

In Situ Epoxidized Natural Rubber: Improved Oil Resistance of Natural Rubber

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Received 1 October 2002; accepted 30 December 2002

ABSTRACT: This study sought to synthesize an *in situ* epoxidized natural rubber (NR) from 20% dry rubber content latex stabilized by nonionic surfactant, 5 phr of Terric 16A16, in the presence of hydrogen peroxide and formic acid at the temperature of 50°C. The molar ratios of H₂O₂ and HCOOH to isoprene unit were equal, 0.75 : 0.75. Reaction was carried out for 3 to 8 h. This reaction yielded products of various epoxide contents depending on reaction time. Based on DSC characterization, epoxide contents of the *in situ* epoxidized natural rubbers (ENRs) were about 22–39 mol %. Tensile properties and tear resistance of the *in situ* ENRs were equal to, or better than, those of NR and commercial ENRs. The *in situ* epoxidation improved resistance to petroleum ether, but not to toluene. Changes in volume

and weight of specimens immersed in ASTM no. 3 oil and automobile oils (various trade names: Shell engine oil, Shell gear oil, and Toyota motor oil) exhibited significant decrease after epoxidation, except in Shell brake fluid. Similar results were obtained from tensile testing of the oil-immersed specimens. Tensile strength and elongation at break of the *in situ* ENRs were much higher than those of NR after immersion in those oils at room temperature for 7 days, except the immersion in brake fluid. Improved oil resistance of the *in situ* ENRs under severe condition was obtained in gear oil. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 261–269, 2003

Key words: rubber; elastomers; mechanical properties; resists; DSC

INTRODUCTION

Natural rubber (NR) was first reacted with peroxy-carboxylic acid in 1922 followed by attempts to improve the epoxidation method by use of a variety of reagents.^{1–3} In spite of their apparent promise, these reactions often led to materials containing products of subsequent ring-opening reactions and thus proved of little interest. Until the 1980s, epoxidation processes by use of peracetic acid and performic acid were established, and thus the ring-opening reaction could be avoided in all cases. Gelling and colleagues^{4,5} established that the acid concentration and temperature of epoxidation reaction controlled the extent of the secondary ring opening, and this in turn substantially affected the properties of the materials obtained. Peracetic acid was prepared before being added to the latex. The *in situ* epoxidation of NR latex using hydrogen peroxide and formic acid also yields epoxidized natural rubber (ENR), a method that was first copyrighted in 1982 (British Patent 2113692).² After these effective methods, ENR has turned out to be an attrac-

tive material once again. Since 1988 commercial ENRs have been produced in Malaysia: the products include 25 and 50 mol % epoxidized NR, referred to as ENR25 and ENR50, respectively.

In theory, any level of epoxidation can be achieved, but it is thought that only up to 50 mol % would be used in practice. The most interesting effects of epoxidation on NR lie in the physical properties of vulcanizates. As the level of epoxidation is increased, the glass-transition temperature (T_g) is raised by approximately 0.92°C/mol % epoxidation,³ attributed to decreases in room-temperature resilience and in low-temperature crystallization. ENR also shows an inherent reinforcement with silica (without coupling agents). The epoxidation process reduces gas permeability. Furthermore, the epoxidation process improves the oil and solvent resistance of NR. Some oil resistance is exhibited in ENR25, which would make it suitable for certain applications where components are only splashed with oil in service. The change in molecular structure brought about by the epoxidation of NR opens up a range of new uses. Compared to common tread rubbers, ENR exhibits both high wet grip and low rolling resistance properties and in these respects is an attractive tread compound. The low air permeability properties of ENR50 suggest application in tire inner liners and inner tubes. The combination of high strength and oil resistance properties of ENR are

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Contract grant sponsor: Prince of Songkla University, Hatyai Campus.

being evaluated in such applications as oil-resistant cut thread, oil suction hose, seals, and oil-well pipe protectors. The high wet grip properties are being investigated to produce nonslip flooring materials and sports shoe soling compounds. Blends of ENR/poly(vinyl chloride) (PVC) and ENR/NR are also being developed. The high fatigue lives of ENR compounds have been found to be attractive in an oil-resistant flexible conveyor and in combination with higher damping properties in vibration-isolation mounts. Its potential in applications in the field of adhesives appears to be promising.

As described earlier, there are two effective methods for epoxidation: (1) by adding peracetic acid into latex and (2) by forming the *in situ* performic acid. The latter provides a product free from secondary ring-opened structure.² Several researchers synthesized ENR by using this method^{6–13}; all employed 20% dry rubber content (drc) latex and 3–5 phr of nonionic surfactant. Reaction temperature used was room temperature or at 50°C. Major differences between these methods are type of nonionic surfactant, concentration of formic acid and hydrogen peroxide, and reaction time, which varied from a few hours to several days. None of them reported about oil resistance of ENR, although Bac et al.⁸ reported the solvent resistance. Swelling behavior in solvents of compounded ENR was previously reported.^{14–18} There are a few studies that have reported oil resistance of commercial ENR.^{4,5,19,20} The polarity of ENR increases with the level of epoxidation and hence the pattern of oil/solvent resistance changes. The general conclusion may be drawn that epoxidation of NR improves the oil resistance of NR.

The present work aims to synthesize ENR by our own method and systematically study the oil/solvent resistance and physical/mechanical properties of the synthesized ENR, compared to commercial ENR and NR. The present method differs from previous methods^{6–13} as follows: (1) latex was not neutralized to adjust pH, (2) reaction temperature was increased to 50°C just before adding hydrogen peroxide, and (3) the mole ratio of formic acid to hydrogen peroxide was 0.75 : 0.75. This novel epoxidation process yields ENR in which the properties are comparable to those of commercial ENR. In this investigation we present the results of our studies on the unfilled vulcanized system. A comparison of the properties of ENR with those of NR is reported.

EXPERIMENTAL

Materials

A commercial-grade, high-ammonia concentrated latex (60% drc) was used. Formic acid (99%) and hydrogen peroxide (30% w/w) used were commercial

grade. A nonionic surfactant, Terric 16A-16, was used as received. All other reagents, solvents, and compounding chemicals used were of reagent grade and used as received. Epoxyrene™ 25 and Epoxyrene™ 50 (Kumpulan Guthrie Berhad, Malaysia), referred to as ENR25 and ENR50, respectively, were used as reference rubbers. Natural rubber sheet obtained by coagulation of high-ammonia graded concentrated latex was used as a control rubber for characterization and swelling behavior of raw rubber. The STR5L-graded Standard Thai Natural Rubber was compounded and tested for mechanical properties for comparison with ENR.

In situ epoxidation of NR latex

The latex was diluted to 20% by adding distilled water and stabilized with 5 phr Terric 16A-16 under continuous stirring. After heating the latex to 40°C, the required amount of formic acid (0.75M of isoprene unit) was added dropwise. Upon increasing the temperature to 50°C, the necessary amount of H₂O₂ (0.75M of isoprene unit) was slowly dropped for about 20–30 min. The reaction temperature was maintained at 50°C throughout the reaction period (3–8 h.). The ENR sample was coagulated with methanol and washed with water and 5% sodium carbonate solution, and water again. The samples were dried at 60°C to a constant weight. ENR samples were called H3, H4, H5, . . . , H8, based on reaction time.

Characterization

Transition temperature of ENR samples was determined by differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA). DSC characterization was recorded at the first heating scan under a heating rate of 10°C/min and in the range of –100 to +40°C. T_g values were determined as onset values of the transition temperature. DMTA was executed as the following condition: 0.1% strain, 20°C/min, and 1 Hz. The degradation temperature was observed by use of thermogravimetric analysis (TGA) under a heating rate of 20°C/min in nitrogen atmosphere.

Compounding

Rubber compounding was performed in a Yasuda Seiki™ 191TM two-roll mill. The chemicals added are listed in Table I. The formulation of each compounded rubber was derived after preliminary tests among various selected recipes to obtain the maximum tensile strength. The objective of this work was to obtain the optimum properties; thus it was not necessary to use the same recipe. The antioxidant and the accelerator employed were Vulkanox™ PAN and Vulkacit™ CZ,

TABLE I
Formulation of Rubber Compounds (in phr units)

Chemical	NR	ENR25	ENR50	H3-H8
Rubber	100	100	100	100
Calcium Stearate	—	3	3	3
ZnO	5	5	5	5
Stearic acid	2	2	2	2
Vulkanox™ PAN	1	1	1	1
Vulkacit™ CZ	1.5	1.5	0.6	1.5
Sulfur	1.5	1.5	2.5	1.5
Struktol™	—	—	1.5	—

respectively. Struktol™ is a processing aid. The setting temperatures of the two-roll mill were about 75 and 65°C for the front and back rolls, respectively. The front-to-back roll speed ratio was 1:1.23. Compounded rubbers were left overnight at ambient temperature in a desiccator before compression molding. Compression-molded sheets were prepared at 150°C under a pressure of 600 kg/cm². Vulcanization time of each compound was determined by using a Moving Die Rheometer (MDR2000).

Testing: mechanical properties and oil resistance

The testing methods are tabulated in Table II. Testing of tensile properties and tear resistance was conducted at a speed of 500 mm/min. Abrasion resistance was determined from a relative lost weight, calculated by the following relationship:

$$\text{Relative lost weight (\%)} = \frac{W_{500 \text{ cycles}} - W_{4000 \text{ cycles}}}{W_{500 \text{ cycles}}} \times 100$$

where $W_{500 \text{ cycles}}$ and $W_{4000 \text{ cycles}}$ are sample weights after testing for 500 cycles and 4000 cycles, respectively.

Thermal aging resistance was tested at 70°C for 7 days. The aging resistance is expressed as a percentage of the change in tensile properties calculated as follows:

$$P = [(A - O)/O] \times 100$$

TABLE III
Designation of Solvents and Oils Used in Testing

No.	Liquid
L1	Toluene
L2	Petroleum ether
L3	Dimethylformamide
O1	Shell™ brake fluid (SAE J 1703 and Dot 3)
O2	Shell™ engine oil (SAE 15W-40)
O3	Shell™ Helix Plus gear oil (15W-50)
O4	IRM 903™ oil (ASTM oil no. 3)
O5	Toyota™ motor oil (20 W-50SJ)

where P is the percentage change in the property, O is the original value, and A is the value after aging. Increases are indicated as positive and decreases as negative.

Oil and solvent resistance was carried out in the form of uncompounded and compounded rubbers. The oils and solvents used are tabulated in Table III. Dumbbell-shaped specimens prepared as ASTM D412 die C and 1-cm-diameter round-shape specimens cut from the molded sheet were used for testing of oil resistance and swelling behavior. The specimens were immersed in oils and solvents for 7 days at room temperature (~ 27–30°C) and 70°C. Oil resistance was reported in terms of tensile properties after immersion, and swelling behavior was reported in terms of changes in volume and weight after immersion. Swelling behavior of green rubbers was reported as the changes in weight after immersion.

RESULTS AND DISCUSSION

Characteristics of *in situ* epoxidized natural rubber

Glass-transition temperatures of ENR samples obtained from DSC are shown in Figure 1 and are tabulated in Table IV (T_g^*/DSC). The T_g of H3-H8 decreased between -50 and -34°C, some were very close to the T_g of ENR25, and all were lower than that of ENR50. This indicates that we could produce 25 mol % ENR within 3–4 h and the maximum epoxide content we obtained is lower than 50 mol %. As previously reported¹⁻³ the T_g of ENR varies linearly with

TABLE II
Standard Test Methods

Property	Standard method	Equipment
Tensile properties	ASTM D412 die C	LLOYD™ 1000S
Tear resistance	ASTM D624 die C	LLOYD™ 1000S
Aging resistance	ASTM D573	Tabai™ gphh-200 gear oven and LLOYD™ 1000S
Hardness Shore A	ASTM D2240	Zwick™ OSK 10162
Resilience	ASTM D2632	Resiliometer (vertical rebound)
Abrasion resistance	ASTM D3389	Akron Abrader
Swelling behavior	ASTM D417	—
Oil resistance	ASTM D417	LLOYD™ 1000S

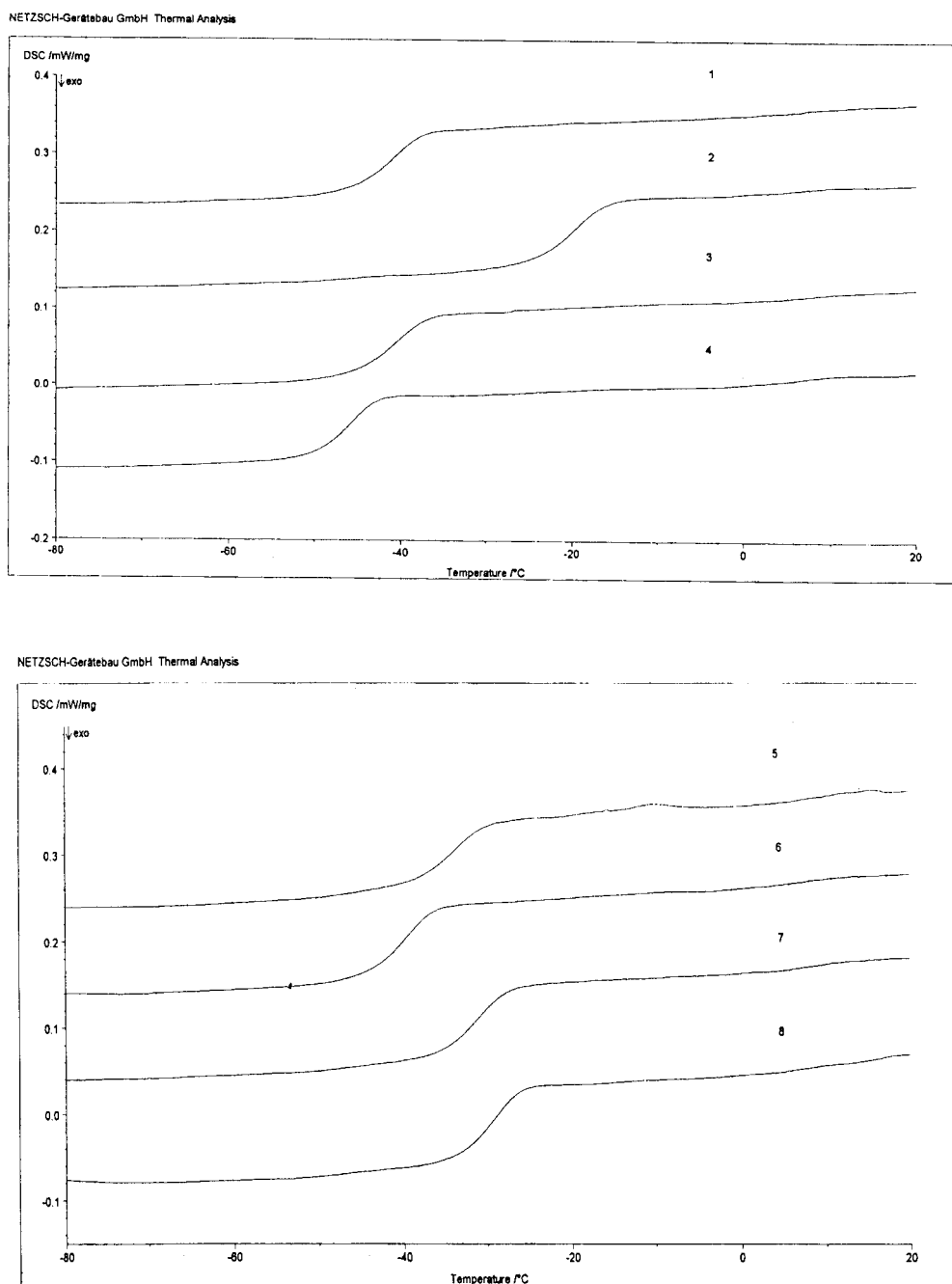


Figure 1 DSC thermograms of commercial and synthesized ENR's: (1) ENR 25; (2) ENR 50; (3) H3; (4) H4; (5) H5; (6) H6; (7) H7; (8) H8.

molar epoxide content and the T_g value increases by $0.92^\circ\text{C}/\text{mol}\%$ ³; thus we could calculate epoxide content of ENR samples. Given that the T_g of NR is -70°C , the epoxidation level of H3–H8 lies between 22 and 39 mol % (Table IV). It appears that T_g and epoxide content of the present study seemed to be higher as the reaction time increased (i.e., H3 versus H8), although the data did not show linear changes with reaction time. This may be the result of an experimental error. Nevertheless, the results showed the trend in the right direction, as we expected. The width of the T_g

also supplies information.³ Normally it is somewhat 10°C wide, but if there is inhomogeneity in the epoxidation, resulting in different polymer chains being modified to different extents, this will show as a broadening of the T_g . ENR samples produced in the present study showed homogeneity in the epoxidation, indicated by a narrow width ($<10^\circ\text{C}$) of the T_g , as shown in Figure 1. This agrees with another result based on the $^1\text{H-NMR}$ spectra that showed no peak between 3 and 4 ppm, which is the evidence of a ring-opened structure.

TABLE IV
Glass-Transition Temperature Investigated by Using DSC and DMTA and Thermal-Degradation Temperature Investigated by Using TGA

Rubber	T_g^*/DSC (°C)	T_g/DMTA (°C)	$T_{\text{deg}}/\text{TGA}$ (°C)	Epoxide content (mol%) ^a
NR	-70.0	n/a	368	0
ENR25	-45.6	-40.6	402	26.5
ENR50	-25.2	-16.1	397	48.7
H3	-45.5	-41.0	396	26.6
H4	-49.8	-44.7	396	22.0
H5	-39.4	-30.2	390	33.3
H6	-44.4	-36.8	398	27.8
H7	-36.3	-26.6	399	36.6
H8	-34.3	-23.2	389	38.8

$$^a \text{Epoxide content (mol \%)} = \frac{T_g^* \text{ of ENR} + 70}{0.92} \text{ (Ref. 3).}$$

We also confirmed the success in epoxidation with the DMTA experiment for the vulcanized ENR samples. Data obtained from DMTA coincide with those obtained from DSC, demonstrated in Table IV. Transition temperature (T_g/DMTA) of H3, H4, and H6 samples was in the range of the value of ENR25. Obviously, the DSC experiment yielded a lower transition temperature than that of the DMTA experiment. Undoubtedly, vulcanizates used in the DMTA experiment were supposed to show higher transition temperature than that of raw ENR samples used in the DSC experiment. Raw ENR samples also exhibited a higher thermal-degradation temperature than that of NR, about 21–31°C, illustrated in Table IV ($T_{\text{deg}}/\text{TGA}$). This was attributed to the presence of the epoxy group in the rubber molecules. Thermal stability of H3, H4, H6, and H8 was close to that of ENR25 and ENR50.

We established that the present epoxidation process is satisfactory, and it appears that the level of epoxidation was below 50 mol %. Thus we focused on the samples containing 25 mol %. For this reason, H4 and H6 were selected to compare with ENR25. Based on DSC results, the epoxide content in H4 and H6 is about 22 and 28 mol %, respectively. Results of ¹H-NMR analysis showed that H4 and H6 consisted of 23 and 31 mol %, respectively. Although H8 showed the highest epoxide content, it is not a promising sample because of an overly long reaction time (8 h).

Mechanical properties

We did preliminary experiments to select the optimum recipe for rubber compounding, and the selected recipe for each rubber compound is shown in Table I. Based on our study, a semi-EV system was selected for all rubber samples except ENR50, given that the conventional high-sulfur cure system offered better tensile properties in ENR50. Although we applied the

different formulations for NR and ENR50, it was reasonable to make comparisons for all compounded rubbers because every formula listed in Table I showed the best tensile properties in this work. In practice, different rubbers may be compounded with different formulas. Figure 2 represents tensile properties of NR, H4, H6, and commercial ENRs. Modulus at 300% strain of all samples was in the same range (1.5–1.7 MPa), except ENR50, which showed higher modulus (2.4 MPa). Tensile strength values of H4 (26 MPa) and H6 (25 MPa) were very close to that of NR (26 MPa), whereas ENR25 and ENR50 showed slightly lower strength, 22 and 23 MPa, respectively. Elongation at break of H4 and H6 was higher than that of NR and commercial ENRs. As we know, ENR is able to perform strain-induced crystallization as NR; thus high tensile strength should be observed in ENR. A comparison of our results to those of Poh and Khok²¹ showed that the tensile strength of the commercial ENRs, ENR25 and ENR50, in the present study harmonized with their results, and were in the same range. The tensile strength of NR and the *in situ* ENR (H4 and H6) in the present study were slightly higher than that of ENR25 and ENR50 reported by Poh and Khok.²¹ The elongation at break of the present rubbers was much higher than that of ENR25 and ENR50 reported by Poh and Khok.²¹ It should be noted that they used the conventional cure system and that recipe was the same as the one we used in ENR50, whereas the rest of our rubbers were compounded under a semi-EV system. Conclusively, the *in situ* ENR

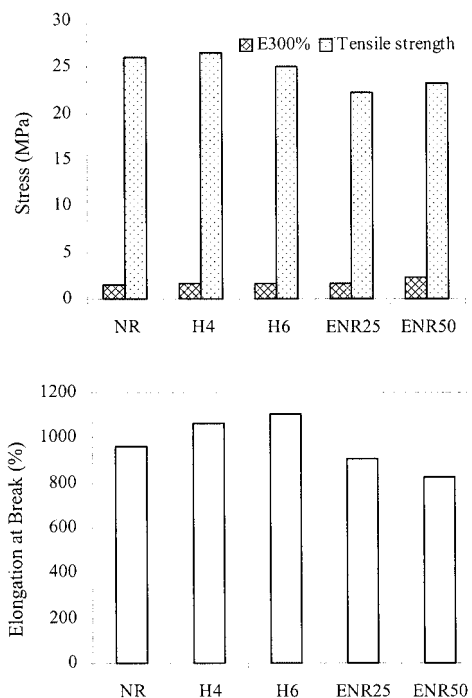


Figure 2 Tensile properties of NR and ENR: (a) modulus at 300% and tensile strength; (b) elongation at break.

TABLE V
Tear Resistance, Hardness, Abrasion, and Resilience of Rubbers

Rubber	Tear resistance (kN/m)	Hardness (Shore A)	Abrasion resistance (%) ^a	Resilience (%)
NR	34	36	3.73	55
H4	32	41	2.25	38
H6	32	38	2.4	32
ENR25	29	n/a	n/a	n/a
ENR50	41	n/a	n/a	n/a

$$^a \text{Relative lost weight (\%)} = \frac{W_{500 \text{ cycles}} - W_{4000 \text{ cycles}}}{W_{500 \text{ cycles}}} \times 100.$$

of the present study showed similar tensile properties to those of commercial ENR, and the tensile properties of the *in situ* ENR fell in the same range as those of NR.

Tear resistance of the *in situ* ENR was similar to that of NR, whereas hardness and abrasion resistance of the *in situ* ENR were slightly higher (Table V). Epoxidation in the present study had no significant effect on tear resistance, hardness, or abrasion resistance. As expected, resilience of the *in situ* ENR was lower than that of NR because the resilience of ENR decreases with the extent of epoxidation in line with the changes in T_g .³

In general, for rubbers that react with oxygen resulting in crosslinking, the accelerated tests would result in increases in tensile stress at a given elongation and decreases in ultimate elongation. For rubbers that react with oxygen resulting in chain scission, the accelerated aging tests would result in decreases in tensile stress at a given elongation and either increases or decreases in ultimate elongation, depending on the extent of degradation. The decrease in tensile strength after aging is attributed to the breakdown of crosslinks, mainly the polysulfidic ones.²¹ The decrease in crosslinks would therefore cause the decline in tensile strength of the present system after aging at 70°C for 7 days (Fig. 3). The best system would be the one that gave the lowest change in properties in the accelerated aging tests. The 25 mol % epoxidation (ENR25 and H4) decreased aging resistance of NR, as shown in Figure 3. Higher epoxide content such as H6 and ENR50 seemed to be better, showing behavior similar to that of NR. It should be noted that all samples in the aging test had no antioxidant. The present method could synthesize ENR (H6), which yields aging resistance similar to that of NR. As stated earlier, the negative value of these changes depicts the presence on thermal degradation in all rubber samples. The mechanisms of degradation are beyond the scope of the present study. The results of the present study agree with the results of Poh and Khok,²¹ that is, percentage changes in tensile properties were less than 20%.

Regarding the results of the above properties, the *in situ* ENR (H4 and H6) is better than, or at least is comparable to, NR and commercial ENR. This also indicates that we obtained the suitable compounding formulation in the present study. Furthermore, the compounding method of the *in situ* ENR was as easy as the compounding method of NR, in that no processing aids were necessary. It becomes clear that the *in situ* ENR shows promise as a new rubber material. However, preparation of the *in situ* ENR is costlier than producing NR. Therefore it is essential to test the swelling behavior and oil resistance of the *in situ* ENR, based on the fact that ENR exhibits better oil resistance than NR.

Swelling behavior and oil resistance of raw rubbers

Uncompounded rubbers were weighed and immersed in oils and solvents at room temperature for 7 days. We selected some common solvents and oils for this testing, as listed in Table III. Toluene is a good solvent for NR, whereas petroleum ether and dimethylformamide have different polarity, the latter of which has greater polarity. Oils used in this testing included automobile-grade oil and ASTM no. 3 oil (IRM903). The swelling characteristic was determined as a change in weight calculated as follows:

$$\text{Change in weight (\%)} = \frac{W_t - W_o}{W_o} \times 100$$

where W_t is the weight after immersion and W_o is the original weight.

Because the samples dissolved and fragmented into many pieces in L1, L2, and L3, after immersion these samples were dried in a vacuum oven at 80°C until the weight was constant, about 15 h. On the other hand, the samples immersed in oils (O1 and O2) were not dried like the previous samples because they only swelled; the test pieces were removed from the oils and wiped with tissue paper to remove excess oil from

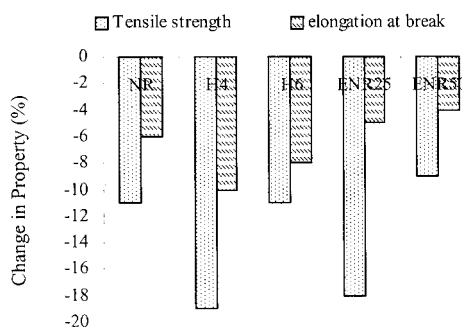


Figure 3 Changes in tensile strength and elongation at break (%) of rubber samples after aging in the Gear oven at 70°C for 7 days.

TABLE VI
Changes in Weight (%) of Uncompounded Rubbers After Immersion at Room Temperature for 7 Days

Rubber	L1	L2	L3	O1	O2
NR	-55	-32	-2	6	225 ^a
ENR25	-90	-1	-4	35	29
ENR50	-90	-4	-3	63	4
H3	-50	-2	-4	28	35
H4	-95	-6	-3	23	28
H5	— ^b	-2	-3	37	15
H6	-43	-1	-2	37	14
H7	-47	-1	-3	51	14
H8	-41	-1	-4	46	9

^a Jelly surface after immersion.

^b Dissolved rubber was very sticky, attached to the container.

the surface. Table VI presents changes in the weight of rubber samples. Negative values obtained from L1–L3 indicate the presence of dissolution of samples, whereas positive values indicate a swelling characteristic. All the uncompounded rubbers dissolved in all solvents. H5 in toluene (L1) was well dissolved, such that small pieces adhered to the wall of the container. The NR sample immersed in motor oil (O2) showed a jellylike surface after immersion. It seems that all samples dissolved well in toluene (L1). We believe that there is no significant difference among percentage changes of all samples in L1. The higher number in ENR25, ENR50, and H4 may be attributable to an error in the experiment. Because much fragmentation of test specimens appeared in these samples, it is plausible to lose some test pieces as they were removed from toluene. An increase in swelling resistance after epoxidation appeared in petroleum ether (L2), and the degree of epoxidation showed no significant effect on swelling behavior. All samples exhibited similar behavior in dimethylformamide (L3). These results indicate that epoxidation increases the resistance only in petroleum ether and shows no resistance in toluene and DMF.

Undoubtedly, the brake fluid (O1) that has greater polarity than that of the engine oil (O2) could swell ENR more than NR: the higher the epoxide content, the less swelling resistance in O1. Crucial resistance in engine oil (O2) was derived from the epoxidation process, and the higher epoxide content showed higher oil resistance. Regarding O2, all synthesized ENRs were transformed into improved oil-resistant rubbers, compared to NR. Keep in mind, though, that these data were obtained from raw rubber. In the end-use applications, rubber vulcanizates are employed. Consequently, the swelling behavior and oil resistance of compounded samples must be investigated.

TABLE VII
Changes in Volume (%) of Compounded Rubbers After Immersion at Room Temperature for 7 Days

Rubber	L1	L2	L3	O1	O2	O3	O4	O5
NR	415	164	5	5	116	80	259	129
ENR25	419	52	44	20	18	n/a	n/a	n/a
ENR50	282	64	63	25	9	n/a	n/a	n/a
H4	417	82	33	25	21	39	114	40
H6	335	26	97	64	3	22	82	33

Swelling behavior and oil resistance of vulcanizates

Changes in volume and weight of vulcanizates after immersion in solvents and oils at room temperature for 7 days are shown in Table VII and Figure 4, respectively. As expected, epoxidation of NR should increase resistance in certain solvents and oils. ENR showed much less swelling than NR in petroleum ether (L2), engine oil (O2), gear oil (O3), ASTM oil (O4), and motor oil (O5). The degree of epoxidation must be high enough to decrease swelling in toluene (L1). It is established²⁰ that 50 mol % epoxidation could lead to oil resistance equal to that of NBR. ENR was inferior to NR in DMF (L3) and brake fluid (O1). Our results coincided with data reported by Gelling,⁴ although more severe testing conditions were used. The vulcanizates were immersed in oils at 70°C for 7 days. Changes in volume and weight are displayed in Figure 5. Epoxidation improves oil resistance in all oils, except in brake fluid. So far, it has been shown that the *in situ* epoxidation of NR improves resistance to hydrocarbon oils, whereas the reverse is true for more polar liquids such as brake fluid (O1).

Tensile properties of the vulcanizates after immersion in oils are shown in Figure 6. Although ENR swelled more than did NR in brake fluid (O1), its degree of swelling was not so high. Therefore, the influence of O1 on tensile strength and elongation at break of NR and ENRs does not generate a significant difference. On the other hand, less swelling of ENR in O2–O5 was attributed to the higher tensile properties

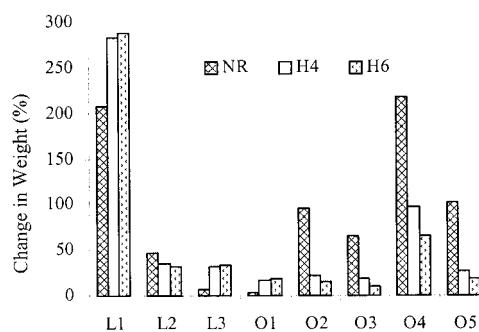


Figure 4 Changes in weight (%) of compounded rubbers after immersion in solvents/oils at room temperature for 7 days.

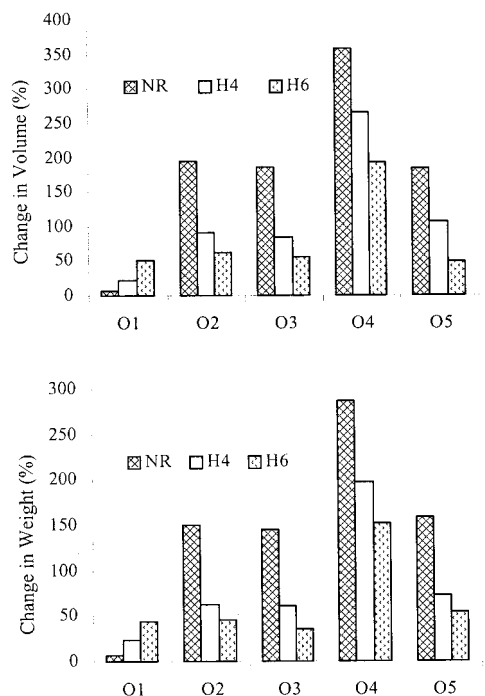


Figure 5 Changes in property (%) of compounded rubbers after immersion in oils at 70°C temperature for 7 days: (a) changes in volume; (b) changes in weight.

representing higher oil resistance. Increase in oil resistance of the *in situ* ENR is outstanding when using engine oil (O2) and motor oil (O5). H4 seems to be better than H6 because it showed tensile properties

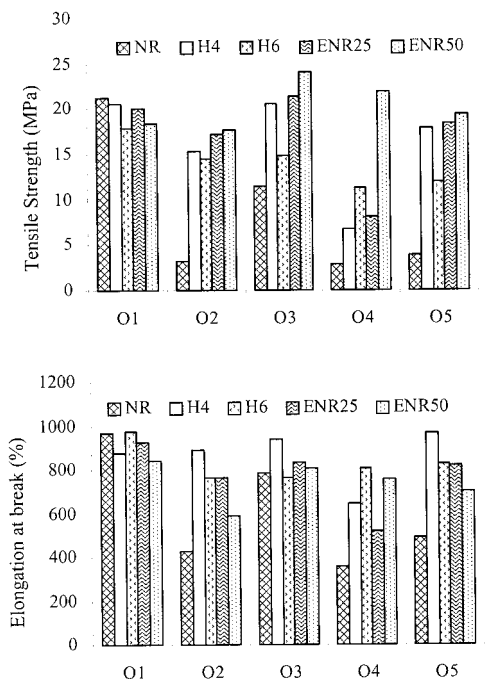


Figure 6 Tensile properties of compounded rubbers after immersion in oils at room temperature for 7 days: (a) tensile strength; (b) elongation at break.

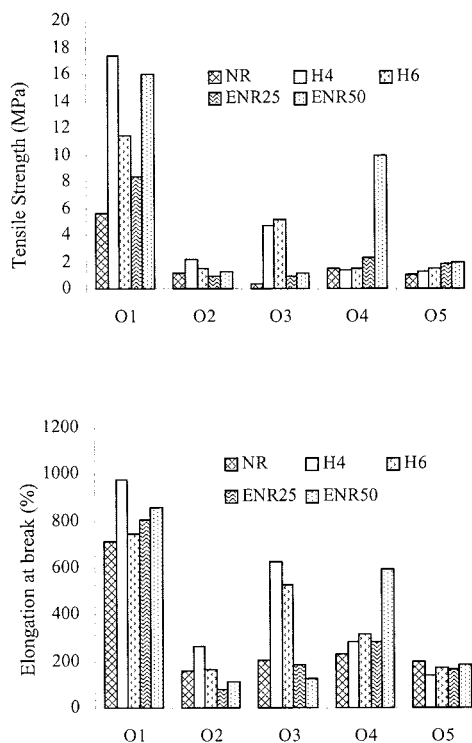


Figure 7 Tensile properties of compounded rubbers after immersion in oils at 70° for 7 days: (a) tensile strength; (b) elongation at break.

similar to those of the commercial ENR. Only ENR50 exhibited high tensile strength and elongation at break after all oils and particularly after ASTM oil (O4). Testing at elevated temperature was performed. Surprisingly, H4 and ENR50 showed high tensile strength in O1, whereas the rest became low, and NR showed the lowest strength (Fig. 7). This condition is so severe that all samples were transformed into weak rubbers, except in O1. Although it appears that H4 and H6 seem to be satisfactory in O3 and ENR50 seems to be satisfactory in O4, their tensile strength was too low (<10 MPa). However, based on the normal condition as shown in Figure 6, it suggests that the H4 and H6 showed improved oil resistance as we assumed.

CONCLUSIONS

1. The *in situ* epoxidation of 20% drc latex was well synthesized to obtain 25 mol % epoxide content within 3–4 h. Neutralization of latex with an acid is not essential.
2. The *in situ* ENR shows tensile properties as good as those of NR and commercial ENR, but shows better abrasion resistance than that of NR. No notable differences in tear resistance and hardness were observed. ENR with 25 mol % epoxide content showed lower aging resistance than that of NR.

- Oil resistance of natural rubber is greatly increased in certain automobile oils by the present method of *in situ* epoxidation.

Although ENR is processed as commercial rubber only in Malaysia, its properties are very interesting. It is an intermediate material for value-added natural rubber. Therefore, future work will focus on preparing the *in situ* ENR by using higher dry rubber content, doing more testing with other oils, and modifying it to be a flame-retardant rubber.

The authors thank Sumalee Suwan, Peerapong Songnui, Pennapa Na-Phatthalung, Phuwanart Premkaew, Nakarin Satajkul, and Weerasak Liangrattanakul for necessary help. This project was supported by a grant from Prince of Songkla University, Hatyai Campus.

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