

Oil Resistance and Physical Properties of In Situ Epoxidized Natural Rubber from High Ammonia Concentrated Latex

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ABSTRACT: Epoxidized natural rubber (ENR) was prepared via in situ epoxidation from high ammonia concentrated natural rubber latex with formic acid and hydrogen peroxide in the presence of a surfactant at 50°C for 4, 8, and 12 h. The obtained ENRs containing 20, 45, and 65 mol % of epoxide groups were denoted ENR20, ENR45, and ENR65, respectively. The differential scanning calorimetric study revealed that they exhibited higher glass transition temperatures than that of natural rubber (−62.4°C), at −38.2°C for ENR20, −27.8°C for ENR45, and −19.7°C for ENR 65. It was clearly seen that their glass transition temperatures increased as the amount of epoxide groups increased. The prepared ENRs were compounded and vulcanized to pre-

pare test specimens for determination of oil resistance and various physical properties. It was found that the swelling of ENRs in oils was substantially less than that of natural rubber. The oil resistance of ENR65 was comparable to that of nitrile rubber, commonly used as oil resistant rubber. ENR65 also showed higher hardness than other ENRs. Contrarily, ENR20 possessed superior tensile strength and compression set when compared with other ENRs. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3948–3955, 2006

Key words: epoxidized natural rubber; nitrile rubber; modification; physical properties; oil resistance

INTRODUCTION

The chemical modification of natural rubber (NR) has been studied for many years, as a means of value-adding to this natural product. Epoxidation of natural rubber leads to interesting new forms of NR, which possesses several improved properties, especially the oil resistance.¹ Epoxidized natural rubber (ENR) can be prepared by epoxidation of natural rubber latex with formic acid and hydrogen peroxide, under the proper condition.^{2,3}

Epoxidation raises the glass transition temperature (T_g) by ~1°C for every mol % epoxidation.⁴ Strength and fatigue properties are still high as ENR is capable of strain-induced crystallization. As the level of epoxidation increases, damping, gas permeability, absorption of microwave energy, and compatibility with silica reinforcement increase. Reduction in swelling in hydrocarbon oil is also observed. In terms of processing, ENR does not appear to harden on storage and premastication is not generally required as the breakdown on a mill or in an internal mixer is rapid. ENR requires conventional antioxidants for optimum resistance to oxidation. Incorporation of a base is recommended to protect against

possible acid-catalyzed reactions during processing and in service. Calcium stearate is normally used at loadings of 2–5 phr and processing advantages are observed. Sodium carbonate can also be used at 0.2–2 phr, but higher levels reduce processing safety. When properly compounded with base and antioxidant, the aging characteristics of ENR will match or surpass those of natural rubber.^{5–7}

The aims of this research were to investigate properties of ENRs prepared via in situ epoxidation method under various reaction times. ENR was prepared via in situ epoxidation from high ammonia

TABLE I
Rubber compounding

| Chemicals | Amount (phr) |
|---|--------------|
| Rubbers | 100.0 |
| —ENR | |
| —NR: STR-5L | |
| —NBR | |
| Zinc oxide | 5.0 |
| Stearic acid | 2.0 |
| Silica | 40.0 |
| Polyethylene glycol 3350 | 1.0 |
| Styrenated diphenylamine: Wingstay L | 10.0 |
| N-cyclohexylbenzothiazylsulphenamide: CBS | 102 |
| Tetramethyl thiuram disulphide: TMTD | 0.2 |
| Sulfur | 2.0 |

^a Part per hundred of rubber.

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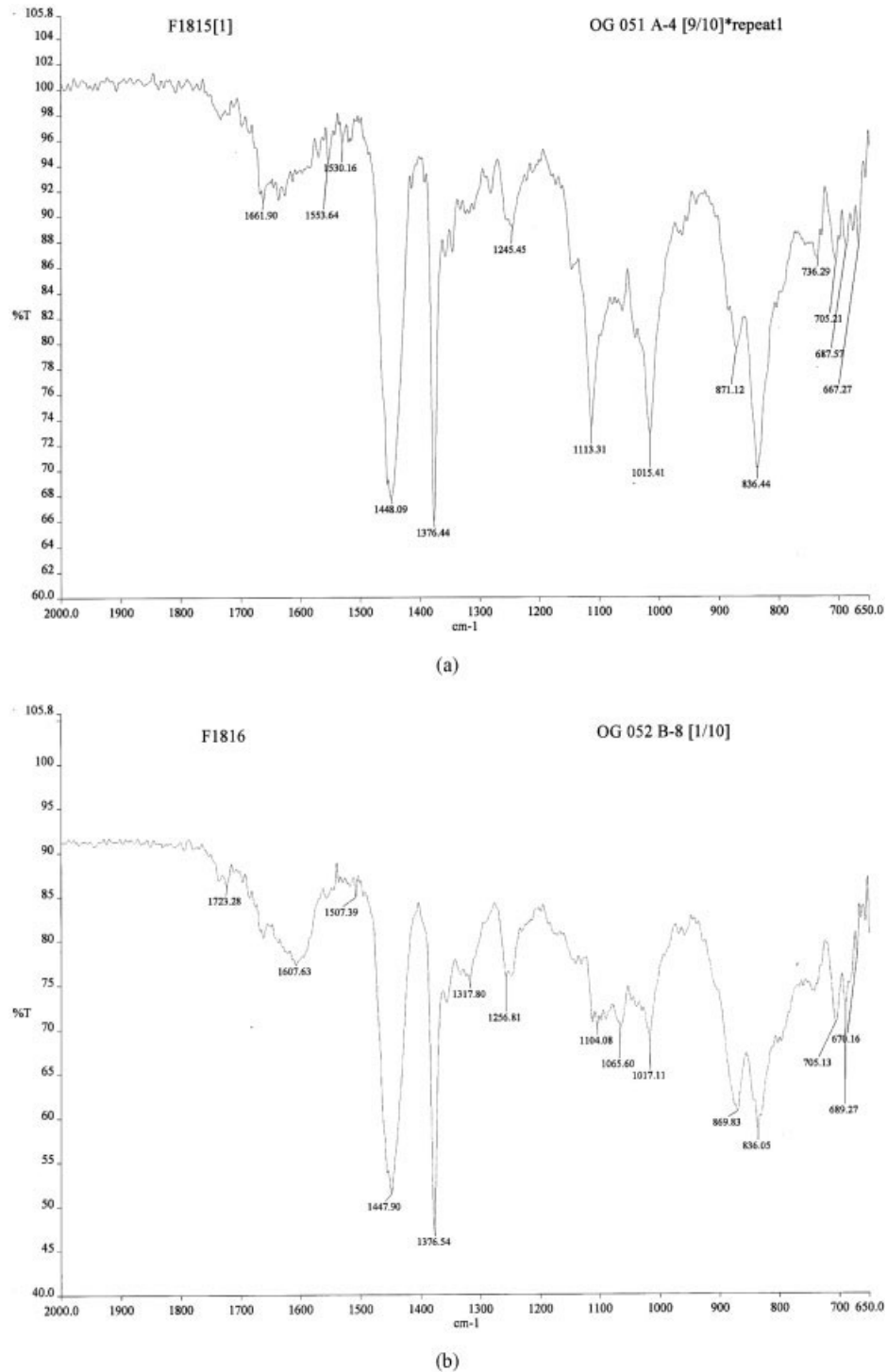


Figure 1 IR spectra of (a) ENR20 (b) ENR45, and (c) ENR65.

concentrated natural rubber latex with formic acid and hydrogen peroxide, using various reaction times. Additionally, a nonionic surfactant, namely, polyalcohol ethyleneoxide condensate, was used as a stabilizer. The obtained ENR was compounded and processed into test specimens. Physical and mechanical properties, i.e., glass transition temperature, oil resistance, hardness, tensile properties, and compression set, of

the prepared ENRs were examined and then compared with those of natural rubber and nitrile rubber.

EXPERIMENTAL

Preparation of ENR

High ammonia concentrated natural rubber latex (HA), supplied by Thai Rubber Latex Co., Ltd., was

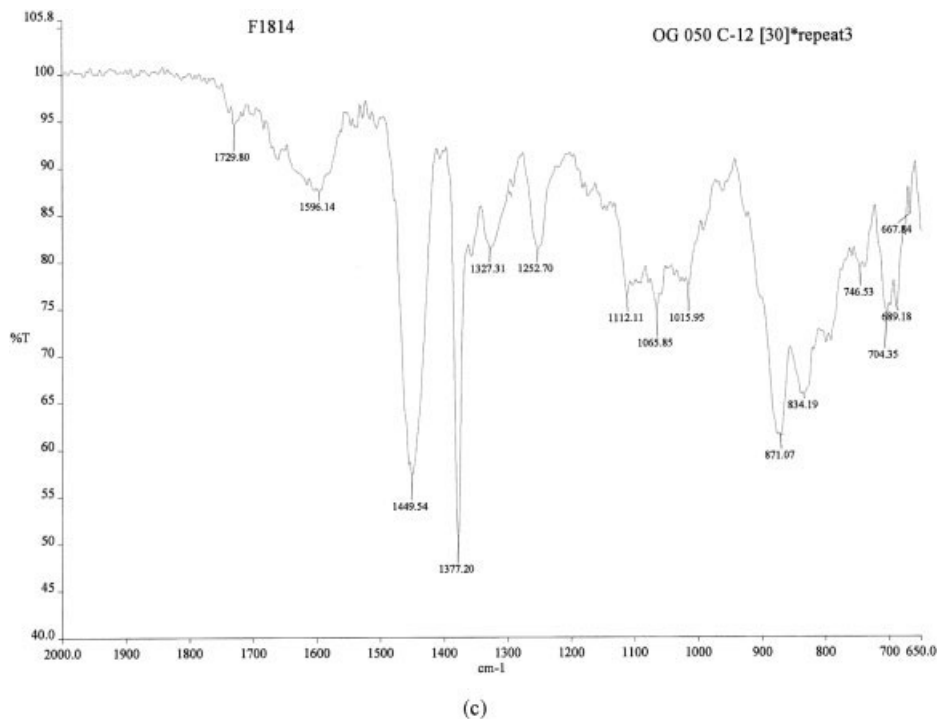


Figure 1 (Continued from the previous page)

diluted with distilled water so as to reduce its dry rubber content (DRC) from 60 to 20%. To stabilize the latex, 5 parts per hundred (phr) dry rubbers of polyalcohol ethyleneoxide condensate (Terric 16A16: Huntsman) was added and stirred for 1 h. The stabilized rubber was then added with 0.75M of 98% formic acid. The temperature was elevated to 50°C³ prior to the addition of 0.75M of 50% hydrogen peroxide. The reaction was carried on for 4, 8, and 12 h to obtain ENRs with different amount of epoxide groups. The epoxidized products were coagulated with 95% v/v methanol. Sodium carbonate solution and water were used to clean the rubber before drying at 60°C. An infrared spectrophotometer (Perkin-Elmer System 2000 FT-IR) was used for determination of epoxide contents. Glass transition temperature (T_g) was determined using a differential scanning calorimeter (Netzsch DSC 200) under N₂ atmosphere with heating rate of 5°C/min.

Compounding and processing

Epoxidized natural rubbers were compounded using a two-roll mill (Model R11-3FF, Japan) with various chemicals, according to the ratio shown in Table I. Natural rubber grade STR-5L and NBR were obtained from Rubber Research Institute, Thailand. Zinc oxide, Stearic acid, and Polyethylene glycol 3350 were purchased from Fluka. Silica, Styrenated diphenylamine, *N*-cyclohexylbenzothiazylsulfenamide (CBS), Tetramethyl thiuram disulphide (TMTD), and sulfur were

obtained from Cabot Corp. (Thailand), Goodyear Chemical, Monsanto, Sunny World (Thailand), and Dyna Trade (Thailand), respectively.

For comparison purpose, solid natural rubber (NR) and nitrile rubber (NBR) were also compounded using the same recipe. Scorch times and cure times of rubber compounds were determined using a rheometer (Rheotech Protech, USA). Based on the determined cure time, the rubber compounds were then processed into test specimens using compression molding machine. Some specimens were aged under elevated temperature at 100°C for 22 h.

Determination of oil resistance and physical properties

Oil resistance was determined by measurement of change in volume, as indicated by ASTM D471 using ASTM oil No.1 supplied by Japan Sun Oil as well as IRM 903 oil from the same supplier. Hardness of cured rubbers and aged rubbers was determined using a Shore durometer according to ASTM D2240. Standard test method ASTM D412 was employed to determine tensile properties of cured rubbers and heat-aged rubbers, using an universal testing machine (Instron Series IX Model 1011) with a test speed of 500 mm/min. A compression set tester (ATS, Italy) was used as described in ASTM D395-98.

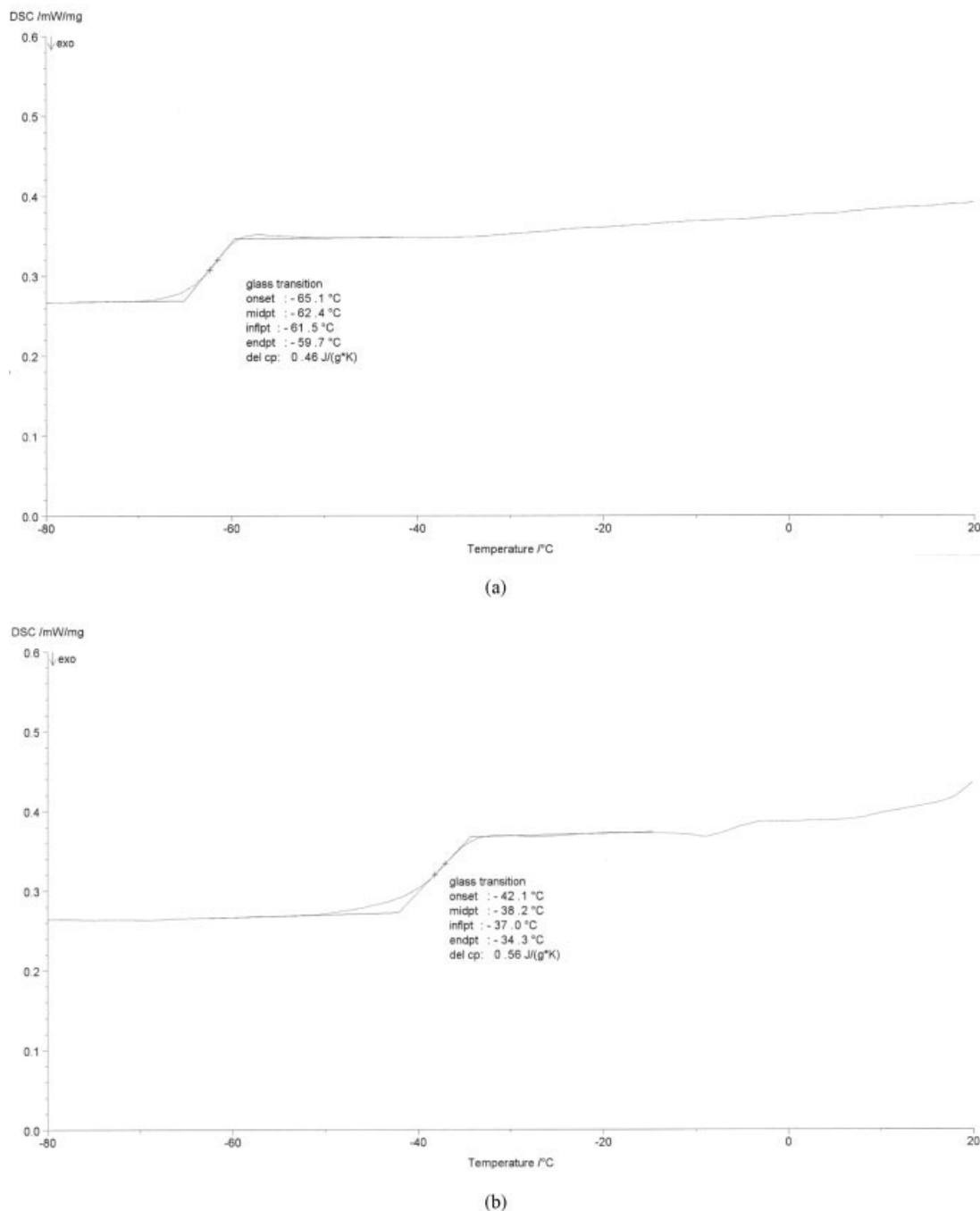


Figure 2 DSC thermograms of (a) NR (b) ENR20 (c) ENR45, and (d) ENR65.

RESULTS AND DISCUSSION

ENRs were prepared using in situ technique using different reaction time. The obtained rubbers were investigated by IR spectroscopy. The results are shown in Figure 1. It was revealed that there were absorption band of epoxide group at 870 and 1240 cm^{-1} . Absorption band of carbonyl group was not found at all, indicating that opening of epoxide ring was not present. The amount of epoxide is determined as the absorbance ratio between absorbance at 870

cm^{-1} and absorbance at 835 cm^{-1} , indicating C—H bonding with —C=C— of *cis*-1,4-polyisoprene.³ The calculation from IR spectra revealed that amounts of epoxide groups in mol % were 17.6, 43.8, and 63.9 for ENRs that reacted for 4, 8, and 12 h, respectively. Accordingly, they were denoted as ENR20, ENR45, and ENR65. It can be concluded that as the epoxidation reaction time increased, the amount of epoxide groups was increased, for the reason that formic acid and hydrogen peroxide had more time to react with

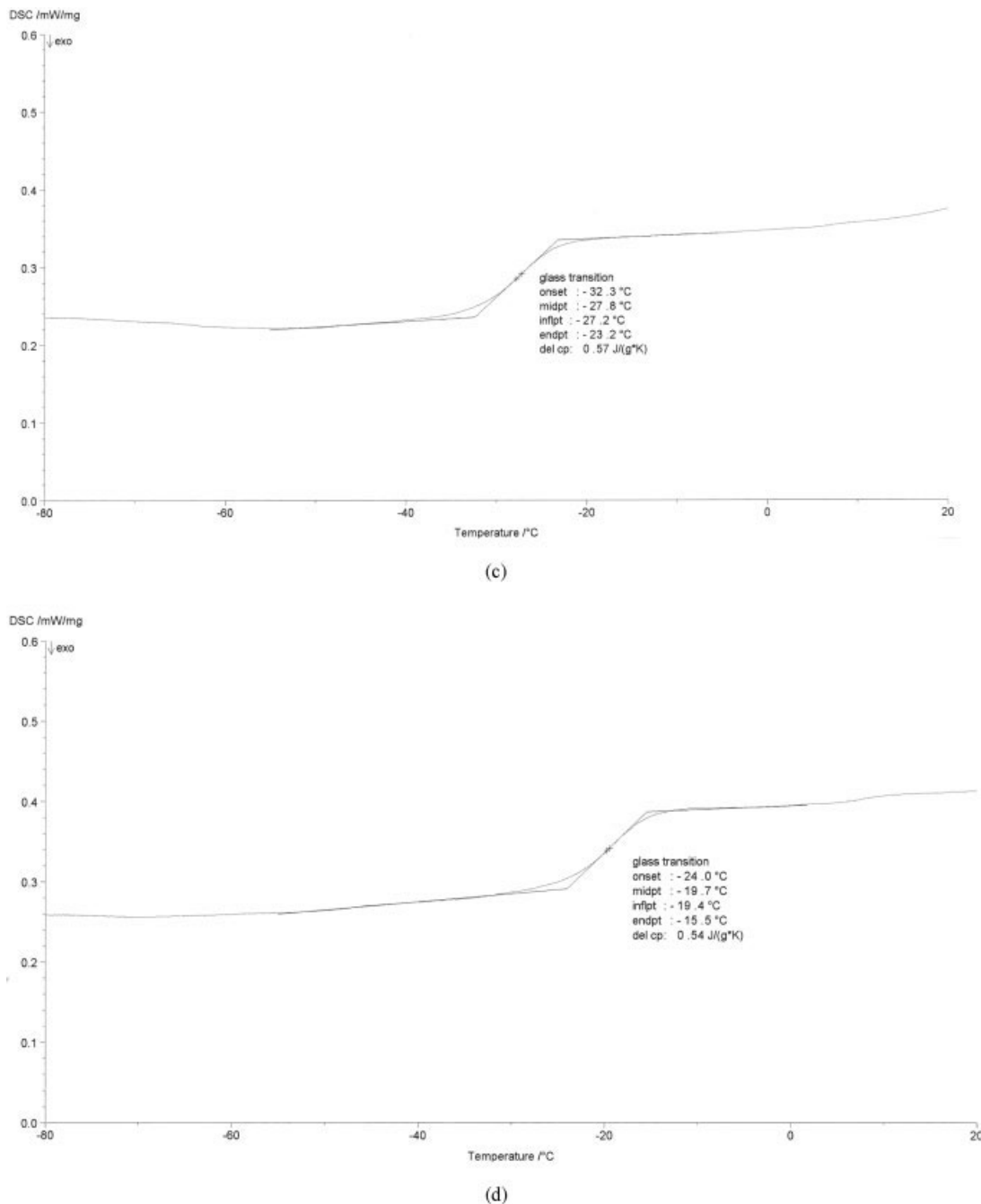


Figure 2 (Continued from the previous page)

the latex. However, if the reaction is longer than 14 h, the obtained latex would not be able to solidify.

From DSC analysis shown in Figure 2, it was found that T_g of ENR20, ENR45, and ENR65 was -38.2°C , -27.8°C , and -19.7°C , respectively. That is T_g of ENRs increased as the amount of epoxide groups increased and was higher than that of natural rubber (-62.4°C). This was due to the fact that chain rigidity was increased when epoxide groups increased.

Scorch times and cure times of compounded ENRs, NR, and NBR are reported in Figure 3. NBR

has the shortest scorch time, followed by ENR65, ENR45, ENR20, and NR, which has the longest scorch time. As epoxide groups activated the nearby double bonds in the molecular chain, scorch time was shorter as the amount of epoxide groups increased.⁸ The cure time of NBR is the longest among our samples, followed by that of NR, ENR20, ENR45, and ENR65. As ENRs have fewer amounts of double bonds compared with those of NR, there are less sulfur crosslinks and the vulcanization reaction reaches the optimum point faster.

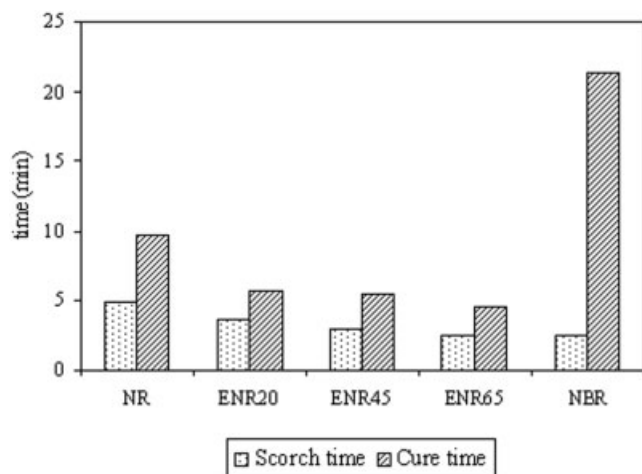


Figure 3 Scorch time and cure time of NR, ENRs, and NBR.

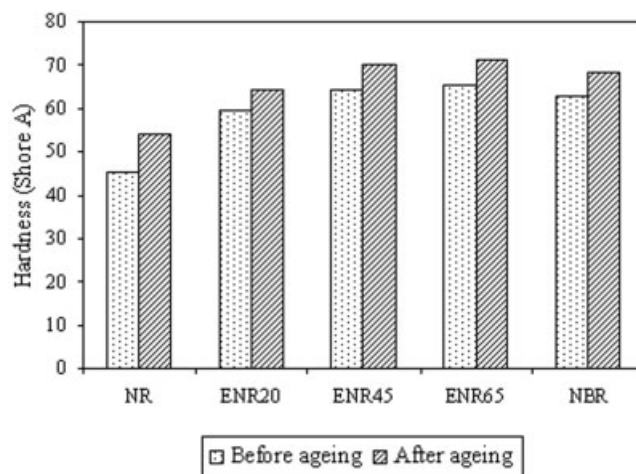


Figure 5 Hardness of NR, ENRs, and NBR before and after heat aging.

Natural rubber is known to have poor oil resistance. Epoxidation has brought about substantial improvement in oil resistance. Figure 4 shows the change in volume of ENRs and NBR after being immersed in ASTM oil No.1 and in IRM 903. There was no result for NR as it dissolves in this standard oil. ASTM oil No.1 is low polar hydrocarbon oil having high aniline point at 123.8°C. As the amount of epoxide groups in ENR increased, swelling degrees were decreased markedly indicating superior oil resistance. For ENR65, its oil resistance was found to approach that of NBR. As both ENRs and NBR are high polar rubber, in more polar hydrocarbon oil (IRM 903), which pos-

sesses lower aniline point at 89.5°C, ENRs and NBR were found to have larger change in volume than in ASTM oil No.1.

Hardness of cured NR, ENR20, ENR45, and ENR65 and NBR before and after heat aging is shown in Figure 5. It was evident that, before heat aging, ENRs were harder than NR but as hard as NBR. As the amount of epoxide groups increased, the chain was less flexible so that ENR65 was harder than ENR45, which was in turn harder than ENR20. After aging, hardness of all rubbers was increased due to embrittlement of the specimens upon exposure to aging, although the trends were the same as unaged rubbers.

Figure 6 shows tensile strength of rubbers before and after aging. For unaged rubbers, ENRs exhibited higher tensile strength than that of NR and NBR. Although, strain-induced crystallinity was observed in both ENRs and NR, epoxide groups contributed to

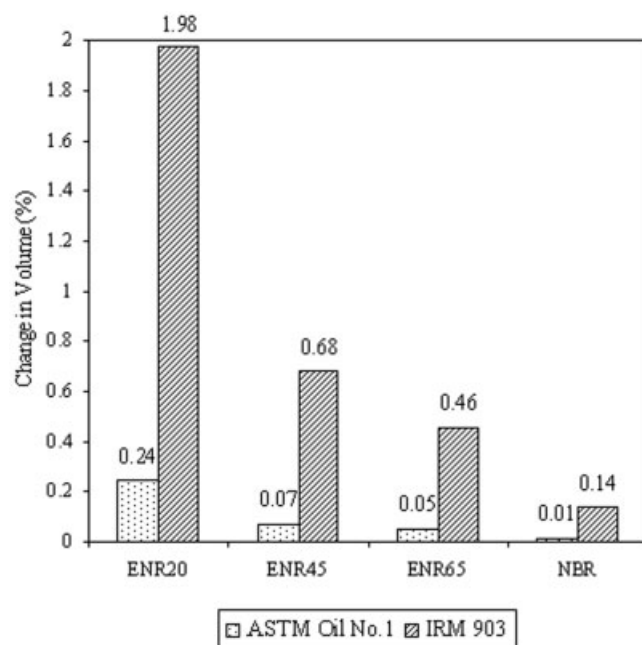


Figure 4 Change in volume of ENRs and NBR in ASTM Oil No.1 and IRM 903.

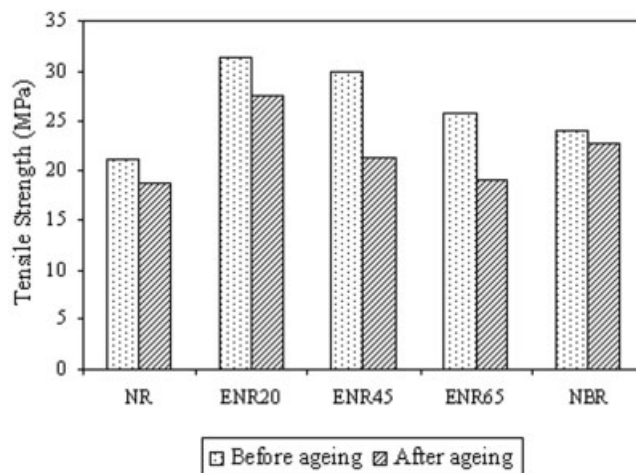


Figure 6 Tensile strength of NR, ENRs, and NBR before and after heat aging.

the chain rigidity resulting in higher tensile strength. The maximum tensile strength occurred at ENR20 after which, the tensile strength of ENRs dropped as the amount of epoxide increased. This was because ENR20 contains more double bonds than ENR45 and ENR65, hence, more crosslinks were obtained. In addition, strain-induced crystallinity was decreased when the amount of epoxide increased as suggested by Davies and Wolfe.⁹ Strain-induced crystallinity was not obtained in NBR. For the aged rubbers, a drop in the tensile property associated to the breakdown of the crosslinks, mainly the polysulfidic ones, during aging. This decrease in crosslinks would therefore cause the drop in tensile strength of aged rubbers. However, the results were in the same tendency as in unaged rubbers.⁵ The effects of aging are more significant in the case of ENR as compared with NR and NBR. This probably is due to the fact that double bonds in ENR molecular chains are activated by the neighbor epoxide groups.⁸ Elongation at break of ENRs, NR, and NBR before and after aging is shown in Figure 7. For the unaged samples, as NR chain is more flexible, it showed better elongation at break than did ENRs and NBR. Elongation at break of ENR20 was found to be higher than that of ENR45 and ENR65 as a consequence of higher crosslinking level in the molecular chains. As well as tensile strength, the aged rubbers expressed poorer elongation at break compare with that of unaged rubbers. Modulus at 300% elongation is shown in Figure 8. It was found that NR posses lower modulus than those of ENRs and NBR. The modulus was increased as the amount of epoxide groups increased due to higher crosslinking level in the molecular chains. After aging, the modulus of each specimen was decreased since crosslinks were decreased.

The higher the compression set percentage, the lower its resiliency. As shown in Figure 9, ENRs pos-

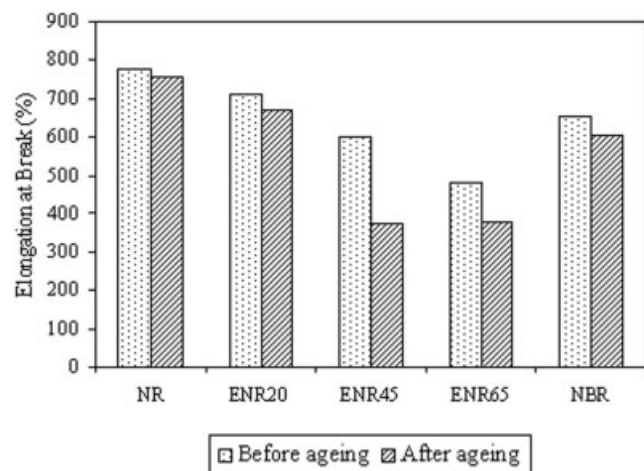


Figure 7 Elongation at break of NR, ENRs, and NBR before and after heat aging.

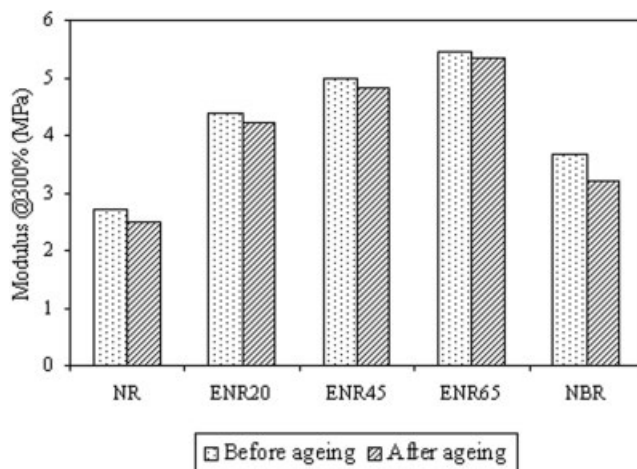


Figure 8 Modulus at 300% elongation of NR, ENRs, and NBR before and after heat aging.

sesses better resiliency than NR and NBR. As the amount of epoxide groups increased, the resiliency was decreased due to higher intramolecular interaction caused by epoxide groups.

CONCLUSIONS

Epoxidized natural rubbers were successfully synthesized via in situ epoxidation from high ammonia concentrated natural rubber latex with formic acid and hydrogen peroxide in the presence of a surfactant at 50°C for 4, 8, and 12 h. When the reaction time increased, the amount of epoxide groups was increased. The prepared ENRs were denoted as ENR20, ENR45, and ENR65 corresponding to ENR with 17.6, 43.8, and 63.9 mol % of epoxide groups, respectively. As the amount of epoxide increased, the glass transition temperature, hardness, and oil resistance were increased. However, scorch time, cure time, tensile strength,

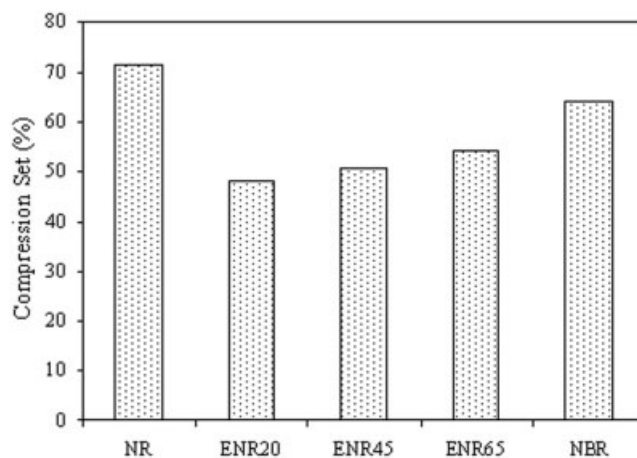


Figure 9 Compression set of NR, ENRs, and NBR.

elongation at break, and resiliency were decreased. After aging, all rubbers showed higher hardness and deteriorated tensile strength and elongation at break. Oil resistance of ENRs was significantly better than that of natural rubber, especially, oil resistance of ENR65, which was comparable to that of nitrile rubber.

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