

Study on Structure and Physico-chemical Properties of Surficial Epoxidized Deproteinized Natural Rubber/silica blend

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Abstract

The blends of epoxidized natural rubber/silica were prepared and characterized the properties which are necessary for the coating application. The epoxidized natural rubber was prepared by epoxidation of deproteinized natural rubber with fresh peracetic acid in latex stage. The blends of epoxidized natural rubber and silica were prepared from epoxidized natural rubber latex and tetraethyl orthosilicate. The structural characterization of products was carried out through latex state NMR and FT-IR spectroscopy and SEM observation. The contact angle of water drop on the surface of the blends and water uptake were investigated. The results from structural characterization showed that epoxy group was successfully introduced to natural rubber chain and silica particle was formed in epoxidized natural rubber matrix. The blend of epoxidized natural rubber containing 15 %mol of epoxy group content and 5 %w/w of tetraethyl orthosilicate was found to attain the highest hydrophobicity.

Keywords: Epoxidized natural rubber, Silica, Structural characterization, Surficial physico-chemical properties.

1. Introduction

Epoxidized natural rubber is the material of great interest since it is a green polymer with high mechanical properties, weather resistance, oxygen resistance and so forth [1]. Moreover, thanks to the ability to form crosslink of epoxy group, epoxidized natural rubber may be used as an adhesive or coating [2]. The preparation and characterization of epoxidized natural rubber were reported in literature [3,4].

In order to improve the properties of epoxidized natural rubber and extend its application field, various fillers were usually used to blend with epoxidized natural rubber. In published works, silica was added to epoxidized natural rubber to enhance the properties [5,6]. It was reported that silica particle can reinforce the hydrophobicity of the sample. This material may be used for coating application. However, silica was added into EDPNR in melt stage which is high viscosity. Therefore, it was difficult to well disperse silica, which could not afford the significant improvement of EDPNR properties. Furthermore, the physico-chemical properties of surficial epoxidized natural rubber/silica blend which is important to coating application were not investigated.

When blend of epoxidized natural rubber/silica is prepared in latex stage, we may achieve the materials with good dispersion since the latex stage is much less viscos than melt stage. In addition, the preparation of material in latex may be scaled up in industry and establish a green technology of natural rubber field.

In this work, we prepared blend of epoxidized natural rubber and silica. Since proteins naturally present in natural rubber may affect the epoxidation, the removal of proteins from natural rubber was carried out, followed by epoxidation of natural rubber in latex stage. Fresh peracetic acid was used as epoxidation agent due to its efficiency. Epoxidized natural rubber/silica blend was prepared by adding tetraethyl orthosilicate into epoxidized deproteinized natural rubber latex. The structure of resulting materials was characterized through latex-state ¹³C-NMR spectroscopy and FT-IR spectroscopy. Contact angle of water drop on the surface of materials and water uptake were investigated. The optimal epoxy group content and silica amount in epoxidized natural rubber/silica blend were found in term of high hydrophobicity of the materials.

2. Experimental

2.1. Preparation of materials

High ammoniated natural rubber (HANR) latex (Dau Tieng Company, Vietnam) was incubated with 0.1 %w/w urea and 1 %w/w sodium dodecyl sulfate

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(SDS - Kishida Reagents Chemicals Co. Ltd.) for 1h followed by centrifugation at 10^4 g. Cream fraction was washed twice by dispersed in solution of 0.5 %w/w SDS. Thereafter, washed cream was re-dispersed in solution of 0.1 %w/w SDS to obtain deproteinized natural rubber (DPNR) latex.

Epoxidation of DPNR latex was carried out with fresh peracetic acid. Fresh peracetic acid was prepared by adding hydrogen peroxide (Nacalai Tesque Inc., 30%) into acetic anhydride (Nacalai Tesque Inc., 99%) at 273K, followed by stirring gently at 40°C for 90 minutes. The concentration of fresh peracetic acid was 33 %w/v.

DPNR latex whose dried rubber content (DRC) was adjusted to 10% w/w was epoxidized in latex stage with fresh peracetic acid at 283K for 3 hours. After completion of the reaction, the resulting latex was neutralized by ammonia solution (Nacalai Tesque Inc., 28 %w/w) then centrifuged at 10,000g for 30 minutes. The obtained cream was re-dispersed into solution of 1% SDS to obtain EDPNR latex.

Blend of EDPNR and silica was prepared in latex stage. Tetraethyl orthosilicate (TEOS) (Nacalai Tesque Inc.) was dropped into EDPNR latex.

EDPNR and EDPNR/silica blend were dried in reduced pressure at 50 °C for a week.

2.2. Characterization of material

^{13}C -NMR measurements were made for DPNR and EDPNR in latex stage with several drops of D_2O (Nacalai Tesque Co., Ltd) in an ECA-400 spectrometer operating at 100 MHz at 303K. The spectra were recorded with pulse repetition times of 5 seconds and 1000 accumulations.

The samples of DPNR, EDPNR and EDPNR/silica were dissolved in chloroform to prepare solution whose concentration was 2% w/w. The solution was dropped in KBr plate to make cast film. FT-IR spectrum was scanned at room temperature in absorption mode with wave number from 400 to 4000 cm^{-1} , at a resolution of 4 cm^{-1} and 64 scans.

Scanning electron microscope (SEM) image of the samples was observed in SEM SM-200 (Jeol). The samples were covered with gold. The electron beam was accelerated at the voltage of 15 kV.

The contact angle of distilled water over EDPNR and EDPNR/silica films was measured by Dataphysics OCA20 system equipped with SCA20 software at 298 K. The image of drop was immediately taken by CCD camera, and then this image was sent to the computer for analysis.

Water uptake was determined as follows. The samples ($1 \times 1 \times 1$ cm) were immersed into 100 ml deionized water at room temperature for a week. After that, the water on the surface of swollen samples was removed with Whatman no.1 paper and weighed. Percentage mass increase ($\% \Delta m$) was calculated as follow:

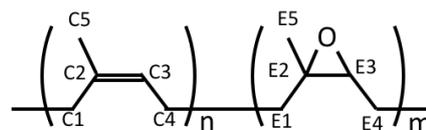
$$\% \Delta m = \frac{m - m_o}{m_o} \times 100 \quad (1)$$

3. Results and discussion

3.1. Epoxidation of DPNR latex

Latex-state ^{13}C -NMR spectrum

Fig. 1 shows the latex-state ^{13}C -NMR spectrum of DPNR and EDPNR. In the spectrum of DPNR, the signal at 134.9, 125.1, 32.8, 26.5 and 23.3 ppm were assigned to C2, C3, C1, C4 and C5 of the *cis*-1,4-isoprene unit, respectively. After the epoxidation, the signal at 134.9 and 125.1 ppm were found to diminish. The new signals present at 60.5 and 64.0 ppm were the characteristic signals of C3 and C2 of epoxidized *cis*-1,4-isoprene unit, respectively. This evidence may confirm that the epoxy group was successfully introduced to the chain of natural rubber.



The epoxy group of EDPNR was calculated from latex-state ^{13}C -NMR spectrum according to the following equation [7]:

$$\text{Epoxy group content } [\% \text{mol}] = \frac{I_{60.5} + I_{64.0}}{I_{134.9} + I_{125.1}} \times 100 \quad (2)$$

where $I_{60.5}$, $I_{64.0}$, $I_{134.9}$ and $I_{125.1}$ is intensity of the signal at 60.5, 64.0, 134.9 and 125.1 ppm, respective.

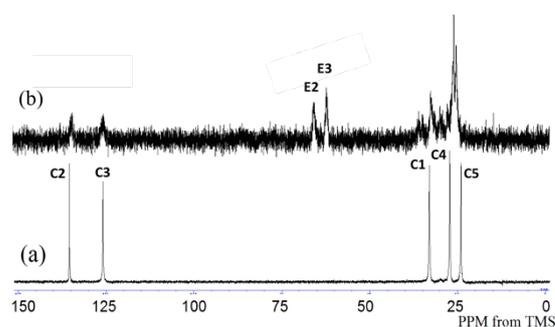


Fig. 1. Latex state ^{13}C -NMR spectrum

(a) DPNR (b) EDPNR.

In order to prepare the sample of EDPNR with different epoxy group content, we used various volume of peracetic acid 33 %w/v. The epoxy group content was calculated from ^{13}C -NMR spectrum.

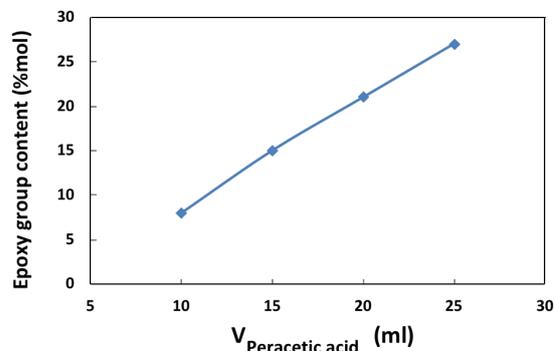


Fig. 2. The graph of volume of peracetic acid (33 %w/v) vs. epoxy group content.

The relationship between volume of peracetic acid (33 %w/v) and epoxy group content is expressed in Fig.2. When using various amount of peracetic acid, we obtained EDPNR with epoxy group contents of 8, 15, 21 and 27 mol%. The denotation of EDPNR is EDPNR8, EDPNR15, EDPNR21 and EDPNR27, respectively.

The content of epoxy group increased monotonically when the volume of peracetic acid increased. In other words, the dependence of epoxy group content on the amount of peracetic acid was found to be linear. This result may imply that the order of reaction of natural rubber and peracetic acid is zero in the given condition.

The image of EDPNRs is shown in Fig.3. When the epoxy group content increased, the color of the sample became darker. EDPNR8 and EDPNR15 still had the characteristics of rubbery materials. The films made of EDPNR8 and EDPNR15 were elastic and their surfaces were smooth. In the published works, it was reported that the high epoxy group content in epoxidized natural rubber was, the more adhesive the sample was [2]. However, when the epoxy group content was too high, it was easy to make crosslink during aging or storage, so the materials became hard. We found it difficult to prepare films of EDPNR21 and EDPNR27. The films were ready to crack during drying and these materials were very hard and brittle. Therefore, EDPNR21 and EDPNR27 were not suitable for the coating application.

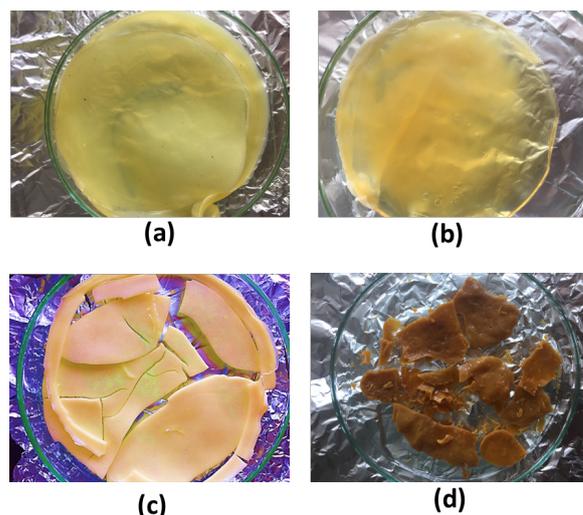


Fig. 3. The samples of EDPNR with various epoxy group contents (a) EDPNR8, (b) EDPNR15, (c) EDPNR21, (d) EDPNR27.

In the following section, we used EDPNR15 for further investigation.

3.2. Blend of EDPNR/silica

The EDPNR/silica blends with various amount of silica were prepared. TEOS was added into EDPNR15 latex and the amounts of TEOS were 1, 5 and 9 w/w%. The resulting samples were denoted as EDPNR/silica-1, EDPNR/silica-5 and EDPNR/silica-9 respectively.

Contact angle determination

Fig.4 shows the image of water drop on the surface of EDPNR15 and EDPNR/silica blends. The contact angle of water drop on EDPNR15 is 69.41° . As for water drop on EDPNR/silica-1, EDPNR/silica-5 and EDPNR/silica-9, the contact angle is 72.25° , 82.29° and 77.16° , respectively. The contact angle of water drop on EDPNR/silica blends is higher than that on EDPNR. In the other word, the surface of EDPNR/silica blends is more hydrophobic than EDPNR. This may be explained due to the strong interaction between silica and epoxy group. As the result, the water - EDPNR interaction reduced and the hydrophobicity of the material was enhanced [8,9]. In addition, when the amount of added TEOS was 5 %w/w, the contact angle of the resulting sample was the highest. It was probably considered that when the TEOS amount increased, the coagulation of silica particle occurred to decrease the interaction between silica and epoxy group. Therefore, 5 %w/w of TEOS was found to be the optimal amount to disperse in EDPNR.

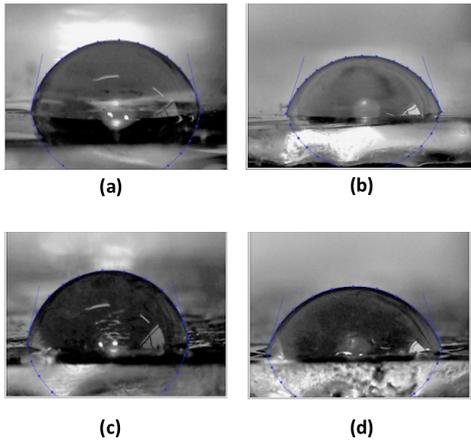


Fig. 4. The image of water drop on the surface of (a) EDPNR15, (b) EDPNR/silica-1, (c) EDPNR/silica-5 and (d) EDPNR/silica-9.

Water uptake measurement

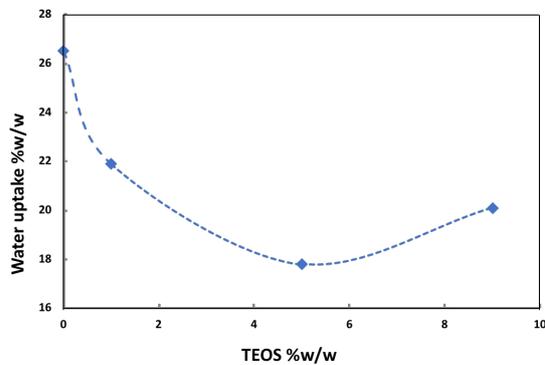


Fig. 5. The plot of water uptake vs. amount of TEOS.

The water uptake is an important index of the materials used for coating application. When the water uptake of sample is low, it may indicate that the material is waterproof and suitable for coating. The water uptake of EDPNR/silica blend was found to be lower than that of EDPNR. This result may confirm that the strong interaction of EDPNR – silica affected not only the surface of EDPNR but also the structure of EDPNR. EDPNR/silica became more hydrophobic compared with EDPNR itself. Moreover, the water uptake of EDPNR/silica-5 was the lowest. This is consistent with the result from contact angle.

We used EDPNR/silica-5 to elucidate the structure and morphology of the sample.

FT-IR spectroscopy

Fig.6 depicts FT-IR spectrum of EDPNR15 and EDPNR/silica5. As can be seen in the figure, the characteristic signals of EDPNR are present in EDPNR/silica5. The signal at 3500 cm^{-1} may be

attributed to vibration of O-H in H_2O which remains in the samples. This result might imply that the structure of EDPNR did not change after blending with TEOS.

However, the worthy of note was that in FT-IR spectrum of EDPNR/silica5, the shoulder of peak at 770 cm^{-1} and peak at 1006 cm^{-1} appeared. They are characteristic signal of SiO_4 tetrahedral and stretching vibration of the Si-O-Si linkage, respectively. The presence of these peaks may suggest that the hydrolysis of TEOS occurred in EDPNR latex to form Si-O-Si.

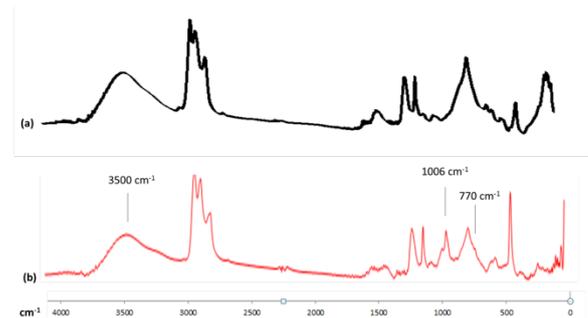


Fig. 6. FT-IR spectrum of (a) EDPNR15, (b) EDPNR/silica5.

SEM observation

In order to elucidate the formation of Si-O-Si in EDPNR, the SEM image of EDPNR/silica-5 was examined. The dark domain is rubber phase and the bright domain is silica particle. It can be clearly seen in Fig.7, the silica particle is small and well dispersed in EDPNR matrix. This evidence may confirm that the hydrolysis of TEOS occurred to form small silica particle. This was the efficient method to disperse silica in EDPNR.

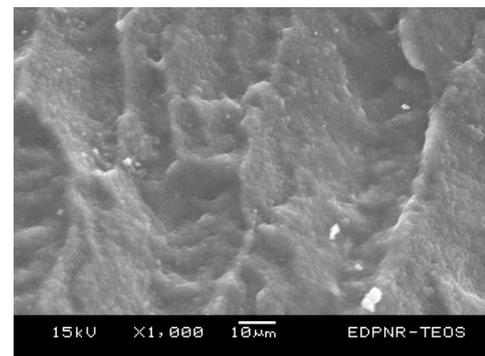


Fig. 7. SEM image of EDPNR/silica5.

4. Conclusion

The preparation of EDPNR and EDPNR/silica was carried out in latex stage. Silica particle was formed through the hydrolysis of TEOS in EDPNR latex and dispersed well in EDPNR matrix. The blends of silica and EDPNR with 15 %mol of epoxy group content were made. When the amount of TEOS was 5 %w/w, the blend EDPNR/silica achieved highest hydrophobicity.

Acknowledgments

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