR is investigated in term of tensile properties. The stress at break of in situ silica-reinforced natural rubber was about 3 times higher than that of non-reinforced natural rubber. TEM images show that the silica particles with the size less than 200 nm were well dispersed in NR matrix.

Keywords: natural rubber, VTES, graft copolymerization, in situ nanosilica, morphology

1. Introduction

Silica-reinforced natural rubber (NR) is a very unique material which provide several advantages such as low-rolling resistance and strong wet-skid resistance compared to carbon black [1]. Commonly, silica-reinforced NR is achieved by mechanical mixing or latex mixing, i.e. masterbatch. However, the first always makes silica particle aggregate since the active hydroxyl groups on silica surface are easily condensed. The latter, on the other hand, needs a silane coupling agent to create the linkages between silica and NR particle. In order to solve these problems, in situ synthesis of silica particles within NR matrix using sol-gel method has been explored. The sol-gel method is believed to be the novel method to control the silica particle size and morphology and it can be done in solid state, solution state or latex state. In the solution state, it was applied to introduce silica in various materials such as Styrene Butadiene Rubber (SBR) [2], epoxydized NR [3], isoprene rubber [4] and carboxylated acrylonitrile-butadiene rubber. However, a lot of organic solvents used limits its practical application. Yoshikai [5] applied sol-gel process in latex state to prepare silica-reinforced SBR. However, during a process to prepare raw reinforced rubber, they found that a lot of silica particles separated out from latex during coagulation due to poor interaction between silica and SBR.

Recently, graft copolymerization of vinyl monomer provides a very useful technique to introduce silica into rubber by the formation of chemical linkages. Nurul et al. used this method to prepare filler nanomatrix structure and found that the molulus of graft copolymer increased after grafting with vinyltriethoxysilane (VTES) [6,7]. However, no structural information of the material was investigated.

In the present work, we investigated graft copolymerization of VTES onto DPNR and do structural characterization to elucidate the formation of functional groups in resulting materials. The mechanical reinforcement of NR is associated with in-situ silica morphology.

2. Experimental

2.1 Materials

The high ammonia natural rubber latex (HANR, pH=9-10, 60% DRC) was received from Dau Tieng rubber company. Vinyltriethoxysilane (VTES), tert-butyl hydroperoxide (TBHP) and tetraethylenepentamine (TEPA) were products of Tokyo Chemical Industry of Japan. Sodium dodecyl sulfate (SDS, 99%) was purchased from Kao

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chemicals company (Taiwan). Urea (99.5%) was purchased from Merck (Germany). The other chemicals were purchased from Sigma-Aldrich.

2.2 Graft copolymerization

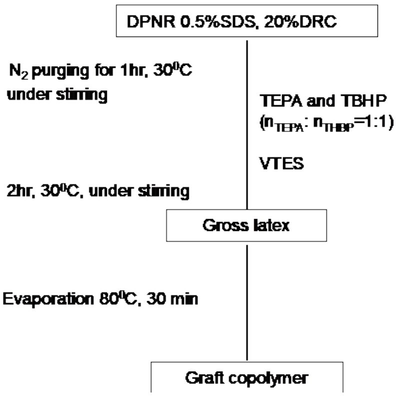


Fig. 1. Graft copolymerization of VTES onto DPNR

Graft copolymerization of VTES onto DPNR was carried out as shown in Figure 1. First, deproteinized natural rubber (DPNR) was prepared by deproteinization of high ammonia natural rubber (HANR) with 0.1 w/w% urea and 1w/w% sodium dodecyl sulfate (SDS). After three times of centrifugations, the final DPNR latex was adjusted to 20% DRC and SDS content was kept at 0.1 w/w%. Before graft copolymerization, SDS was added to the DPNR latex up to 1 w/w%. Graft copolymerization was carried out with 1.05, 1.5 and 2.0 mol/kg-rubber of VTES at 0.033 and 0.066 mol/kg-rubber of each initiator. The reaction system was stirred at 400 rpm at 30^0C for 2 hours after N_2 bubbling DPNR latex for 1 hour at a speed of 300 rpm. Afterward, unreacted monomer and free initiators were removed using a rotary evaporator at 80^0C for 40 min. The gross polymer was cast into a thin film and dried for a week in a heating oven and one week in vacuum oven at 50^0C.

2.3 Silica content determination

Silica content was determined by burning method. Weight of sample about 1g rubber was burned in an electrical furnace at 600°C for 2 hours in a clean porcelain cup (which is previously burned at 600°C for 1 hour). The weight of cup before and after burning was measured to determine ash of sample. Ash after buring DPNR is also determined and it will be substrated from ash of sample to determine the actual silica content. The silica content was calculated as the following equation:

$$silica\ content\ (phr) = \frac{ash\ of\ sample - ash\ of\ DPNR}{weight\ of\ sample} * 100$$

From silica content, VTES conversion is estimated as following equation:

$$\text{VTES conversion (\%)} = \frac{\text{silica content} * \text{weight of rubber}}{\text{weight of VTES}} * \frac{190}{60}$$

where 190 and 60 are molecular weights of VTES and SiO_2, respectively. VTES conversion in this work is defined as how much VTES converted into SiO_2.

2.4. FT-IR measurement

FT-IR measurement is performed in a JASCO FT-IR 4600 spectrometer. The preparation of samples is described as follows: a very thin film was prepared by casting latex on a petri-dish and dried for 1 week. Then it was placed on a KBr plate and inserted into the FT-IR machine. The measurement is set for 100 scans, from 400 cm^{-1} to 4000 cm^{-1} at a resolution of 4 cm^{-1}.

2.5 Mechanical properties

The tensile strength of samples was measured at room temperature using a Tokyo Instron 5300 according to JIS K6251. The samples were cut by a dumbbell-shaped no.7, the thickness of samples was controlled around 1 mm measured by thickness gauge (dial type) (Mitutoyo, Japan) under a crosshead speed of 200 mm/min. Each sample was measured at least three times.

2.6 Morphology observation

Morphology observation of resulting samples was made using TEM (JEM-2100, JEOL) at accelerating voltage of 200kV. The ultrathin section of graft copolymer was cut by using a glass knife equipped in a Reichert-Nissei FC S ultra-microtome (Leica, Wetzlar, Germany) under liquid N_2.

3. Results and discussion

3.1 VTES conversion

In order to prepare various graft copolymers, graft copolymerization of VTES was performed with two initiator concentrations, that is 0.033 and 0.066 mol/kg rubber and at each initiator concentration, monomer concentration is varied from 1.0, 1.5 and 2.0 mol/kg rubber.

Table 2 shows the silica contents and VTES conversions for six conditions of graft copolymerization. It could be seen that the silica content depends on the VTES concentration and insignificantly dependent on the initiator concentration. On the other hand, at small VTES concentration (1.0 and 1.5 mol/kg-rubber) the VTES conversions are similar to each other but at higher VTES conversion (2.0 mol/kg-rubber) it is decreased. This suggests that when too much VTES is added to the reaction, the conversion is decreased. The reason may be due to the steric hindrance of Si-O-Si groups onto the hydrolysis and condensation of other ethoxy groups and silanol groups, respectively. Therefore, it can be inferred that low VTES concentration (such as 1.05 and 1.5 mol/kg rubber) are the suitable concentrations to achieve high conversion.

Table 2. Silica contents and VTES conversions of graft copolymers

Samples	Silica content (phr)	VTES conversion (%)
DPNR-g-VTES-0.033-1.05	5.25	82.9
DPNR-g-VTES-0.033-1.5	7.45	82.5
DPNR-g-VTES-0.033-2.0	9.64	80.0
DPNR-g-VTES-0.066-1.05	5.20	82.5
DPNR-g-VTES-0.066-1.5	7.50	83.9
DPNR-g-VTES-0.066-2.0	9.28	76.7

3.2 FT-IR spectroscopy

To elucidate the structure of graft copolymer, FT-IR measurement was carried out. Figure 2 shows the FT-IR spectra for DPNR and DPNR-g-VTES 0.033-1.05. The characteristic absorption bands of DPNR were maintained and still appeared in the FT-IR spectrum for DPNR-g-VTES. However, there are several new absorption vibration bands appeared in spectrum of DPNR-g-VTES. These characteristic absorptions were registered in Table 2. Absorption at 3000-3500 cm^{-1} was attributed to Si-OH; absorption at 1035-1206 cm^{-1} was attributed to Si-O-Si as well as Si-O-C groups. The arisen of these absorption bands were evident to confirm that the in-situ silica was successfully formed in NR matrix. It is noted that the band at 1206 cm^{-1} belongs to the vibration of Si-O linking to ethoxy groups in VTES and the band at 960 cm^{-1} belongs to Si-OH in silanol [8,9]. This implies that absorption peak at 1206 cm^{-1} is due to the incomplete hydrolysis of ethoxy groups and the peak at 960 cm^{-1} is due to the free OH groups linking to Si atom. It is consistent with the broad absorption band in the region of 3000 to 3500 cm^{-1}, which belongs to the OH group. FT-IR spectrum is confirmed to give very useful information on the hydrolysis and condensation of ethoxy groups and therefore the formation of silica structure in the elastomer matrix.

Table 2. Assigments of FT-IR absorption bands for graft copolymer

Wave number (cm^{-1})	Assigments
3400	Si-OH
1206	Si-O-C (VTES)
1124	Si-O-Si
1035	Si-O-Si
950	Si-OH (silanol)

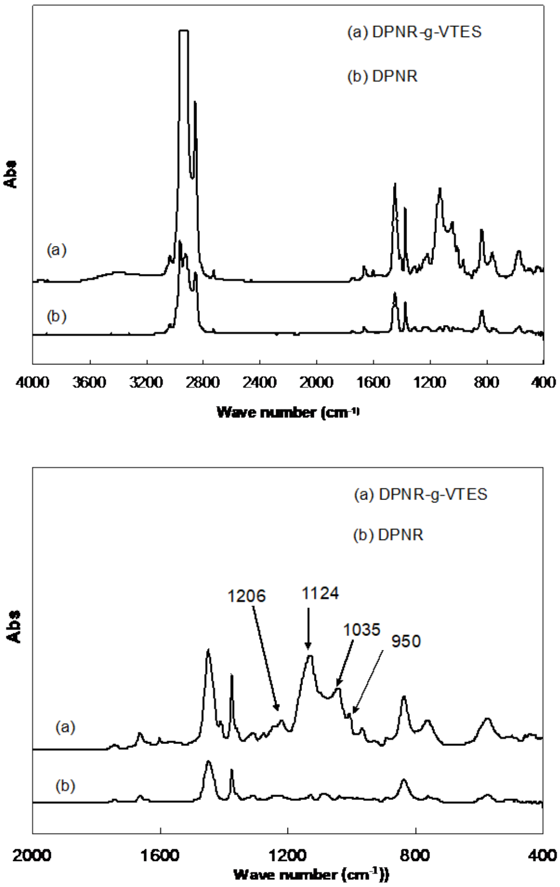


Fig. 2. FT-IR spectra of DPNR and DPNR-g-VTES (a) from 400-4000 cm^{-1} and (b) from 400-2000 cm^{-1}

The formation of *in situ* silica was proposed to occur during graft copolymerization as illustrated in Figure 3, where we assume the graft copolymerization took place followed by the hydrolysis and condensation to generate the silica particle on the NR molecule. Through the chemical linkages formed by graft copolymerization, the *in situ* silica is expected to enhance NR properties without using silane coupling agent.

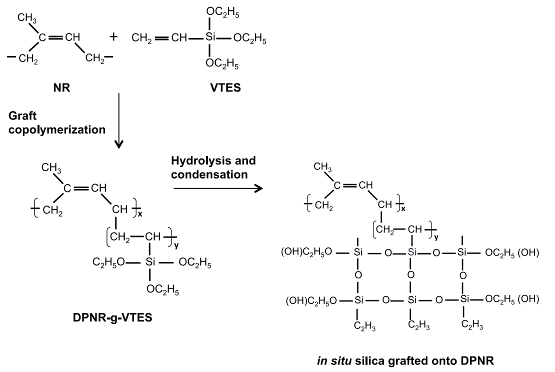
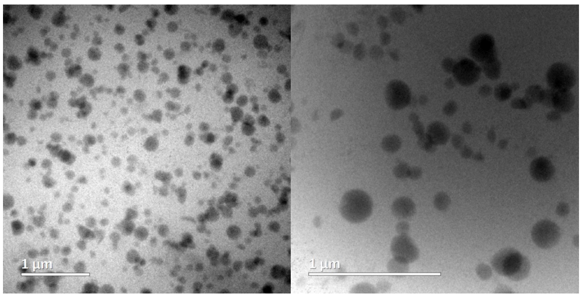


Fig. 3. Formation of *in situ* silica in during graft copolymerization of VTES

3.3 TEM

The presence of *in situ* silica in graft copolymer is further confirmed by morphology observation with Transmission Electron Microscopy (TEM). Figure 4 exhibits TEM images of DPNR-g-VTES 0.033-1.5 at magnifications of 10,000 and 5000. In Figure 4, the dark domains represent silica particle and the bright domains represent NR. As can be seen, the silica particles are well dispersed in NR matrix. When we increase magnification, it is clear to estimate the size of silica particle is less than 200 nm.

In addition, the *in situ* silica particles are the sphere in shape. This may be due to the hydrophilic nature of silica particle, which is not compatible with the hydrophobic nature of NR particle. Therefore, the growth of silica particle during graft copolymerization is frequently hindered by molecular interaction between them. Therefore, silica particles tend to decrease their surface area. The formation of sphere silica particles is the result of such molecular interaction.



(a) x 5000 (b) x10,000

Fig. 4. TEM images of DPNR-g-VTES 0.033-1.5 at two magnifications (a) x5000 and (b) x10,000

3.4 Tensile strength

To investigate the reinforcement of *in situ* nanosilica on mechanical properties of graft copolymer, the stress-strain curves of the materials were made.

Figure 5 shows the stress-strain curves for DPNR-g-VTES at various VTES concentrations at 0.033 mol/kg rubber of initiator concentration. It could be seen that the graft copolymer prepared with VTES concentration of 1.05 mol/kg-rubber achieved the highest stress at break (9 MPa), which is nearly three times higher than that of DPNR. Furthermore, the stress at same strain for each sample is dependent on the VTES concentration.

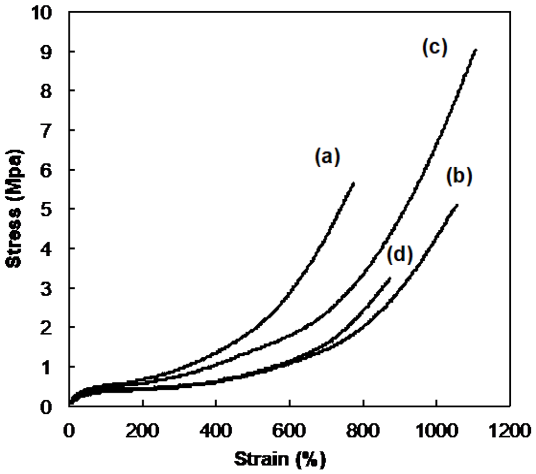


Fig. 5. Stress-strain curves for DPNR-g-VTES (a) 0.033-2.0; (b) 0.033-1.5; (c) 0.033-1.05 and (d) DPNR

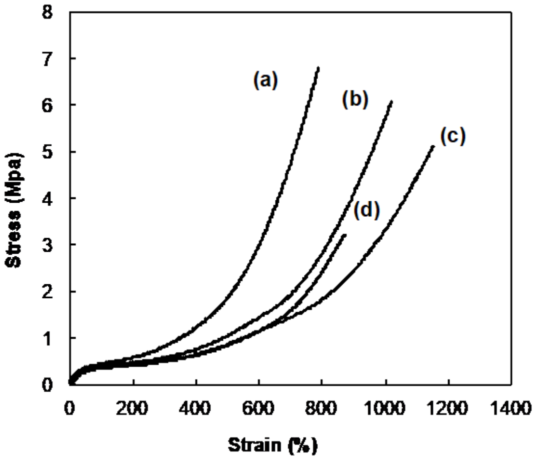


Fig. 6. Stress-strain curves for DPNR-g-VTES (a) 0.066-2.0; (b) 0.066-1.5; (c) 0.066-1.05 and (d) DPNR

Figure 6 displays the stress-strain curves for DPNR-g-VTES prepared with initiator concentration of 0.066 mol/kg-rubber. It is found that the stress at break of the samples increased as the monomer concentration increased, which are different from those prepared at initiator concentration of 0.033 mol/kg rubber. The stress at same strains of the samples depends on VTES concentration, similar to those prepared with initiator of 0.033 mol/kg rubber The stress at break of samples at 0.066 mol/kg rubber of initiator has higher than those at 0.033 mol/kg rubber, except sample prepared at initiator concentration of 0.033 mol/kg rubber and VTES concentration of 1.05 mol/kg rubber. The highest tensile strength for DPNR-g-VTES 0.033-1.05 maybe explained to be due to the high conversion during graft copolymerization and may be the good distribution of silica particles in NR matrix.

4. Conclusion

In situ nanosilica was successfully formed in NR during graft copolymerization of VTES onto NR. The silica content is found to depend on VTES concentration but not depending on the initiator concentration. The conversion decreased as VTES concentration increased. From structural characterization by FT-IR, silica particles still contain silanol groups and unhydrolysed ethoxy groups with a small amount. The silica particles have been found to be homogeneously distributed in NR matrix with the sphere shape and size less than 200 nm. The reinforcement of nanosilica is significantly enhanced through formation of chemical linkages between silica and NR. Graft copolymerization is, therefore, a useful tool to incorporate *in situ* silica to achieve good reinforcement without using silane coupling agent.

Acknowledgments

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