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Epoxidized Natural Rubber for Adhesive Applications

Rangrong Yoksan

ABSTRACT

ENR-based adhesives were prepared under the concepts of (i) crosslinking at epoxirane rings and/or (ii) curing at α-carbon positions along the rubber chain. The crosslinking at epoxirane rings was accomplished when two crosslinking agent/catalyst systems, i.e., diamine/bisphenol A and anhydride/imidazole were used. However, the crosslinking efficiency of the anhydride/imidazole crosslink system was higher than that of the diamine/bisphenol A crosslink system. The curing of ENR at the α-carbon positions was carried out by conventional vulcanization (CV). The mechanical testing of three formulations of ENR-toluene based adhesives, i.e., (i) ENR-PA adhesive, (ii) ENR-S adhesive, and (iii) sulfur cured ENR-PA adhesive showed that ENR-S adhesive gave the highest tensile strength. The fourth formulation of adhesive was, hence, prepared by adding tackifier (resin PX1150) to the ENR-S adhesive (ENR-S-resin PX1150 adhesive). The effect of resin PX1150 on the mechanical properties of ENR-S-resin PX1150 adhesives was studied to find that when the amount of tackifier increased the tensile strength and tensile modulus of the adhesive also increased, while the %elongation at break decreased.

Key words: natural rubber, epoxidized natural rubber, phthalic anhydride, adhesive, tackifier

INTRODUCTION

Natural rubber (NR) is one of the most important economic commodities in Thailand produced from Para rubber tree, *Hevea brasiliensis*. NR exhibits unique physical and chemical properties such as elasticity, stickiness, resilience, etc., which are suitable for various products, e.g., tires, under the bonnet products, gloves, balloons, rubber bands, condoms, adhesives, etc. However, most applications of NR are limited owing to the low stability to heat, oxygen, sunlight, etc. and the high solubility in most hydrocarbon/hydrophobic solvents including oils. Those limitations result from NR chemical structure (cis 1,4-polyisoprene), which contains double bonds and hydrocarbon atoms (Figure 1).

The chemical modification at double bonds and introduction of hydrophilic groups along NR backbone are alternative strategies to improve the stability of NR and to provide widespread applications. Epoxidized natural rubber (ENR) (Figure 1) is an ideal material for the present work since the introduction of epoxirane ring not only reduces the number of double bonds but also increases the hydrophilicity of NR. The preparation of ENR by using peracids, e.g., performic (Heping *et al*., 1999; Okwu *et al*. 2001; Tanrattanakul *et al*., 2003) and peracetic acids (Kinklai *et al*., 2003) was reported. The

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Division of Physico-Chemical Processing Technology and Department of Packaging Technology and Materials, Faculty of Agro Industry, Kasetsart University, Bangkok 10900, Thailand. e-mail: rangrong.y@ku.ac.th

degree of epoxidation is controlled by the amount of peracid, reaction temperature, and reaction time. Similar to epoxy resin, ENR can be crosslinked by di- or multi-functional group substances such as amines (Hashim *et al.*, 1994; Hong *et al.*, 1998; Hong *et al.* 2004), carboxylic acids, anhydrides (Masse, 1999; Masse *et al.*, 1999), etc. to provide a network structure.

Adhesive is one of the major applications of NR used in many industries such as shoes, bags, tires, automotives, furniture, etc. NR-based adhesives were classified into two principal types, i.e., latex adhesives (water-based adhesives) and solution adhesives (solvent-based adhesives) (Pocius, 1997). Although latex adhesives are cheap, handled easily, non-toxic, and little incendiary risk, some properties such as tackiness and water resistance including adhesive shelf-life should be considered. The solution adhesives, generally containing a solvent such as toluene, naphtha, or trichloroethane, are inflammatory and toxic when one uses without skills. However, solvent-based adhesives provide higher tackiness and longer shelf-life.

The present work, thus, focused on the preparation and characterizations of ENR and also studied on its vulcanization at α-carbons and crosslinking at epoxirane rings. In addition, the solvent-based ENR adhesives were prepared and tested for their mechanical properties.

MATERIALS AND METHODS

Materials

Concentrated NR (Batch No. T2 091047, 60 %DRC) was obtained from Num Rubber & Latex Co., Ltd., Thailand. Resin PX1150 was provided by Yasuhara Chemical Co., Ltd., Japan. Formic acid, 30% hydrogen peroxide (H_2O_2), sodium sulfite, 25% ammonia solution, methanol (MeOH), sodium carbonate (Na_2CO_3), bisphenol A, *p*-phenylenediamine, hexamethylenediamine, phthalic anhydride (PA), and 2-ethyl-4-methylimidazole (EMI) are analytical grade and used without further purification. Emulwin W, Terric 16A-16, ZnO, stearic acid, titanium dioxide (TiO_2), Wingstay-L, sulfur, and zinc-diethyldithiocarbamate (ZDEC) are industrial grade.

Preparation and characterizations of ENR

ENR was prepared by performic epoxidation (Figure 1). Concentrated NR was diluted with distilled water to have 20 %DRC. Nonionic surfactant (Emulwin W or Terric 16A-16) was gradually added to maintain the stability of latex. Formic acid (0.75 mole equiv. to isoprene unit) and 30% H_2O_2 (0.75 mole equiv. to isoprene unit) were, then, slowly dropped while the mixture was heated to 50°C. The mixture solution was stirred at 50°C for 2-9 hours. After the reaction, the mixture was cool down to room temperature and added sodium sulfite to remove an excess H_2O_2 following by neutralization with 25% ammonia solution. MeOH was, then, added to precipitate the product. A white solid bulk was washed with water several times, rinsed with MeOH, and dried under reduced pressure. The obtained products were, then, characterized by FT IR (Vector 3.0 Bruker Spectrometer and PerkinElmer Spectrum 100 FT IR spectrometer), ^1H NMR (Bruker DPX300), and SEM techniques

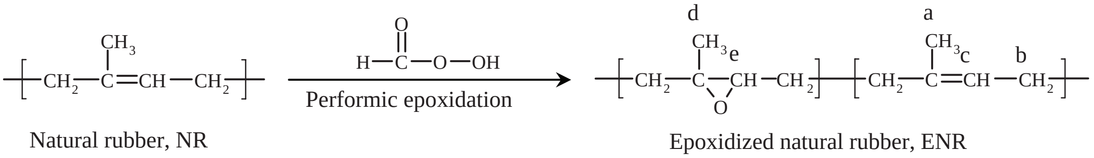

Figure 1 Performic epoxidation of NR.

(Jeol JSM 5600 LV). The mol %epoxidation was determined by ^{1}H NMR technique using Equation 1.

$$\text{Mol \%epoxidation} = [A_{2.7} / (A_{2.7} + A_{5.14})] \times 100$$

Equation 1

When $A_{2.7}$ = Peak integral at δ 2.7 ppm representing methine proton (*e*) of epoxide group

$A_{5.14}$ = Peak integral at δ 5.14 ppm representing olefinic proton (*c*) of unreacted NR

Study on crosslinking of ENR at epoxirane rings

The crosslinking of ENR with 25 mol %epoxidation (ENR25) via ring opening reaction was studied by using two crosslink systems, i.e., (i) diamine/bisphenol A (formulation A and B) and (ii) anhydride/imidazole crosslink systems (formulation C) (Table 1). ENR compounds were prepared at 50°C by two-roll mill. The curing characteristic of compounds was studied at 160°C for 90 minutes by Rheometer (RDA III, ARES of Rheometric machine).

Preparation and characterizations of ENR-S-resin PX1150 adhesives

Tackifier used in the present work was resin PX1150 (terpene polymer). The ENR-S-resin PX1150 adhesives were prepared in toluene with various ENR25:resin PX1150 ratios, i.e., 1:0, 1:0.5, 1:1, 1:1.5, 1:2, 1:3, and 1:4. Compound S was firstly prepared by mixing ENR25 (10 g) with all chemicals for sulfur vulcanization (ZnO (0.3 g), stearic acid (0.2 g), TiO_2 (0.1 g), Wingstay-L (0.1 g), and sulfur (0.1 g)), except ZDEC (accelerator). The mixing was carried out at 70°C by two-roll mill. Compound S was, then, dissolved in a ZDEC-resin PX1150-toluene solution with accelerator/sulfur (A/S ratio) of 0.4 and toluene:ENR25 of 5 mL:1 g.

The mechanical properties of all adhesives were tested using the modified ASTM D2095-2096. The adhesive was applied to a cubic wood (11×11×38 mm^3) on one surface (11´11 mm^2). The wood was stick with another wood and then dried with two different drying conditions, i.e., (i) room temperature for 2 days and (ii) 150°C for 10 min following by room temperature for 2 days. The mechanical properties were tested in a tension mode (EZ Graph, Shimadzu Corporation, Japan) with a loading rate of 3×10^5 Pa/sec (0.3 N/mm^2/sec).

Table 1 Amount of chemicals used for the preparation of crosslinked ENR.

Chemicals	Formulations[a]		
	A	B	C
ENR25	100	100	100
Na_2CO_3	3	3	
Bisphenol A	10	10	
p-Phenylenediamine	5		
Hexamethylenediamine		5	
PA			5
EMI			1

[a] Unit in phr: part per hundred dried ENR

RESULTS SND DISCUSSION

Preparation and characterizations of ENR

ENR was successfully prepared by performic epoxidation as confirmed from a new peak at 870 cm^{-1} (asymmetric epoxide ring stretching) and the decrease in peak intensity at 3036 ($R_1R_2C\underline{=CH}R_3$) and 835 cm^{-1} (=CH-, bending) (Figure 2). The successful epoxidation also supported by ^{1}H NMR technique as seen from new peaks at δ 1.2 ($-CH_3$ (*d*)) and 2.7 ppm (-CH- (*e*)) (Figure 3). It should be noted that the mole %epoxidation increased as the reaction time increased and was not dependent on the types of surfactants used, i.e., Terric 16A-16 and Emulwin W (Figure 4). The changes in appearance and physical properties were obtained in the case of ENR with high mol%epoxidation, e.g., the

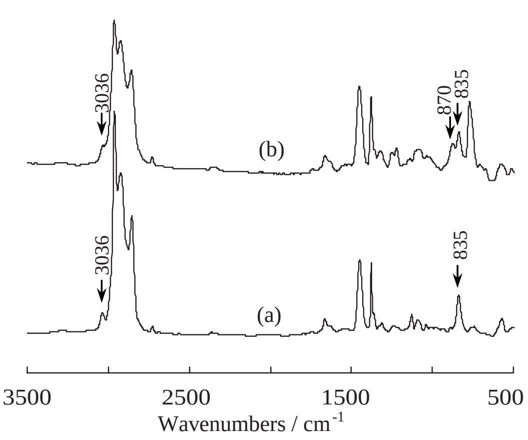

Figure 2 FT IR spectra of (a) NR and (b) ENR.

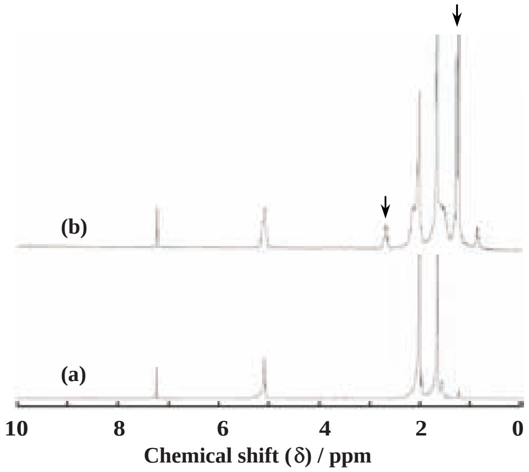

Figure 3 ^{1}H NMR spectra of (a) NR and (b) ENR.

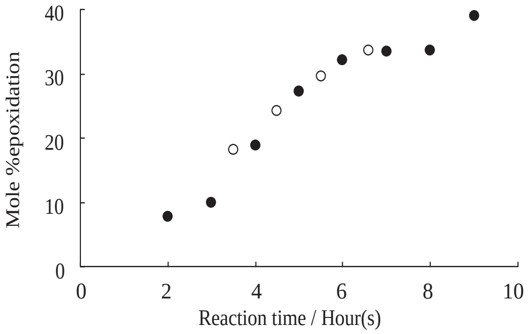

Figure 4 Mole %epoxidation of ENR as a function of reaction time; (●) Terric 16A-16 and (○) Emulwin W.

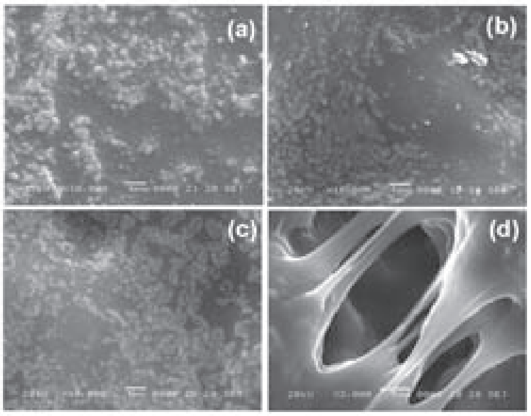

Figure 5 SEM micrographs of (a) NR, (b) ENR-Tr-5h, (c) ENR-Tr-7h, and (d) ENR-Tr-9h.

products were crumbly and easy to tear. SEM showed that the surface of NR is porous with an average pore size of 300-400 nm (Figure 5a); however, those pores are bigger for ENR with longer epoxidation time, e.g., 500 nm, 600 nm, and > 5 µm for the epoxidation time of 5, 7, and 9 hours, respectively (Figure 5b-d). This might result from the destruction of rubber matrix by performic acid, excess H_2O_2, and/or excess formic acid. In order to maintain the appearance (i.e., the small pore size of the matrix) and properties (e.g., not crumbly), the ENR with 25 mole %epoxidation (ENR25) (epoxidation time of 5 hours) was used in the present work.

Crosslinking of ENR at epoxirane rings

By considering the chemical structure, ENR can be either vulcanized by sulfur at α-carbons or ring opening crosslinked by di- and multi-functional group substances, e.g., amines

(Hashim *et al*., 1994; Hong *et al*., 1998; Hong *et al*. 2004), carboxylic acids, anhydrides (Masse, 1999; Masse *et al*., 1999), etc. The crosslinking of ENR at epoxirane rings was accomplished when diamine/bisphenol A (compound A and B) and anhydride/imidazole (compound C) were used as crosslinker/catalyst (Figure 6). The curing characteristic was studied at 160°C to find that the torque decreased for the first few minutes for all ENR compounds. This might be resulted from the softness of the compounds under heating. The torque, then, increased as a function of time pointing out that the crosslinking was proceeding. The rate of crosslinking depended on the crosslinker/catalyst system; for example, the rate was slow for the first 25 minutes and thereafter higher for compound A and B (Figure 6a-b). On the contrary, compound C showed very fast crosslinking rate for the first 10 minutes and after that the rate was significantly decreased (Figure 6c). It should be noted that the torque of compound C was higher than that of compound A and B implying that the anhydride/imidazole system showed higher crosslinking efficiency than the diamine/bisphenol A system (Figure 6).

ENR adhesives

Herein, three ENR/toluene-based adhesives were prepared, i.e., (i) ENR crosslinked by phthalic anhydride (ENR-PA adhesive), (ii) ENR vulcanized by sulfur (ENR-S adhesive), and (iii) ENR crosslinked by PA and vulcanized by S (S cured ENR-PA adhesive). The mechanical properties of those adhesives were tested using wood as a testing material to find that ENR-S adhesive gave the highest tensile strength (data not shown).

ENR-S-resin PX1150 adhesives

To improve the adhesive strength of ENR-S adhesive, the resin PX1150 was applied as a tackifier at various amounts. Figure 7 showed that naked resin PX1150/toluene (2 g/mL) gave higher tensile strength and tensile modulus than ENR-S-resin PX1150 adhesives, whereas %elongation at break was lower. This implied that the tackifier was strong and stiff. The tensile strength of ENR-S-resin PX1150 adhesives increased when the amount of tackifier increased; however, the reduction of tensile strength was observed when ENR:resin PX1150 was 1:3 (Figure 7a). This might be due to the limitation of ENR solubility in high concentration of tackifier solution. It should be noted that the adhesives dried at 150°C for 10 minutes gave higher tensile strength than those at room temperature. This might result from the vulcanization. In addition, the number of adhesive applications also affected the tensile strength, i.e., two applications gave higher tensile strength than one application. The

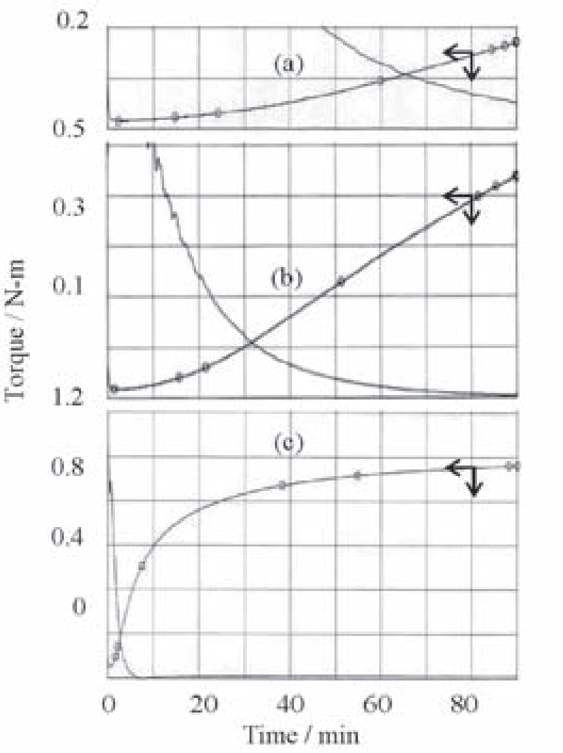

Figure 6 Plots of torque vs. time of samples crosslinked at 160°C; (a) compound A, (b) compound B, and (c) compound C.

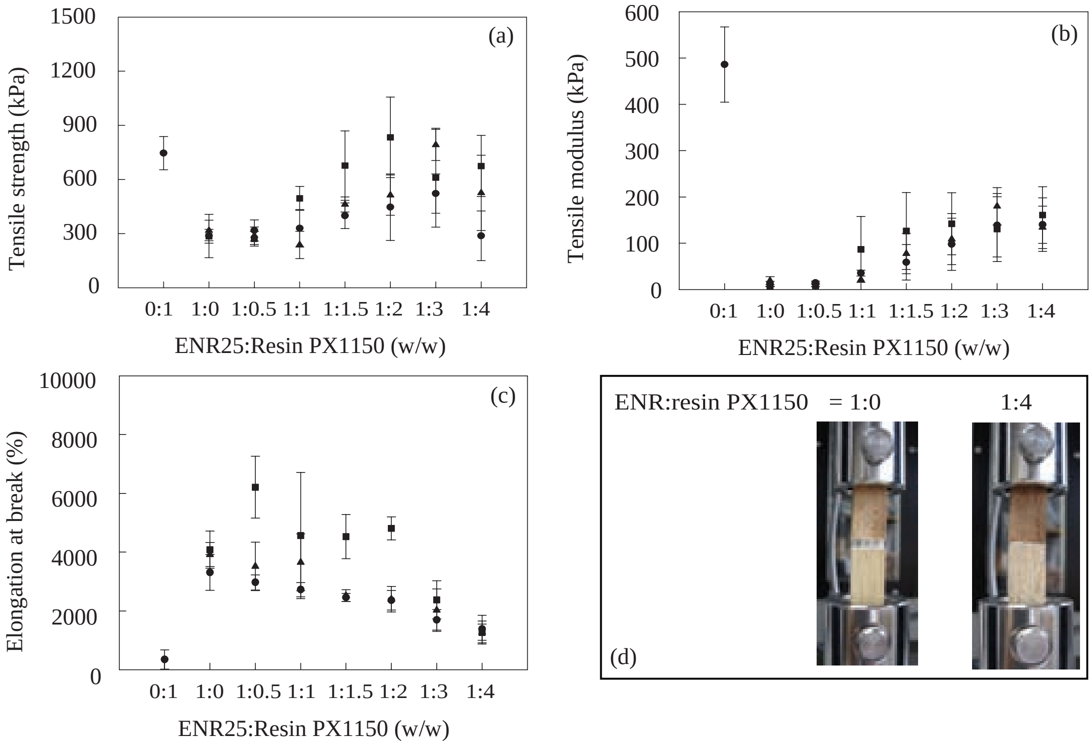

Figure 7 (a) Tensile strength, (b) tensile modulus, (c) elongation at break, and (d) photographs representing the separation of wood pieces joint with ENR-S-PX1150 adhesives during mechanical testing in tension mode; ●: one adhesive application and drying at room temperature, ▲ : one adhesive application and drying at 150°C for 10 min, ■ : two adhesive applications and drying at 150°C for 10 min.

result supported the fact that a large amount of rubber provides higher strength. The optimum ratio of ENR:resin PX1150 was 1:2 for applying adhesive twice and 1:3 for applying adhesive once. It should be pointed out that the %elongation at break decreased when the amount of tackifier increased and two adhesive applications enhanced the elongation of adhesive (Figure 7c). The adhesive with high amount of tackifier was stiff and difficult to elongate (Figure 7d). This supported the fact that tackifier provides adhesive strength, but not cohesive strength (elongation).

After mechanical testing, the surfaces of woods were investigated by SEM to find that the adhesive still remained on the wood surfaces implying that ENR-S and ENR-S-resin PX1150 adhesives showed failure in cohesion. The appearances of adhesives on the wood surfaces were different depending on the ratio of ENR:resin PX1150, e.g., elastic-like characteristic was observed when there was no tackifier in adhesive formulation (Figure 8b) or when small amount of tackifier was used (Figure 8c). When the amount of tackifier increased, the elastic-like characteristic disappeared little by little and the surface appearance became stiff flake-like (Figure 8d-f) and more rigid (Figure 8g-h), respectively.

It is interesting that the adhesive viscosity decreased when the amount of resin PX1150 increased; however, ENR could not be dissolved well when the ENR:resin PX1150 was 1:4. This might be due to the saturation of adhesive solution.

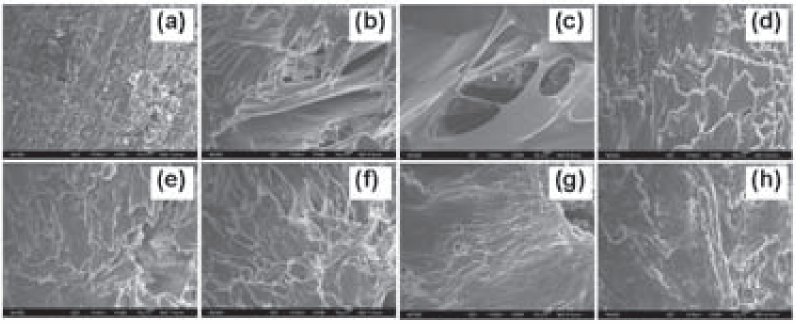

Figure 8 SEM micrographs of (a) naked wood surface and (b-h) wood surface joint with ENR-S-resin PX1150 adhesives after mechanical testing in a tension mode; when the ratios of ENR:resin PX1150 are (b) 1:0, (c) 1:0.5, (d) 1:1, (e) 1:1.5, (e) 1:2, (f) 1:3, and (g) 1:4.

This might be another reason that the tensile strength of ENR-S-resin PX1150 adhesive reduced when the amount of resin PX1150 was too high, e.g., adhesives with ENR:resin PX1150 ratios of 1:3 and 1:4.

CONCLUSION

ENR25 was successfully prepared by the performic epoxidation at 50°C for 4-5 hours. The crosslinking of ENR25 at epoxirane rings was markedly accomplished when phthalic anhydride (PA) and 2-ethyl-4-methylimidazole were used as crosslinking agent and catalyst, respectively. The adhesive prepared from sulfur cured ENR25 showed higher tensile strength than the one from PA crosslinked ENR25. The tensile strength and tensile modulus of sulfur cured ENR25 adhesive was enhanced by the addition of tackifier (resin PX1150). The optimum ratio of ENR:resin PX1150 was 1:2-3.

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