SOME CHARACTERISTICS OF EPOXIDIZED
NATURAL RUBBER AND THE WOOD COATED BY IT

Nguyen Thu Ha[*], Nguyen Hong Quan, Cao Hong Ha,
Nguyen Pham Duy Linh, Phan Trung Nghia

School of Chemical Engineering, Hanoi University of Science and Technology,
No.1 Dai Co Viet street, Hai Ba Trung district, Ha Noi

[*]Email: *ha.nguyenthu5@hust.edu.vn*

ABSTRACT

Epoxidized natural rubber was prepared by epoxidation of natural rubber with fresh peracetic acid in latex stage. The epoxidized natural rubbers with epoxy group contents of 8, 15 and 27 mol% were prepared by adjusting the amount of fresh peracetic. The characterization of obtained materials was carried out through NMR spectroscopy, gel content determination and particle size measurement. The epoxidized natural rubber with various epoxy group contents were coated on the surface of the wood substrate by spin coating technique. The contact angle measurement and bending strength measurement were carried out for wood coated by epoxidized natural rubbers and epoxidized natural rubber/silica. The results showed that the obtained epoxidized natural rubber and epoxidized natural rubber/silica are liquid resistance which is expressed by high contact angle of water and poly(ethylene glycol) solution on the rubber surface. The bending strength of wood was improved by coating epoxidized natural rubber and epoxidized natural rubber/silica. The material with epoxy group content of 15 mol% is suitable for the protection of the wood surface.

Keywords: epoxidized natural rubber, surface, contact angle, bending strength.

1. INTRODUCTION

Natural rubber has been widely recognized to be suitable for coating application [1]. Due to the high adhesion, high hydrophobicity and superior water resistance, natural rubber is the ideal material to protect surface from severe environment condition. However, natural rubber is quite difficult to be the coating for wood material, because wood material contains various highly-polar compositions such as cellulose, hemicellulose and lignin [2]. In order to improve the adhesion of natural rubber on the polar surface, the modification of natural rubber was carried out.

The introduction of epoxy group to natural rubber is a method to obtain polar polymers from natural rubber. Epoxidized natural rubber is the potential material for coating of wood material surface, since the epoxy group is ready to interact with polar groups in wood [3,4]. Moreover, the addition of silica into epoxidized can support the adhesion and other physico-

chemical properties which are useful for coating. This green material is anticipated to replace formaldehyde based resin in coating and adhesive application.

In the previous works, the preparation of epoxidized natural rubber was carried out in solution or latex stage [5, 6]. The epoxy group content was adjusted by the amount of epoxidation agent or reaction time. Vietnamese researchers also paid very much attention on epoxidized natural rubber [7,8]. The preparation of epoxidized natural rubber was conducted in latex or CH_2Cl_2. The structural characterization of epoxidized natural rubber was carried out through FT-IR or NMR measurements. The mechanical properties, e.g. tensile strength, elongation at break, and thermal properties of epoxidized natural rubber were characterized. It has been reported that the properties of epoxidized natural rubber depends on epoxy group content [9]. Nevertheless, the physico-chemical properties of epoxidized natural rubber and epoxidized natural rubber/silica which are important for coating application have not been investigated and the optimal epoxy group content for coating wood has not been determined. The attempt to use epoxidized natural rubber/silica blend for coating wood has not been made.

The characterization of their physico-chemical properties which are important for coating application has not been investigated. In addition, the optimal epoxy group content for coating wood has not been determined. The proteins in natural rubber having an influence on epoxidation reaction have not been removed in research work of Vietnamese researchers.

In the present work, we prepared epoxidized natural rubber as well as its blends with silica, and we characterized their properties which are necessary for the coating wood material. We removed proteins from natural rubber by using urea and surfactant, then carried out the epoxidation in latex stage. The epoxidized natural rubbers with epoxy group contents of 8, 15 and 27 mol% were prepared in latex stage by adjusting the amount of fresh peracetic. Silica was dispersed into epoxidized natural rubber latex. The NMR spectroscopy was used to calculate the epoxy group content. The characterization of resulting materials was carried out through particle size measurement, gel content determination, contact angle measurement and bending strength measurement.

2. MATERIALS AND METHODS

2.1. Materials

High ammoniated natural rubber (HANR) latex was provided by Binh Duong company (Vietnam) with dried rubber content (DRC) of about 60 w/w%. Sodium dodecyl sulfate (SDS) and urea was purchased from Merck (Germany). Hydrogen peroxide (30 w/w%), anhydride acetic (99 w/w%), ammonia solution (28 w/w%), toluene, tetraethyl orthosillicate (TEOS) and poly(ethylene glycol) (PEG) were supplied by Nacalai Tesque (Japan). The reagents were used without further treatment.

2.2. Epoxidation of natural rubber in latex stage

The removal of proteins from natural rubber latex was carried out, followed by the epoxidation. Deproteinization of HANR latex was made in pilot scale by incubation of HANR latex with 0.1 w/w% urea and SDS 1 w/w% for several minutes, followed by centrifugation at 7,000 g. The resulting material is deproteinized natural rubber (DPNR) latex. The nitrogen content, which is proportional to protein content, of HANR and DPNR is 0.33 and 0.18 w/w%, respectively.

DPNR latex adjusted DRC to 10 w/w% was epoxidized in latex stage with various amounts of fresh peracetic acid (concentration of 33 w/w%) which was prepared by adding dropwise hydrogen peroxide into acetic anhydride at 0 °C, followed by stirring gently at 40 °C for 90 minutes. The epoxidation of DPNR latex was carried out at 10 °C for 3 hours. After the completion of reaction, the pH of resulting solution was adjusted to 7 by ammonia solution, then followed by the centrifugation at 9,000 g for 30 minutes to obtain epoxidized deproteinized natural rubber (EDPNR). TEOS with 5 w/w% was dropped into EDPNR latex. The resulting samples were dried in reduced pressure at 50 °C for a week.

2.3. Preparation of EDPNR-coated wood

Wood of *erythrophloeum fordid* with 1 mm in thickness was dried in the flow of nitrogen gas for an hour, followed by keeping in a desiccator in a week. Thereafter, a EDPNR sample was coated on the surface of the substrate by spin coating technique and followed by drying in room temperature for 24 hours. The thickness of EDPNR on the wood surface was adjusted to about 100 μm.

2.4. Characterization

2.4.1. NMR measurement

^{1}H-NMR measurements were carried out with CDCl$_3$ solutions of DPNR, EDPNR with a JEOL FT-NMR ECA-400 spectrometer. The measurements were operated at 400 MHz at 25 °C with pulse repetition times of 7 s and 128 accumulations. The chemical shift was referred to signal of CHCl$_3$. The content of epoxy group in EDPNR was calculated from the intensity ratio of the signals at 2.7 and 5.1 ppm, according to the equation:

$$X_{epoxy} = \frac{I_{2.7}}{I_{2.7}+I_{5.1}} \times 100 \qquad (1)$$

where I$_{2.7}$ and I$_{5.1}$ is the intensity of the signal at 2.7 and 5.1 ppm, respectively [10].

2.4.2. Particle size measurement

The particle size distributions of natural rubber latex before and after epoxidation were analyzed though the Dynamic Light Scattering (DLS) technique using a HORIBA SZ100 instrument. The scattering angle was 90 degree. The measurement was carried out at 25 °C.

2.4.3. Gel content determination

Gel contents of samples were determined by immersing 0.04 g of the rubber in 80 g of toluene. The mixture was kept in the dark without shaking for a week, followed by centrifugation at 10000 rpm, 15 °C for 30 min in order to separate gel fraction. Gel remaining was dried under reduced pressure at 50 °C for a week and weighed [11]. The calculation for gel content is as follow:

$$\% \text{ Gel content} = \frac{Weight\ of\ gel}{Weight\ of\ samples} \times 100 \qquad (2)$$

2.4.4. Contact angle measurement

The contact angles of distilled water and a solution of polyethylene glycol (20 w/w%) on wood substrates coated by EDPNR and EDPNR/silica were measured. A drop of the liquid (4 µL) was placed on the surface of substrate.
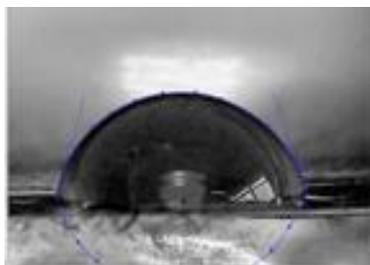

Figure 1. The drop of liquid on substrate used for contact angle measurement.

The contact angle was measured by Dataphysics OCA20 system equipped with SCA20 software. The measurement was carried out at 298 K. The image of drop was immediately taken by CCD camera, and then this image was sent to the computer for analysis. The contact angle was calculated by software SCA20.

2.4.5. Bending strength measurement

The bending strength of samples was determined according to ISO 178-1993 by an Instron 5582 Universal Tester. The samples with 1 mm in thickness were cut into 10x1 cm. The measurement was carried out at 25°C with the bending speed of 2 mm/min. The measurement was repeated five times for each sample. The bending strength was calculated as the following equation:

$$\sigma = \frac{3FL}{2bd^2} \qquad (3)$$

where σ: bending strength (MPa), F: load applied to sample (N), L: the distance of support span (mm), b: width of sample (mm), d: thickness of sample (mm).

3. RESULTS AND DISCUSSION

3.1. NMR spectroscopy

The ^{1}H-NMR spectra for DPNR and EDPNR are shown in Figure 1. In ^{1}H-NMR spectrum for DPNR, three signals at 5.14, 2.05 and 1.67 ppm were assigned to methine (CH=), methylene (-CH$_2$-) and methyl (–CH$_3$) groups of *cis*-1,4-isoprene units, respectively. After epoxidation, signals at 1.2, 1.55 and 2.7 ppm appeared. Those signals were assigned to methyl, methylene and methine groups of epoxidized-*cis*-1,4-isoprene units, respectively [10]. The presence of these signals confirmed that the epoxy group was formed in natural rubber.

We prepared EDPNRs with various epoxy group content by adjusting the amount of fresh peracetic acid using for epoxidation. The epoxy group content of EDPNR was calculated according to the equation (1). In the present study, the resulting EDPNRs with epoxy group content of 8, 15 and 27 mol% which are abbreviated as EDPNR8, EDPNR15 and EDPNR27, respectively, were prepared.
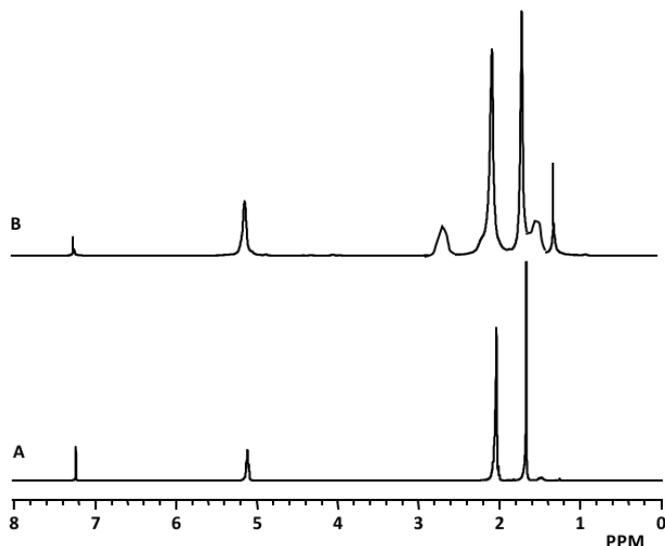
172

Figure 2. ^{1}H-NMR spectrum for (A) DPNR and (B) EDPNR.
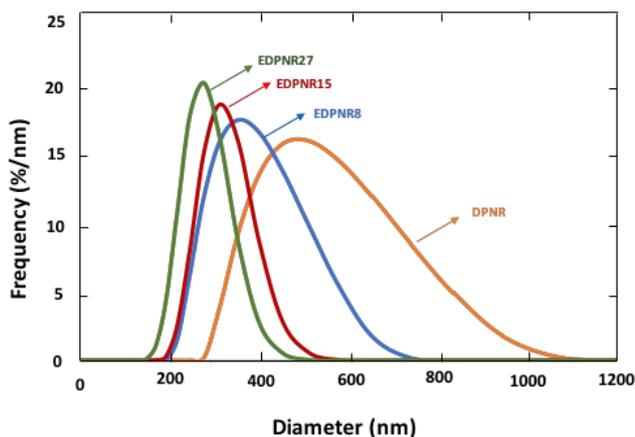
3.2. Particle size

Figure 3. Particle size of natural rubber and epoxidized natural rubber.

Figure 3 depicts the particle size distribution of DPNR, EDPNR8, EDPNR15 and EDPNR27. The range of particle size DPNR latex is from 280 nm to 1075 nm. As can be seen in Figure 3, the size of natural rubber particle decreased after epoxidation. The higher epoxy group content in EDPNR contained, the smaller rubber particle size was. In addition, the particle size distribution reduced as the epoxy group content increased. It was possible to consider chain scission occurred during epoxidation reaction [9]. Therefore, the rubber particle size decreased. The result may indicate that EDPNR is suitable for coating application since the material with small particle size can afford the shiny surface [12].

3.3. Gel content

Table 1. Gel content of the samples.

Sample	DPNR	EDPNR8	EDPNR15	EDPNR27
Gel content (w/w%)	28.0	54.1	71.0	63.9

The gel content of DPNR and EDPNRs is shown in Table 1. The gel content of natural rubber, which is attributed to branching points in natural rubber, was found to increase after epoxidation reaction. When the epoxy group content grew up to 15 mol%, the gel content of EDPNR was 71 w/w%. However, when the epoxy group content was 27 mol%, the gel content slightly went down to 63.9 w/w%. This may be explained that during the epoxidation, the 3D network formed thanks to the presence of epoxy group and the gel point which is naturally present in natural rubber deformed due to the reaction. In fact, when the content of epoxy group was higher than 15 mol%, the sample was readily cracked. Therefore, EDPNR with 15 mol% of epoxy group content may be considered to contain the highest gel content.

3.4. Contact angle

The contact angle of water and PEG solution on several substrates, i.e. wood and wood covered with EDPNRs is shown in Table 2.

Table 2. Contact angle of liquid on various substrates.

Sample	Water	PEG solution
Wood	40.02^{o}	41.40^{o}
Wood coated with EDPNR8	66.13^{o}	77.24^{o}
Wood coated with EDPNR15	69.41^{o}	79.68^{o}
Wood coated with EDPNR27	65.50^{o}	75.44^{o}
Wood coated with EDPNR15/silica	82.29^{o}	88.75^{o}

Wood surface is hydrophilic as indicated by the small contact angles with distilled water and PEG solution. When wood is coated by EDPNR, the surface becomes more hydrophobic. It is worthy of note that the contact angle of water and PEG solution on the surface of wood coated with EDPNR15 attains the highest value. It may be associated with the highest gel content of EDPNR15 as mentioned above. The 3D network structure in EDPNR15 as indicated by highest gel content may result in the more hydrophobicity of the surface.

In order to enhance the hydrophobicity of wood surface, an attempt to coat wood surface with EDPNR15/silica was made. The result reveals that contact angle of water and PEG solution on wood coated with EDPNR15/silica sharply increases. This result may be explained that when TEOS was added to EDPNR latex, the hydrolysis occurred to form silica particle [13]. The strong interaction between silica and epoxy group was supposed to strengthen gel point in EDPNR. Therefore the structure of the material was tighter and the hydrophobicity of wood surface was improved in spite of small amount of added TEOS, i.e. 5 %w/w.

3.5. Bending strength

The bending strength of the samples is tabulated in Table 3. The value of bending strength of wood coated with EDPNR raises compared to that of wood. It was probably caused by the strong interaction between epoxy groups of EDPNR and polar groups of wood. As for wood

coated with EDPNR15, the bending strength achieved the highest value. The results are consistent with those of gel content and contact angle. It was supposed that the high content of branching point in EDPNR structure enables the increase of bending strength of sample. The epoxy group content of 15 mol% was found to be the optimal content for EDPNR using for coating wood.

Table 3. Bending strength of the samples.

Sample	Bending strength (MPa)
Wood	27.2
Wood coated with EDPNR8	35.5
Wood coated with EDPNR15	55.9
Wood coated with EDPNR27	47.6
Wood coated with EDPNR15/silica	64.1

When wood was coated with EDPNR15/silica, the bending strength of the material considerably increases. Although the silica content used was 5 w/w%, the bending strength of wood coated with EDPNR15/silica is about 2.5 times higher than that of wood. We supposed that silica particle was well dispersed in EDPNR thanks to the method of dispersion in latex stage. Thus, silica particle in sample dissipates the applied force during bending. As the result, the bending strength of wood coated with EDPNR15/silica improves in spite of using only the small amount of silica.

4. CONCLUSIONS

In this work, the characteristics of epoxidized natural rubber and the wood coated from it were investigated. The particle of epoxidized natural rubber was smaller and more uniform than that of natural rubber. Gel content and silica were found to play an important role in the properties of EDPNR using for coating wood. EDPNR with 15 mol% of epoxy group content possesses the outstanding liquid resistance and improvement of bending strength of wood. Silica blended with EDPNR enhanced the liquid resistance and bending strength of wood.

REFERENCES

1. Wake W. C. - Natural rubber and reclaimed rubber adhesive, Van Nostrand Reinhold, New York, 1977, 552-554.

2. Thongnuanchan B., Kokkaew K., Kaesaman A., Nakason C. - Epoxidized natural rubber - bonded para rubber wood particleboard, Polymer Engineering and Science **47** (2007) 421-428.

3. Yoksan R. - Epoxidized natural rubber for adhesive applications, Thailand Journal of Natural Science **42** (2008) 325 - 332.

4. Pocius A. V. - Adhesion and adhesives technology: an introduction, Carl Hanser Verlag, Munich, 1997, 230-231.

5. Klinklai W., Kawahara S., Mizumo T., Yoshizawa M., Sakdapipanich J. T., Isono Y. and Ohno H. - Depolymerization and ionic conductivity of enzymatically deproteinized natural rubber having epoxy group, European Polymer Journal **39** (2003) 1707-1712.

6. Tanrattanakul V., Wattanathai B., Tiangjunya A. and Muhamud P. - In-situ epoxidized natural rubber: improved oil resistance of natural rubber, Journal of Applied Polymer Science **90** (2003) 261- 269.

7. Le X. H., Hoang N. T., Tran T. V. – Epoxidation of liquid natural rubber using peracetic acid, Vietnam Journal of Chemistry **37** (1998) 2-4 (in Vietnamese).

8. Le D. G., Pham H. L. – Epoxidation of liquid natural rubber having epoxy group in terminal unit by 3-chloro perbenzoic acid, Vietnam Journal of Science and Technology **49** (2011) 49-54 (in Vietnamese).

9. Gelling I.R. – Epoxidised natural rubber, Journal of Natural Rubber Research **6** (1991) 184 - 205.

10. Saito T., Klinklai W., Kawahara S. - Characterization of epoxidized natural rubber by 2D NMR spectroscopy, Polymer **48** (2007) 750 - 757.

11. Amnuaypornsri S., Nimpaiboon A., Sakdapipanich J. - Role of phospholipids and proteins on gel formation and physical properties of NR during accelerated storage, Elastomer and Plastics (Germany) **3** (2009) 88-92.

12. Bohren C. F., Huffman D. R. - Absorption and scattering of light by small particle, John Wiley and Son, Toronto, 2008, 83-129.

13. Kim K. D., Kim H. T. - Formation of Silica Nanoparticles by Hydrolysis of TEOS Using a Mixed Semi-Batch/Batch Method, Journal of Sol-Gel Science and Technology **25** (2002) 183-189.