Mechanical and Aging Properties of Hydrogenated Epoxidized Natural Rubber and Its Lifetime Prediction

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ABSTRACT: Natural rubber (NR) has restricted its application due to its potential for thermal- and oil-resistant materials. The weakness of NR can be eliminated by chemical modification to enhance aging properties. Formic acid and hydrogen peroxide have been used to prepare partially epoxidized natural rubber (ENR) in the latex state. Its residual unsaturated units were then modified using hydrazine and hydrogen peroxide to obtain hydrogenated ENR (HENR). ^{1}H-NMR characterized the resulting products. NR and modified NRs were compounded and then vulcanized using a conventional milling process. This paper compares NR, ENR having 49.5% epoxide group content, and HENR having 49.5% epoxide group content and 24% hydrogenation degree in terms of tensile, thermal, oil, and ozone properties. Morphology and lifetime

prediction were studied. Overall results show that the tensile strength of the HENR composite (14.7 MPa) was 79 and 71% lower than that of ENR (18.6 MPa) and NR (20.8 MPa) composites, respectively. In contrast, the modulus at 100% elongation of the HENR composite (2.0 MPa) was 167 and 200% higher than that of ENR (1.2 MPa) and NR (1.0 MPa) composites, respectively. Morphological studies of the tensile fractured surface of the vulcanizates, using scanning electron microscopy, confirmed a shift from ductility failure to brittle with the presence of the epoxide groups and low unsaturated bonds in the backbone chain. The results demonstrated that HENR could act as an ideal material, providing better thermal, oil, and ozone resistances while maintaining the mechanical properties of the rubber. The kinetic analyses of the thermal degradation of NR, ENR, and HENR were studied using thermogravimetric analysis (TGA) at three heating rates. Kissinger−Akahira−Sunose (KAS) was employed to calculate the activation energy (E_a). The obtained data were used to predict the lifetime under the established temperature range and 0.05 conversion level. Overall, the results represented that HENR had a longer lifetime than NR and ENR for a temperature range between 25 and 200 °C, indicating that HENR had excellent thermal stability than NR and ENR. Therefore, the HENR should extend the applications to include gaskets and seals, especially for the automotive and oil industries.
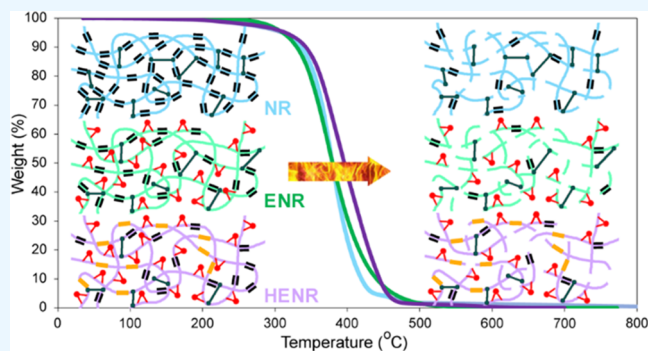
1. INTRODUCTION

Natural rubber (NR), obtained from *Hevea brasiliensis*, consists mainly of a *cis*-1,4-polyisoprene structure that is sticky, soft when warm, and brittle when cold. Unvulcanized rubber has poor mechanical properties and is not very durable. It cannot be used to make products with a good elasticity level. Vulcanization is a chemical process for converting rubber into more durable materials by compounding them with sulfur and curatives with accelerators. Cross-linked NR generally consists of linkages brought about by sulfur-based chemical reactions between sulfur and rubber occurring mainly at the carbon−carbon double bonds (C=Cs).[1] It is renowned for high reversible deformability, excellent tensile strength, and elongation properties due to its ability to crystallize under stretching. Besides all of these good properties, the properties of NR can be greatly affected when exposed to light, heat, oxygen, ozone, and weather due to unsaturated double bonds of NR, which are easily oxidized, leading to poor thermal

stability and resistance to oils and solvents.[2−6] Its service temperature is also limited to about 90 °C.[7] To overcome these limitations and widen the application of natural rubber, the change in the molecular structure brought about by the chemical modification of NR opens up a range of new applications. Modifying the double bonds in NR by epoxidation was originally considered to increase the resistance toward oils and hydrocarbon solvents. Epoxidized natural rubber (ENR) is a chemically modified NR that converts part of the double bonds in NR to epoxide groups using an organic

peracid in latex form and/or a solution stage epoxidation.[8,9] ENR has some new properties when compared with NR, such as lower gas permeability, better oil resistance, and higher polarity[10] while retaining the high strength of NR because of its ability to strain to crystallize upon stretching.[11] Many works have focused on the application of ENR. The oil and hydrocarbon solvent resistances of ENR were significantly better than those of NR.[12−15] However, many works have focused on the thermal degradation of ENR.[16−18] They pointed out that thermal oxidation occurs not only in the double bond region but also involves an epoxide ring-opening reaction to yield oxidative products. Hydrogenation is one of the most efficient methods used to reduce the degree of unsaturation in the polymer chains by adding hydrogen atoms to the unsaturated units, thus enhancing the thermal stability of the polymer. It ultimately governs the mechanical properties, durability, spectral stability, shelf lives, and life cycles of polymers. Many investigations prepared the hydrogenation of different materials such as ENR,[19,20] liquid epoxidized natural rubber,[21] NR,[22] and liquid natural rubber.[23] They reported that the thermal stability of hydrogenated products was improved by a decomposition temperature shift to a higher temperature than the original polymer. Decreasing the double bond decreased the weak point to be attacked by oxygen, which caused a thermooxidative reaction. The preparation of modified NR by both epoxidation and hydrogenation reactions is expected to yield a product with good oil resistance, improved thermal stability, and ozone resistance due to the presence of the epoxide groups and reduction in the unsaturation level. These properties provide more application for the hydrogenation of ENR in the automotive and oil industries. There are many reports of the thermal decomposition behavior of polymeric materials such as nitrile butadiene rubber,[24] LDPE containing cobalt stearate in the concentration range (0.05−0.2% w/w),[25] and poly(ether imide)/carbon fiber composites[26] using thermogravimetric analysis (TGA). The kinetic parameters of degradation were evaluated using model-free kinetic methods. The activation energy has been calculated to predict the thermal life of materials. In many polymer applications, predicting product lifetime is valuable because the costs of premature failure in actual end use can be high. TGA provides a method for accelerating the lifetime testing of polymers so that short term experiments can be used to predict in-use lifetime. Many works have focused on modified NR preparation, mechanical properties, and resistance to oil and heat. However, a detailed study of NR and modified NR undergoing estimation of their lifetime is lacking. The obtained modified NR was compounded and processed into test specimens. Subsequently, the mechanical properties; morphological study; thermal, hydrocarbon oil, and ozone resistances of the prepared ENR and HENR composites were compared with those of the NR composite and investigated to confirm the improvement of NR drawbacks. In addition, the application of TGA with multiple heating rates to evaluate thermal degradation kinetics and estimate lifetime was also studied.

2. EXPERIMENTAL SECTION

2.1. Preparation of Modified NR. The modified NR samples were prepared as described previously by Ngudsuntear et al.[27] Briefly, 500 g of NR latex was diluted with distilled water to reduce its dry rubber content (DRC) from 60 to 20% in a 1 L four-necked round-bottom flask equipped with a

mechanical stirrer. Emulvin WA surfactant (10% w/v) (100 mL) was added and stirred for 1 h to stabilize the latex. The stabilized rubber was added with 0.3 mol of formic acid and 0.9 mol of hydrogen hydroxide (H_2O_2) at 40 °C for 12 h. Then, the latex was left for 24 h at room temperature to obtain ENR latex. The hydrogenation was then continued by adding a proper amount of 30% ammonium hydroxide solution to adjust the pH to 10. After stirring, 0.22 mol of hydrazine hydrate, dissolved 11 mmol of boric acid, and 0.22 g of gelatin were dropped into the ENR latex (DRC about 15%). H_2O_2 (0.22 mol) was added dropwise using a peristaltic pump at 12 mL/min and 40 °C for 6 h. During the addition of hydrogen peroxide, if too many bubbles were formed, 2−3 drops of the silicone oil used as an antifoaming agent were added. The hydrogenated epoxidized natural rubber (HENR) was precipitated in methanol for compounding and washed three times with deionized water. The product was dried under a vacuum at 40 °C to reach a constant weight before further analysis. In addition, epoxidized natural rubber (ENR) was separately prepared as controlled rubber samples using the same condition mentioned above. The chemical structure characterization of NR, ENR, and HENR has been reported in our previous paper.[27] The quantitative conversion of mol percentage of epoxide groups and degree of hydrogenation was calculated using eqs 1 and 2, respectively.[19,28]

mol% epoxide group(% EP)

$$= \frac{A_{2.70}}{(A_{2.70} + A_{5.12} + (A_{0.86}/3))} \times 100\% \quad (1)$$

degree of hydrogenation(%HD)

$$= \frac{(A_{0.86}/3)}{(A_{2.70} + A_{5.12} + (A_{0.86}/3))} \times 100\% \quad (2)$$

where A is the integrated area and subscripts represent a value of the chemical shift.

The ^{1}H-NMR spectra of the NR, ENR, and HENR are shown in Figure 1. Before epoxidation, three signal characteristics of methyl (a), methylene (b), and unsaturated methine protons of cis-1,4-isoprene units (c) appeared at 1.68, 2.05, and 5.10 ppm, respectively, as shown in Figure 1a. After
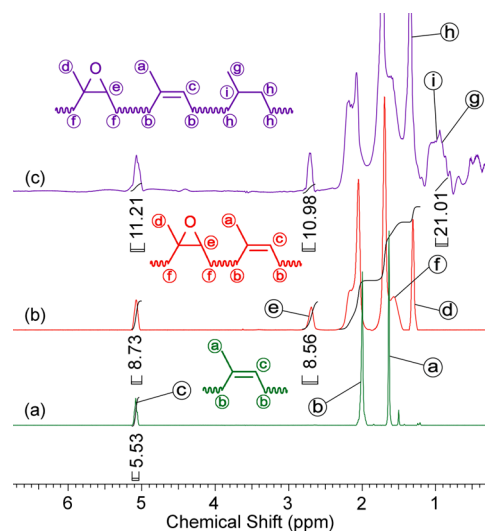

Figure 1. ^{1}H-NMR spectra of (a) NR, (b) ENR, and (c) HENR.

epoxidation, the other three signals appeared at 1.29, 1.58, and 2.70 ppm, which were assigned to methyl (d), methylene (f), and oxirane methine protons (e) of the resulting epoxide group, respectively. The results reveal that the increasing signals at 2.70 resulted from the increment of the epoxide group, as shown in Figure 1b. After the hydrogenation of ENR, the signals of 5.10 ppm decreased as the hydrogenation proceeded.[28,29] The new signals appeared around 1.30−1.40, 1.10, and 0.86 ppm after hydrogenation of ENR, which were assigned to methylene protons (h), methine protons (i), and methyl protons (g), respectively.

It is shown in Figure 1 that using eqs 1 and 2, as previously mentioned, two types of modified NR could be performed: ENR containing 49.5% epoxide group and HENR containing 49.5% epoxide group and 24% hydrogenation degree.

2.2. Compounding and Processing. The modified NRs were compounded using a laboratory-sized two-roll mill (Kodaira Seisakusho Co., Ltd., Tokyo, Japan) with various chemicals, according to the formulations for mixing, as shown in Table 1. For comparison purposes, NR was also

Table 1. Ingredients Used in the Present Study

ingredient	amount (phr)[a]	grade/supplier
rubber	100	
activator		
zinc oxide (ZnO)	5	Commercial/Thai-Lysaght Co., Ltd., Thailand
stearic acid	2	Commercial/Emery Oleochemicals LLC, Malaysia
accelerator		
N-cyclohexyl-2-benzothiazole sulfonamide (CBS)	1.6	Commercial/Monflex Pte., Ltd., Singapore
tetramethyl thiuram disulfide (TMTD)	0.3	Commercial/Vessel Chemical Co., Ltd., Thailand
sulfur (S)	2.5	Commercial/Azure Link Co., Ltd., Thailand

[a]phr, parts per hundred of rubber.

compounded using the same recipe. First, each rubber was initially masticated for 3 min, followed by the addition of the activators and accelerators. Second, mixing was completed by adding sulfur at 70 °C for 3 min. Each rubber compound was compression-molded at 150 °C with a force of 17.5 MPa using a hydraulic press according to their respective optimum cure time (t_{90}) determined based on the curing characteristics using a rheometer (TECH-PRO, Cuyahoga Falls, Ohio) according to ISO 3414 for 30 min at 150 °C. Vulcanizates were conditioned for 24 h before testing.

2.3. Characterization. Tensile properties were determined on an Instron universal testing machine (model 4466; Instron Corp., Canton, MA) using C-type dumbbell specimens, according to ASTM D412. Tensile specimens were aged at 100 °C for 72 h in an air-circulating aging oven according to ASTM D573 (1994) and were immersed in hydrocarbon oils at room temperature for 72 h. Oils used in this testing, engine oil (PTT, Performa Super Synthetic: SAE 0W-20) and brake fluid (PTT, Synthetic DOT 3), have different polarities, the latter of which has higher polarity. When the specified time was reached, the test specimens were removed from the oil and wiped with tissue paper to remove the excess oil from the

surface. Finally, the tensile properties of the specimens after aging were measured to estimate oil resistance according to ASTM D471-06. The aging resistance is expressed as relative tensile properties calculated using the following eq 3

$$\text{relative tensile property}(-) = \frac{\text{value after aging}}{\text{value before aging}} \tag{3}$$

Ozone aging studies under static conditions were conducted according to ISO 1431-1:2004 in a Hampden (model 1008-AH, Northampton, England). Photographs were taken using an optical microscope Carl Zeiss Stemi 2000 C (Werk Göttingen, Germany) with a magnification of 50.

Scanning electron microscopic studies of the compounds' tensile fracture surfaces were carried out on gold-coated samples using a JEOL microscope (model JSM 5600 LV; Tokyo, Japan) at a magnification of 3000.

Thermogravimetric analysis (TGA) was performed in a Q500 (TA Instruments). TGA was conducted under nitrogen with a flow rate of 50 mL/min. NR, ENR, and HENR composites (about 10 mg) were subjected to heating rates of 10, 20, and 30 °C/min, between 35 and 800 °C, to evaluate thermal stability and degradation kinetics.

2.4. Thermal Kinetics Analysis. Generally, the thermal decomposition reaction is first to measure the weight loss when applying heat with a constant heating rate and to use the fundamental expression considering Arrhenius temperature dependency following eq 4

$$\frac{dx}{dt} = A \cdot e^{-E_a/RT} \cdot f(x) \tag{4}$$

where A, E_a, T, and R of the reaction mechanism model refer to pre-exponential factor (min^{-1}), activation energy (J/mol), temperature (K), and gas constant (8.314 J/mol/K^{-1}), respectively. The value of x can be calculated using the TGA curve (eq 5)

$$x(-) = \frac{W_0 - W_t}{W_0 - W_f} \tag{5}$$

where W_0, W_t, and W_f are the initial weight, weight at time (t), and final weight, respectively.

For each process, the reaction rate is a function of conversion, $f(x)$, representing the reaction model and must be determined from the experimental data.[30] The Friedman (FRD) method is obtained by taking natural logarithm on both sides of eq 4 that becomes eq 6.

$$\ln\left(\frac{dx}{dt}\right) = \text{constant} - \frac{E_a}{RT} \tag{6}$$

Under nonisothermal conditions, in which the samples are subjected to a heating rate (β) = dT/dt in °C/min, the time dependency of eq 4 can be eliminated as expressed in eq 7

$$\frac{dx}{dT} = \frac{A}{\beta} \cdot e^{-E_a/RT} \cdot f(x) \tag{7}$$

More information about the thermal stability and the activation energy (E_a) was calculated using the Coats−Redfern equation[31,32] using the Kissinger−Akahira−Sunose (KAS) method as expressed in eq 8

$$\ln\left(\frac{\beta}{T^2}\right) = \text{constant} - \frac{E_a}{RT} \tag{8}$$

Based on the same degree of thermal degradation at different heating rates, linear plots of $\ln\left(\frac{dx}{dt}\right)$ vs $1000/T$ (FRD method) and $\ln\left(\frac{\beta}{T^2}\right)$ vs $1000/T$ (KAS method) were constructed. The slope of the straight line was used to calculate the value of the Arrhenius activation energy.

The material lifetime was estimated using the E_a obtained for the conversion rate of 5% by an analysis of the lifetime of rubber with different operating temperatures (T_f). A 5% conversion level value usually corresponds to the beginning of the degradation process; this conversion level can cause a significant decrease in a material's mechanical properties. Equation 9 was used for the thermal lifetime estimation proposed by Toop[33]

$$\log t_f = \frac{E_a}{2.303 R T_f} + \log\left(\frac{E_a}{R\beta}\right) - a \tag{9}$$

where t_f is the estimated thermal time to failure for constant conversion level, T_f is the operating temperature, E_a is the activation energy of 5% weight loss, a is the value that is determined using E_a/RT_c from the numerical integration table given in ref 34, and T_c is the temperature of 5% weight loss.

3. RESULTS AND DISCUSSION

3.1. Properties of NR, ENR, and HENR. Table 2 shows that the torque values and tensile strengths of the modified

Table 2. Properties of NR, ENR, and HENR

rubber	NR	ENR	HENR
M_H (lb$_f$·in)	7.21	5.99	5.18
M_L (lb$_f$·in)	0.69	0.42	0.23
$M_H - M_L$ (lb$_f$·in)	6.52	5.56	4.95
tensile strength (MPa)	20.8 ± 0.54	18.6 ± 1.46	14.7 ± 0.20
modulus 100% (MPa)	1.0 ± 0.10	1.2 ± 0.05	2.0 ± 0.01
relative tensile strength (−)			
after thermal aging	0.39	0.29	0.97
after engine oil aging	0.31	0.80	0.87
after brake fluid aging	0.40	0.76	0.80
relative Modulus at 100% elongation (−)			
after thermal aging	1.45	1.21	1.85
after engine oil aging	0.41	1.10	1.15
after brake fluid aging	0.59	1.05	1.10

rubber composites were lower than those of the NR composite, which possessed the highest values, followed by the ENR and HENR composites. In contrast, the modulus at 100% elongation displayed the opposite trend. The HENR composite exhibited the highest modulus at 100% elongation, followed by ENR and NR composites. The torque values determined by the rheometric data indicate the extent of the cross-linked rubber composite during the curing reaction.[35] NR has many double bonds in its molecular chains, which react with sulfur to form a network that makes the rubber stronger and more elastic. Toki et al.[36] investigated the relationship between the network structure and strain-induced crystallization in unvulcanized and vulcanized NR and synthetic polyisoprene rubbers. They found that the presence of a chemical network increased the behavior of strain-induced crystallization, enhancing the strain at the break since the

strain-induced crystalline molecule was longer than the oriented amorphous chain along the stretched direction. Moreover, the superior mechanical property in vulcanized NR has been attributed to the *cis* 1,4 configuration in NR. Because of many products generated in the mixture of rubber, sulfur, activators, and accelerators, the mechanism of sulfur vulcanization is still unclear until the present. A reaction representing the sulfur vulcanization of isoprene repeat units within the hypothesis of a free radical mechanism is illustrated in Scheme 1. During the vulcanization process, in the presence

Scheme 1. Mechanism of Sulfur Cross-Link for NR
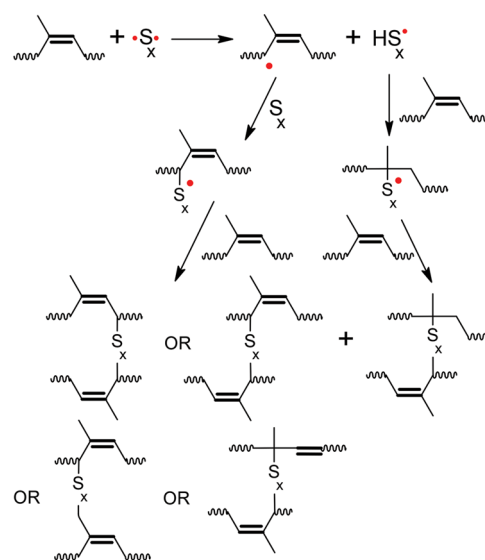
of accelerators and activators, sulfur decomposes into sulfur diradicals, which react with rubber to form the cross-link precursor. Finally, the cross-link precursor subsequently reacts with both saturated and unsaturated sites on the rubber chain resulting in different sulfur cross-link types.[37] A possible reaction mechanism of modified NR vulcanizates for the acid-catalyzed epoxy ring-opening reaction to form ether cross-link is proposed in Scheme 2. The sulfur-containing acid (HX) was

Scheme 2. Mechanism of Ether Cross-Link for Modified NR
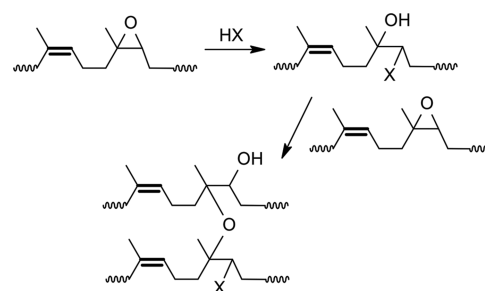
the acid from the oxidation of sulfides produced during vulcanization. Thus, more C=Cs and epoxide groups like NR and ENR vulcanizates had higher tensile strength.

The resistance of rubber-based composites to thermal aging is an essential requirement for better service performance. The effect of thermal aging on tensile strength was presented in terms of the relative value ratio after and before aging (eq 3). Table 2 reveals that all relative tensile strength of various rubber types was lower than 1. The results show that the
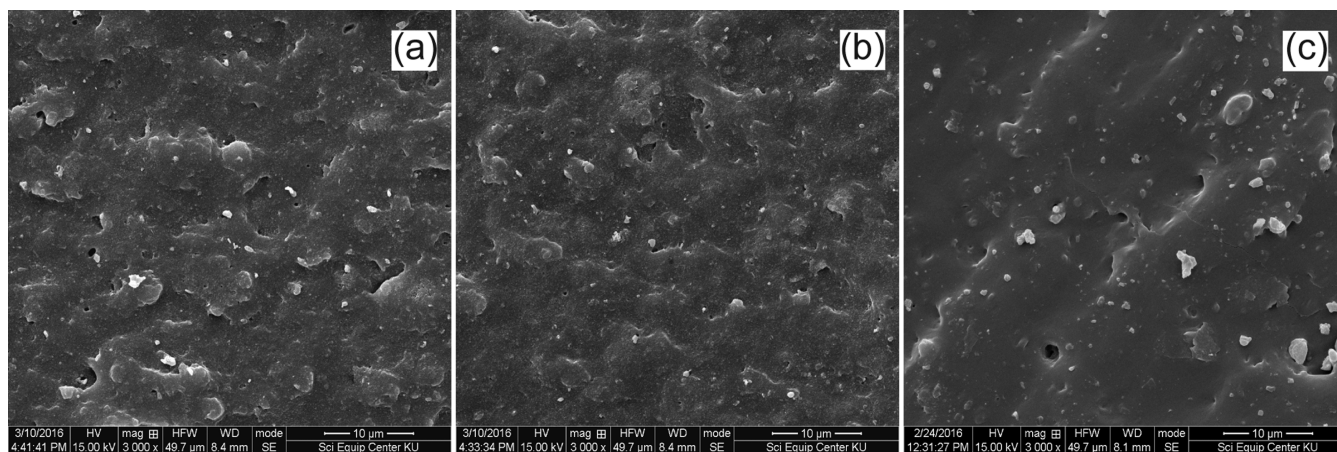
Figure 2. Morphology of the unfilled (a) NR, (b) ENR, and (c) HENR composites of tensile specimens before aging (×3000).
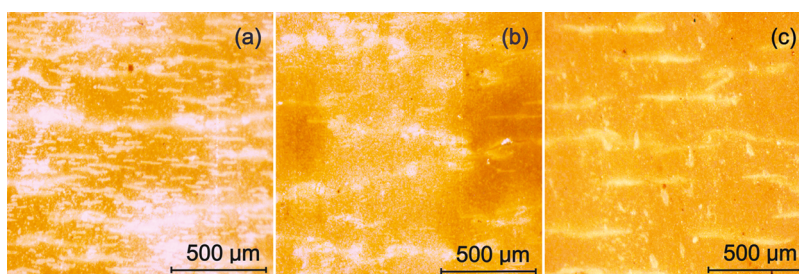

Figure 3. Ozone specimens of the unfilled (a) NR, (b) ENR, and (c) HENR composites (×50).

HENR composite had the greatest relative tensile strength ratio due to having fewer C=Cs in the structure, followed by NR and ENR composites after thermal aging. Generally, thermal oxidation of rubber composite occurred in the C=C region to form oxidative products leading to polymer embrittlement and cracking.[17,38,39] Furthermore, excessive main chain scission reduced the tendency to crystallize with increasing temperature.

The effect of different types of rubber on the relative tensile strength of the composites after being immersed for 72 h in a low polar automotive oil (engine oil) and a more polar automotive oil (brake fluid) is shown in Table 2. The introduction of epoxide groups along the NR backbone reduced the number of C=Cs and increased the polarity of NR. As expected, relative tensile strengths on oil resistance were higher in modified NR composites than in NR composites due to the poor solubility in most hydrocarbon/hydrophobic solvents, including oils. Modified NR with a strong molecular polarity in the more polar hydrocarbon oil (brake fluid) showed a lower relative value than low polar hydrocarbon oil (engine oil). It also implied that the polarity of the rubber was believed to play a significant role in resisting the dissolution of hydrocarbon oil.

These morphological results of the NR, ENR, and HENR composites were well matched with the tensile strength results, as shown in Figure 2. A fracture can be separated into two types: brittle fracture and ductile fracture. Usually, the fracture surface after applying high stress had a rough surface and white fibrils (matrix tear lines with branching), a typical feature of ductile failure. Many fibrils on the failure surface showed that the rubber could receive large deformation before breaking, thus enhancing the tensile strength.[13] The NR [Figure 2a] and ENR [Figure 2b] composites had a rough surface and rich

white fibrils, while the HENR composite [Figure 2c] had a smooth surface and small amounts of white fibrils. The smoothness of the tensile fractured surfaces was related to the brittleness behavior, while under the SEM, these fractures display shorter isolated fibered structure characteristics. Due to fewer reactive sites of unsaturated bonds to form sulfidic cross-links of the HENR composite, it contributed to higher brittleness behavior, which was probably associated with the low unsaturated bonds of the HENR composite and lower tensile strength than the NR and ENR composites. The rougher surface indicated better mechanical properties, while a smoother surface was usually reported for low tensile strength and rather brittleness of the rubber composite.

Modulus is the stress required to obtain a given strain. Therefore, the modulus at 100% elongation is simply the stress required to elongate the rubber twice its reference length and is related to the low mobility of molecular chains. Modulus at 100% elongation before and after thermal and oil aging is shown in Table 2. The HENR composite exhibited the highest modulus at 100% elongation, followed by ENR and NR composites. As discussed, the NR with high cross-link density directly negatively affects the modulus at 100% elongation due to higher elasticity when the composite is stretched.

After thermal aging, the rubber molecule would react with oxygen and be degraded by chain scission, which increased the degree of branch and retarded chain movement due to the increase in the stiffness of the composite. Therefore, the rubber exhibited a higher relative than 1, contrasting with the trend of relative tensile strength. The HENR composite had the highest modulus at 100% elongation value after thermal aging, following NR and ENR composites.

Unlike thermal aging, the modulus of all of the composites decreased at 100% elongation after both oil aging, as shown in

Table 2. The reduction in relative modulus at 100% elongation of the composites after being immersed in both oils may be due to the solvation with surface macromolecules, which took place, and solvents permeated into the inside gaps of the macromolecules. Thus, the composites will swell and become soft. With the introduction of oxirane rings in the polymer backbones, their resistance to low polar oil became stronger, and its swelling capacity in both oils became lower. The NR composite had the highest swelling capacity due to its nonpolar characteristic. As expected, the NR composite demonstrated the lowest relative 100% modulus, followed by the two epoxidized polymers (Table 2). Both modified NR composites displayed less resistance in brake fluid than engine oil, whereas the NR composite showed a different result between both hydrocarbon oils.

Optical photographs of the surfaces of the rubber composites of ozone-exposed samples are presented in Figure 3. A surface crack length was measured in the field at a magnification of ×50 (500-micrometer unit) and has been plotted in Figure 4 for NR, ENR, and HENR, respectively. The
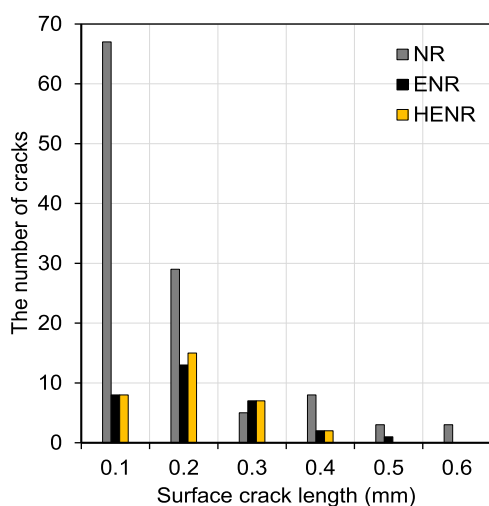

Figure 4. Surface crack length versus the number of cracks.

nature and intensity of cracks depend on the amount of unsaturation in the rubber structure, which becomes susceptible to the free radicals created by ozone and break the bonds. The photograph showed that the highest cracks were deep, wide, and continuous in NR [Figure 3a]. In the case of modified NR, the crack density was less, and the composite showed shorter and shallow cracks represented by the horizontal lines [Figure 3b,c], which confirms that the crack growths were retarded. The reduction of C=Cs in the main chain led to shorter and fewer ozone cracks on the surface of the rubber specimens, as shown in Figure 4. The results indicated that the presence of the polar group in modified NR reduced the penetration of oil into the rubber matrix giving better resistance toward swelling, and converting unsaturated rubber to less unsaturated one improved the thermal and ozone resistances compared to the NR. A similar finding was reported by Saengdee et al.[19] The oil and solvent resistances, including ozone resistance of the modified NRs, were improved compared to the NR. These observations suggest that HENR can overcome the drawbacks of NR, which should extend the applications of NR.

3.2. Activation Energy. Figure 5 displays the percentage mass loss values of rubber mass as a function of temperature at
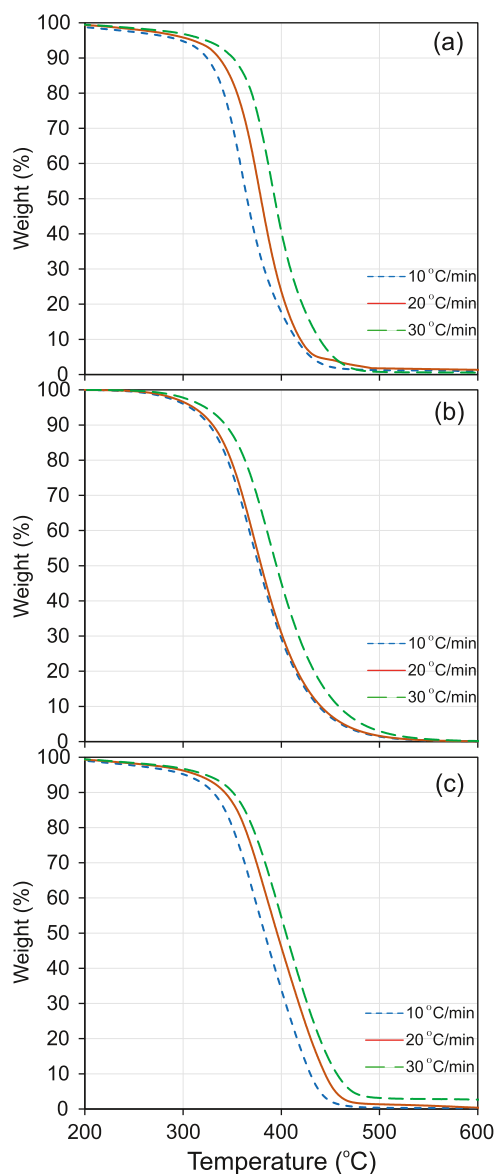

Figure 5. TGA of the unfilled (a) NR, (b) ENR, and (c) HENR composites.

heating rates of 10, 20, and 30 °C/min for NR, ENR, and HENR, respectively. The thermal degradation reaction of all rubbers in nitrogen could be a simple one-step reaction and proceed thoroughly. The model-free methods were applied, and activation energies of rubber were calculated according to eqs 6 and 8 for different conversion levels, varying from 0.05 to 0.5 with intervals of 0.025. Therefore, according to the plots of $\ln\left(\frac{dx}{dt}\right)$ vs $1000/T$ (FRD method) and $\ln\left(\frac{\beta}{T^2}\right)$ vs $1000/T$ (KAS method), the activation energy (E_a) of the degradation process was obtained from the slope of the resulting straight line. The plots are almost parallel straight lines at different conversion levels. The calculated values limited in the conversion level range of 0.05−0.2 were reliable,[40] whereas the values outside the range of 0.05−0.2 were only for reference. The activation energy at different conversion levels from 0.05 to 0.5 for NR, ENR, and HENR calculated from the straight lines in Figures 6
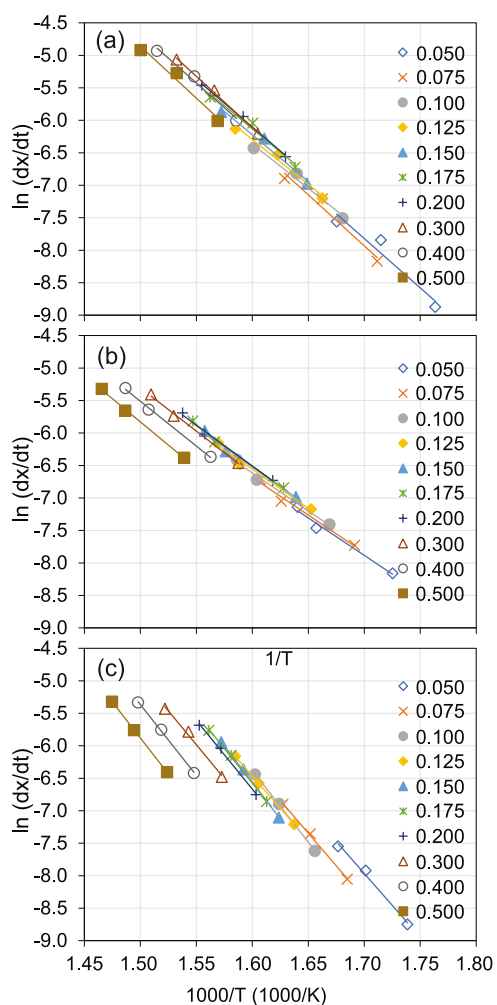
Figure 6. Plots obtained from the TGA curve at different degrees of conversion of (a) NR, (b) ENR, and (c) HENR based on the FRD method.

Figure 7. Plots obtained from the TGA curve at different degrees of conversion of (a) NR, (b) ENR, and (c) HENR based on the KAS method.

and 7 are shown in Figure 8. For comparison, the activation energy values using the KAS method displayed a similar trend to those from the FRD method although they were smaller than the latter (Figure 8). These results increased to a 0.1 conversion level, followed by a gradual increase. For the kinetic analysis of model-free fitting methods, the KAS method gave close E_a values at all of the conversion levels, but the FRD method yielded many deviant results. Results from Figure 8 indicated that the KAS method was considered more accurate than the FRD method. The plots indicate that the HENR composite had the highest E_a, followed by NR and ENR composites, the energy required to degrade the main chains. Thermal degradation above 200 °C led to chain scission and largely depended on impurities generated during their manufacture, like C=Cs.[39] As a result, the significantly improved thermal stability of the HENR is attributed to the reduction of C=C bonds by hydrogenation in the rubber matrix. However, the thermal stability of ENR was worse than that of NR. In the case of ENR, as compared with NR, the chain scissions were more significant because the neighbor epoxide groups activated C=Cs in ENR molecular chains.[15] Consequently, the HENR has better thermal stability than the NR and ENR.
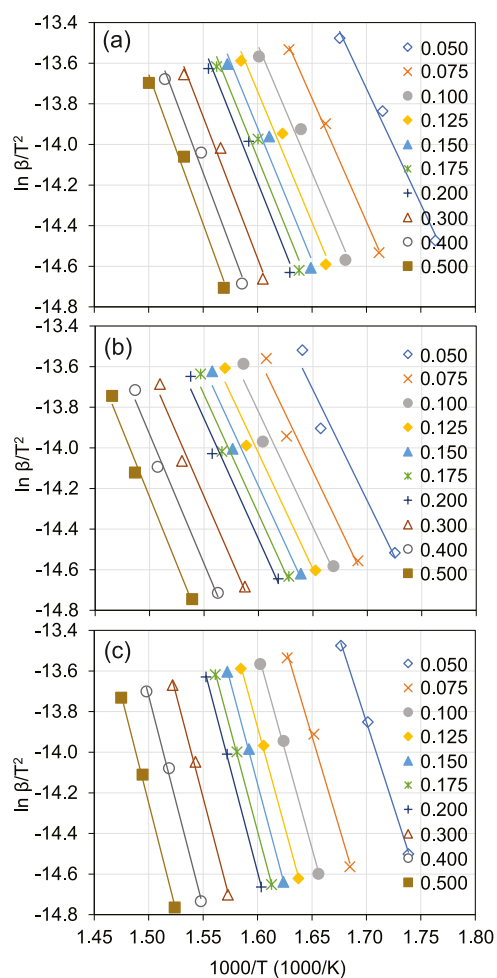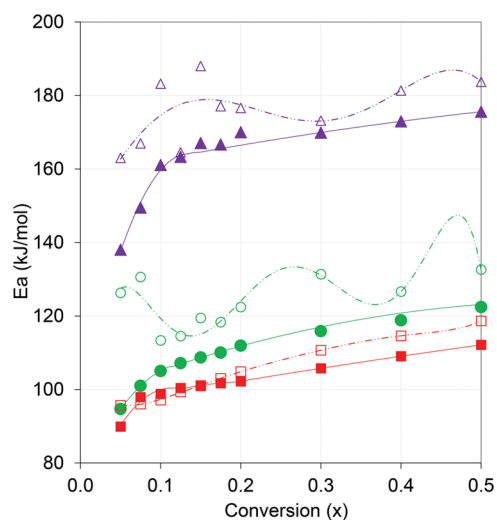

Figure 8. Dependence of activation energy of NR (circles), ENR (rectangles), and HENR (triangles) as a function of the extent of conversion obtained from the FRD method (open symbols) and KAS method (closed symbols) applied to thermal decomposition.

3.3. Lifetime Estimation. The ability to predict a lifetime is valuable to prevent an accident because of the premature failure of the material. In the present case, the lifetime has been

considered when the sample has experienced a 0.05 conversion level on a heating rate of 20 °C/min in the thermogravimetry experiments. The lifetime for a temperature range between 25 and 200 °C has been calculated using eq 9 and is plotted in Figure 9 for NR, ENR, and HENR, respectively. The logarithm
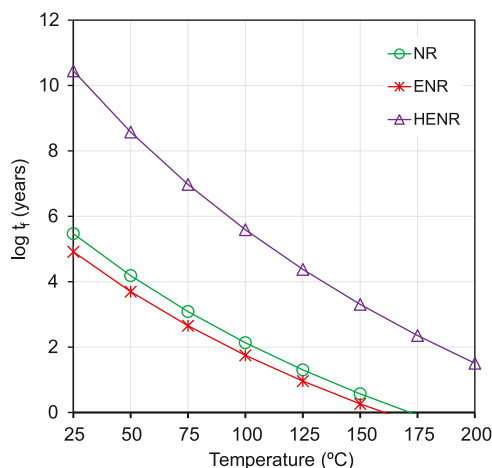

Figure 9. Thermal lifetime estimation for NR, ENR, and HENR as obtained for different operating temperatures at 20 °C/min and $x =$ 0.05.

scale for the lifetime has been chosen for better comparison. Figure 9 shows a sharp lifetime fall with increasing temperature for all samples. Hence, the determined polymer lifetime variation strongly depended on the selected temperature. It is important to emphasize that these TGA analyses were carried out in a nitrogen atmosphere without considering the weather and mechanical stress during aging. Therefore, the temperature played an active role in the overall material lifetime. The increase in temperature tended to decrease material durability. Because a lifetime is based on activation energy, HENR has a longer lifetime than NR and ENR. For instance, when T_f changed from 25 to 200 °C, the lifetime of NR varied from 2.94×10^5 to 2.16×10^{-1} years, ENR varied from 8.22×10^4 to 1.23×10^{-1} years, and HENR varied from 2.81×10^{10} to 3.21×10^1 years.

4. CONCLUSIONS

The epoxidation of NR with performic acid in the latex stage is followed by diimide hydrogenation. The resulting products, ENR (49.5% epoxide group content) and HENR (49.5% epoxide group content and 24% hydrogenation degree), were characterized by ^{1}H-NMR. The ENR and HENR were vulcanized using sulfur compared with the NR composite. The torque values and tensile strength of the NR composite were comparable to those of both modified NR composites. The NR composite showed the highest values, followed by ENR and HENR composites. However, the modulus at 100% elongation of modified NRs was higher than that of the NR composite. These observations suggest that the heat, oil, and ozone resistances of the HENR composite were better than those of NR and ENR composites due to the presence of epoxide groups and a reduction in the number of C=Cs in the rubber chains. The thermal degradation of the rubber composites was studied using TGA. The obtained set of experimental TG data was used to calculate the activation energy (E_a) through the Kissinger−Akahira−Sunose method.

The HENR composite had the highest E_a, followed by NR and ENR composites. Using the kinetics data, HENR had a longer lifetime than NR and ENR in the range of 25−200 °C, indicating that HENR had excellent thermal stability than NR and ENR. Thus, the HENR synthesized from a renewable resource (NR) can provide improved rubber materials focused on the automobile (seals, gaskets, hoses, and belts) and oil industries where durability and thermal- and oil-resistant application properties are the primary concern.

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Notes

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