

Synthesis of Hydrogenated Natural Rubber Having Epoxide Groups Using Diimide

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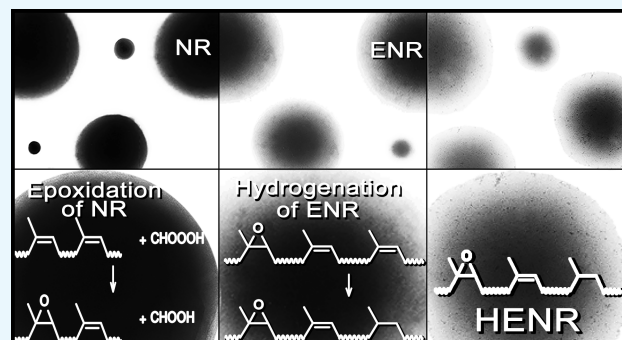
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ABSTRACT: Epoxidized natural rubber (ENR) with 50% mol of epoxide groups was synthesized using performic acid generated from the reaction of formic acid/hydrogen peroxide in latex form followed by hydrogenation using diimide generated from hydrazine (N_2H_4) and hydrogen peroxide (H_2O_2) with boric acid (H_3BO_3) as a catalyst. The resulting products (hydrogenated epoxidized natural rubber, HENR) were characterized by proton nuclear magnetic resonance spectroscopy (1H -NMR), gel testing, transmission electron microscopy (TEM), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). The effects of reaction parameters such as N_2H_4 amount, H_2O_2 amount, H_3BO_3 amount, gelatin amount, reaction time, and reaction temperature on the percentage of hydrogenation degree and gel content were investigated. The transmission electron micrographs of the particles confirmed a core/shell structure consisting of a highly unsaturated concentration region as the core encapsulated by a low carbon–carbon double bond concentration region as the shell, which indicated that the rubber particle seemed to be modified from the outer layer to the center of the rubber particle. Overall, the data showed that an increase in the amount of the individual chemicals, reaction time, and temperature increased the hydrogenation degree. However, a higher level of gelatin retarded an increase in the percentage of hydrogenation degree. As the hydrogenation degree increased, the gel content increased due to the ether linkage and the crosslinking reaction triggered through hydroxyl radicals. From DSC measurements, the glass transition temperatures of hydrogenated products increased above those of original rubbers. The thermal stability of hydrogenated products was improved, demonstrated by a decomposition temperature shift to a higher temperature than ENR, as shown by the results from the thermogravimetric analysis. Therefore, the hydrogenated ENR (HENR) exhibited good thermal stability, which could extend the applications of ENR in the automotive and oil industries.



1. INTRODUCTION

Natural rubber (NR) obtained from *Hevea brasiliensis* is a renewable material possessing excellent characteristics such as high tensile strength due to its ability to crystallize upon stretching.¹ However, the disadvantages of NR are its low heat, oxygen, and oil resistance, mainly because of its unsaturated chain structure.² In addition, it does not perform well when exposed to oils and hydrocarbon solvents due to its non-polar character,³ having limitations in demanding applications. Epoxidation of NR (ENR), using peracid produced *in situ*, is the reaction to convert the unsaturated units into epoxide rings, which have turned out to be an attractive material. It has high polarity due to the epoxide groups in the chain, bringing about an improved resistance toward oils and hydrocarbon solvents⁴ while retaining superior strength and fatigue properties due to undergoing strain-induced crystallization like that of NR. As the percentage of the epoxide group content increases, the glass transition temperature (T_g) increases, thus resulting in decreasing resilience and air permeability. Two grades of ENR, ENR-25 (25% epoxidation) and ENR-50 (50%

epoxidation), have attained commercial importance. ENR-25 can be utilized for tire products because of its good wet-grip and rolling resistance.⁵ In contrast, the oil resistance property of ENR-50 was comparable to that of nitrile-butadiene rubber (NBR) with 34% of the acrylonitrile group.⁶ Natural rubber latex was epoxidized with performic acid generated from a formic acid and hydrogen peroxide reaction under various reaction conditions by Heping et al.⁷ They reported that the glass transition temperature (T_g), thermal degradation temperature, and activation energy of thermal degradation of the ENRs increased with the extent of epoxidation. Tanrattanakul and co-workers⁸ synthesized an *in situ* epoxidized natural rubber (NR

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from 20% dry rubber content NR latex with performic acid at a temperature of 50 °C and systematically studied the oil resistance and mechanical properties of the synthesized ENR. They illustrated that the ENR showed tensile properties and tear resistance as good as NR and improved resistance to oils and solvents such as petroleum ether, ASTM no. 3 oil, and automobile oils. Chuayjuljit et al.³ synthesized ENR via *in situ* epoxidation from NR latex with performic acid using different reaction times. They found that the T_g increased as the epoxide group content increased. The prepared ENRs were compounded and vulcanized. They reported that as the epoxide group content increased, the hardness and oil resistance increased. After aging, all rubbers showed a deteriorated tensile strength and lower elongation at break but higher hardness. The oil resistance of ENRs was significantly better than that of NR, especially the oil resistance of ENR with 63.9% epoxide group content, which was comparable to that of nitrile-butadiene rubber. However, He et al.⁹ examined the thermal oxidative degradation of ENR with 50% epoxide group content (ENR-50) with TGA and DTA. They have reported that the thermal stability of ENR-50 is worse than that of NR, thus limiting its use in outdoor applications. The primary drawback of ENR, like NR, is its poor heat aging properties. Hydrogenation is one of the most efficient methods used to reduce the degree of unsaturation in polymers by adding hydrogen atoms to the unsaturated units, thus enhancing the thermal stability of the polymer. The hydrogenation of ENR is expected to yield a product with improved heat resistance due to the conversion of carbon-carbon unsaturated units to saturated units. There are several methods to hydrogenate polydienes that involve catalytic and non-catalytic procedures. In the catalytic hydrogenation process, polydienes dissolved in an organic solvent are hydrogenated selectively under high pressures of hydrogen at elevated temperatures using a transition metal catalyst.¹⁰ Magnetic Fe_3O_4 nanoparticles embedded in graphene oxide behave as a highly efficient and reusable heterogeneous nanocatalyst for alkene hydrogenation in ethanol at 80 °C temperature using hydrazine hydrate as the hydrogen source to deliver the corresponding alkanes in good to excellent yields together with a 4–20 h reaction time.¹¹ Generally, transition metal ions are not effective as catalysts in latex systems because the metal ions may be isolated from the reactants in the aqueous phase. In the case of non-catalytic hydrogenation, diimide (N_2H_2) is widely used as a hydrogen-donating agent. Diimide is a short-lived intermediate that can be generated by various methods. An efficient method was developed for the hydrogenation with diimide, generated *in situ* from hydrazine hydrate by oxidation with oxygen. The hydrogenation process proceeded for 24–48 h with excellent yields. This procedure offers synthetic advantages over metal-catalyzed hydrogenation.¹² He et al.¹³ studied the conditions for the hydrogenation of styrene-butadiene rubber (SBR) latex via the diimide reduction process. They pointed out that the particle surface is an important parameter in controlling the hydrogenation degree. They also found that the gel fraction of SBR latex increased after the hydrogenation. Samran et al.¹⁴ investigated the hydrogenation of NR and various ENRs using diimide generated *in situ* from the thermal decomposition of *p*-toluenesulfonylhydrazide in *o*-xylene solution at 135 °C. They showed that the T_g of the hydrogenated rubbers was increased by about 10–20 °C compared with the starting rubbers. The effects of reaction conditions for hydrogenated styrene-butadiene rubber (HSBR), such as reaction time and temper-

ature, pH, and concentrations of hydrogen peroxide, hydrazine, and catalysts, have been reported by De Sarkar et al.¹⁵ The reaction conditions directly affect the hydrogenation degree and give rise to an increase in the T_g with an increasing hydrogenation degree due to the development of crystalline segments. Lin et al.¹⁶ investigated the hydrogenation of nitrile-butadiene rubber latex via utilization of diimide, generated by the oxidation of hydrazine (N_2H_4/H_2O_2). They claimed that the hydrogenation efficiency when a copper ion, silver ion, or ferrous ion was used as a catalyst was lower than the hydrogenation efficiency in boric acid. The reaction conditions directly affect the hydrogenation degree and give rise to an increase in the glass transition temperature (T_g) with an increasing hydrogenation degree due to the development of crystalline segments. Unfortunately, hydrogenated unsaturated rubber synthesized via diimide hydrogenation in latex form is prone to a crosslinking side reaction, producing gelled or crosslinked hydrogenated rubber latex particles.¹⁷ It is commonly known that a high gel content has poor mechanical properties and is not beneficial to milling hydrogenated unsaturated rubber when used as dried rubber because extra energy will be consumed to break the crosslinking structures.¹⁸ Roy et al.¹⁹ prepared the hydrogenation of ENR (HENR) with a homogeneous catalyst at 323 K in a solution phase. They reported that HENR reduced both the green strength, a rubber's resistance to deformation and fracture before vulcanization, and the modulus at 300% elongation, whereas the elongation at break was increased marginally. They also reported that HENR showed a better thermal stability and oil resistance. Saengdee and co-workers²⁰ studied the preparation condition of modified NR by prior epoxidation using performic acid followed by hydrogenation using diimide in latex form. Compared to the NR, they reported that HENR showed improved thermal and mechanical properties and oil and ozone resistance. They suggested that HENR can overcome drawbacks of NR, which could extend the applications of NR.

In the present study, we attempt to prepare hydrogenated epoxidized natural rubber (HENR). First, ENR-50 was synthesized by *in situ* epoxidation of natural rubber (NR) using performic acid generated from the formic acid/hydrogen peroxide reaction in the latex stage. The ENR with 50% epoxide group content was then hydrogenated by diimide reduction in a water system using hydrazine reacted with hydrogen peroxide and boric acid as a catalyst. The effects of the amount of the individual chemicals (N_2H_4 , H_2O_2 , H_3BO_3 , and gelatin) and hydrogenation conditions such as reaction time and temperature on the percentage of hydrogenation degree (% HD_{residual double bond}) characterized by proton nuclear magnetic resonance spectroscopy (1H -NMR) were investigated. The possibility of crosslinking (gel content) during a hydrogenation reaction was also mentioned. The thermal properties of the resulting product were examined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

2. EXPERIMENTAL STUDIES

2.1. Materials. The commercial high-ammonia natural rubber latex comprises almost entirely *cis*-polyisoprene, with 60% by weight dry rubber content (DRC). It was produced by Yala Latex Industry Co., Ltd. (Yala, Thailand). Aqueous hydrogen peroxide (50 wt %), formic acid (85 wt %), and hydrazine hydrate (85 wt %, $N_2H_4 \cdot H_2O$) were purchased from Sigma-Aldrich. Polyoxyethylene styrenated phenyl ether ($C_{24}H_{22}O_2$) used as a surfactant under the trade name Emulvin

WA was purchased from Chemical and Materials Co., Ltd., Thailand. Gelatin was purchased from J R F & B Co., Ltd. (Bangkok, Thailand). Methanol (commercial grade), 99.5 wt % boric acid (H_3BO_3), 30 wt % ammonium hydroxide solution (NH_4OH), and an antifoaming agent (silicone oil) were bought from Facobis Co., Ltd. (Bangkok, Thailand). All chemical reagents were used as received. Deionized water was used throughout the work.

2.2. Preparation of *In Situ* Epoxidized Natural Rubber.

Diluted natural rubber latex (500 g) with 20% DRC was mixed with 100 g of 10 wt % aqueous solution of Emulvin WA surfactant in a 1 L three-neck flask mounted with an overhead agitator. After stirring for 1 h, 0.3 mol of formic acid and 0.9 mol of hydrogen peroxide were added dropwise into the reactor slowly and were stirred under a constant reaction temperature of 40 °C for 12 h. The latex was left for 24 h at room temperature to obtain the partially epoxidized natural rubber (ENR) latex, which was used as the starting reactant for the hydrogenation reaction. Then, the pH of ENR latex was adjusted to pH 10 by ammonium hydroxide to convert the residual formic acid to formate ions so not to disturb the following step of hydrogenation. ENR latex was precipitated using methanol to form the coagulated rubber and washed three times with deionized water. The gross polymer was recovered and dried to constant mass in a vacuum oven at 40 °C. The percentage of epoxide group content (% EP) was determined by $^1\text{H-NMR}$ spectroscopy.

2.3. Hydrogenation of Epoxidized Natural Rubber (HENR).

ENR latex (about 15%) prepared by the above method providing about 50% mol epoxidation was put into a 1 L four-neck round-bottom flask. After stirring, hydrazine hydrate and dissolved boric acid and gelatin were dropped into the latex. A water bath was used to maintain the desired temperature. Aqueous hydrogen peroxide was added dropwise using a peristaltic pump at 12 mL/min. Slowing down the addition rate of H_2O_2 can help in achieving a higher efficiency of diimide generation and has a beneficial effect on gel reduction.¹⁷ During the addition of hydrogen peroxide, two to three drops of silicone oil were added to reduce foaming if too many bubbles were formed. When hydrogen peroxide was added, the reaction was left to proceed under a constant stirring rate. The product latex was precipitated using methanol to form the coagulated rubber. The product was washed three times with deionized water. The gross polymer was recovered and dried to constant mass in a vacuum oven at 40 °C. The percentage of hydrogenation degree (% HD_{residual double bond}) was determined by $^1\text{H-NMR}$ spectroscopy.

3. CHARACTERIZATION

3.1. Determination of the Percentage of Epoxide Group and Hydrogenation Degree.

The percentage of epoxide group and hydrogenation degree was examined by proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectroscopy. The sample was dissolved in deuterated chloroform (CDCl_3) at room temperature. After the sample has been dissolved, it was transferred directly to an NMR tube by allowing the solution to pass through a cotton filter. The spectra were recorded on a Bruker 300 MHz spectrometer (Bruker BioSpin Corp., Massachusetts, USA). The qualitative and quantitative analyses of the functional groups of NR and modified natural rubbers were identified by $^1\text{H-NMR}$ spectroscopy, as shown in Figures 1 and 2. The chemical shift was reported in parts per million (ppm). The percentage of epoxide group content before

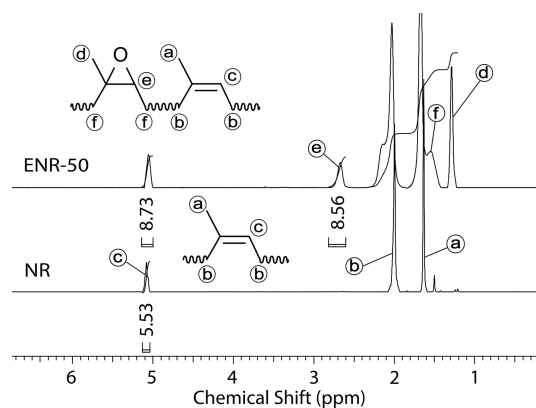


Figure 1. $^1\text{H-NMR}$ spectra of NR and ENR-50.

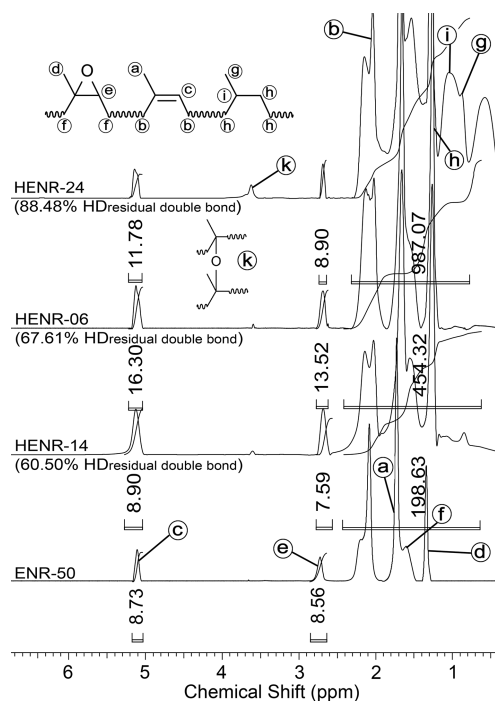


Figure 2. $^1\text{H-NMR}$ spectra of ENR-50 and HENRs.

hydrogenation was calculated, as shown in eq 1.²¹ The conversion of residual carbon–carbon double bond content after epoxidation can be used to calculate the percentage of hydrogenation degree using eq 2.²²

$$\% \text{ epoxide group (\% EP)} = \frac{I_{2.7}}{(I_{2.7} + I_{5.1})} \times 100\% \quad (1)$$

$$\begin{aligned} \% \text{ hydrogenation degree (\% HD}_{\text{residual double bond}}) \\ = \frac{I_{0.8-2.3} - 7I_{5.1}}{(I_{0.8-2.3} + 3I_{5.1})} \times 100\% \end{aligned} \quad (2)$$

where I is the signal intensity and the subscripts represent a value of the chemical shift.

3.2. Determination of Gel Content.

A gel test is the ASTM standard test method for determining the gel content (insoluble fraction) for the polymer's crosslinking linkages, according to ASTM D3616. Approximately 0.4 ± 0.05 g of each sample was weighed and placed on a screen rack (50 mesh) in a borosilicate bottle, and 100 cm³ of toluene was added into the

bottle. The sample was soaked in toluene for 20 h. According to eq 3, the liquid was pipetted to determine the gel content

$$\text{gel content(\%)} = \frac{A - B}{A} \times 100 \quad (3)$$

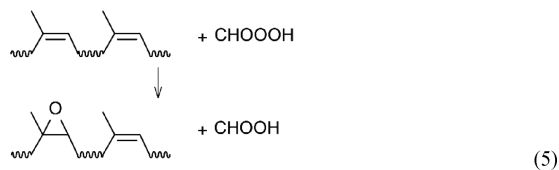
where A is the mass of the original samples and B is the residual mass after solvent evaporation. A test result was regarded as the average of two determinations.

3.3. Morphology Study. Osmium tetroxide (OsO_4) is the most used chemical for staining unsaturated sections to increase the contrast and gradient of the particles. The rubber surface was observed using a JEM-1230 transmission electron microscope (TEM) with a magnification of 30,000 at an accelerating voltage of 80 kV. The diluted rubber latex was dropped on microscope grids and was exposed to OsO_4 vapor in glass-covered dishes at room temperature for 24 h before observation. The relationship between the reaction conversion and particles morphology was studied.

3.4. Thermal Property Analysis. The degradation temperature was obtained from thermogravimetric analysis (TGA) and differential thermal analysis (DTA) (Perkin–Elmer Pyris Diamond, TGA/DTA). The mass of the sample was recorded continuously since the 10 mg sample was placed on a platinum pan. At the same time, the heat was applied to increase the temperature at a constant rate from room temperature to 650 °C under nitrogen at a flow rate of 50 mL/min and heating rate of 10 °C/min. Weight losses occur when volatiles adsorbed by the polymer are driven off and at higher temperatures when degradation of the polymer occurs with the formation of volatile products.²³ The initial, final, and decomposition temperatures at weight loss of 5% (T_{d5}) and 95% (T_{d95}) and maxima of the weight loss (T_{max}) of samples were measured. The glass transition temperature (T_g) was measured by differential scanning calorimetry (DSC, Perkin Elmer Instrument DSC 8500). A sample mass of 10 mg encapsulated in an aluminum pan was measured for the T_g at a temperature of –90 °C to 50 °C at a heating rate of 10 °C/min.

4. RESULTS AND DISCUSSION

4.1. $^1\text{H-NMR}$ Characterization. The *in situ* epoxidation of the NR latex using hydrogen peroxide and formic acid also yields epoxidized natural rubber (ENR). The following reaction scheme is proposed for the epoxidation of the NR latex by the performic acid method:



The characteristics of the NR latex were analyzed based on proton nuclear magnetic resonance ($^1\text{H-NMR}$). As for NR, three signals characteristic of methyl (a), methylene (b), and unsaturated methine protons (c) of *cis*-1,4-isoprene units appeared at 1.68, 2.05, and 5.10 ppm, respectively. After 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. The results reveal that the increasing signals at 2.70 resulted from the increment of the epoxide group, as shown in Figure 1. This provides evidence that a part of the carbon–carbon double

bonds of NR is converted to epoxide groups. The percentage of epoxide group content of the starting reactant ENR-50 was 49.51%.

Two steps achieve the diimide hydrogenation reaction: (1) the reaction between hydrazine and hydrogen peroxide to produce diimide [eq 6] and (2) the reaction between diimide and carbon–carbon double bonds to form hydrogenated ENR [eq 7]

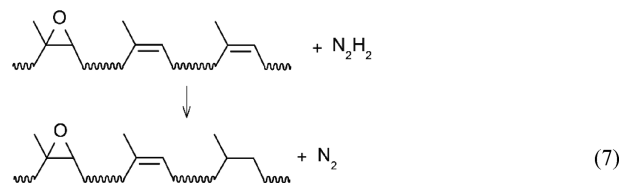
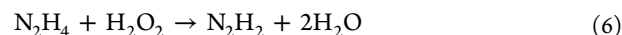


Figure 2 shows the $^1\text{H-NMR}$ spectra of ENR-50, HENR-14 (60.50% $\text{HD}_{\text{residual double bond}}$), HENR-06 (67.61% $\text{HD}_{\text{residual double bond}}$), and HENR-24 (88.48% $\text{HD}_{\text{residual double bond}}$). After hydrogenation of ENR, new signals appeared around 1.30–1.40 ppm, 1.10 ppm, 0.84 ppm, and 3.70 ppm, which were assigned to the methylene protons (h), methine proton (i), methyl proton (g), and ether unit (k), respectively, whereas the signals at 2.70 and 5.10 ppm decreased as the hydrogenation proceeded.^{21,24} The percentages of the epoxide group content and hydrogenation degree were calculated from the integrated peak area of these signals based on the $^1\text{H-NMR}$ spectrum according to eqs 1 and 2, respectively. The percentage of epoxide group content of ENR used in the present study was 49.51% (ENR-50); hence, the estimated residual carbon–carbon double bond content was 50.49%.

4.2. Morphology of HENR Particles. The morphology of NR, ENR-50, and HENR-25 (89.19% $\text{HD}_{\text{residual double bond}}$) particles was observed from the TEM micrographs, as shown in Figure 3. NR, ENR-50, and HENR-25 are spherical and have

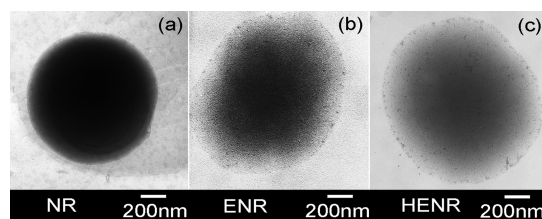


Figure 3. TEM micrographs of (a) NR, (b) ENR-50, and (c) HENR-25 (magnification 30,000 \times).

smooth surfaces. Since the OsO_4 staining agent can only stain at the carbon–carbon double bonds, the lightly colored domain indicates a region of low carbon–carbon double bond content. NR showed a relatively sharp particle edge because of the high OsO_4 amount inside the particle. For ENR-50, the contrast between the core and the shell of the modified NR particle was quite different, as shown in Figure 3b. The dark color domain indicated the particle region with a high carbon–carbon double bond content as the core, while the lighter color domain at the outer layer as the shell indicated a low carbon–carbon double bond content for OsO_4 staining. HENR-25 exhibited a much lighter color domain due to the small carbon–carbon double bond content, as shown in Figure 3c. The epoxidation and hydrogenation reaction occurred from the outer surface to the

center of the rubber particle, suggesting a heterogeneous structure (core/shell morphology).

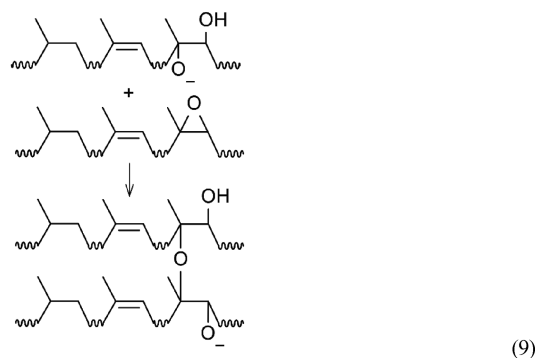
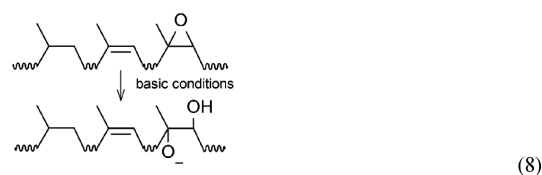
4.3. Effect of Reaction Time on the Hydrogenation of ENR. The reaction time usually plays a significant role in a chemical reaction. The effect of reaction time on the percentage of hydrogenation degree and gel content was studied over the range of approximately 0 to 10 h while keeping the concentration of all other reagents constant under a reaction temperature of 40 °C, as shown in Table 1. The residual double

Table 1. Effect of Reaction Time on the Hydrogenation of ENR^a

samples	time (h)	% HD _{residual double bond}	gel content (%)
ENR-50	0	0.00	27.54
HENR-01	2	34.43	30.52
HENR-02	4	61.53	35.99
HENR-03	6	73.52	45.65
HENR-04	8	77.38	62.11
HENR-05	10	77.59	63.63

^aConditions: N₂H₄·H₂O, 0.22 mol; H₂O₂, 0.22 mol; H₃BO₃, 11 mmol; gelatin, 0.22 g; T, 40 °C.

bond conversion and gel content were sharply increased and almost unchanged for a reaction time greater than 8 h. According to eq 6, it can be seen that diimide was formed as an active species at the surface of the particle and was consumed toward the surface of the unsaturated region of the latex particles. Then, the residual double bond content was reduced due to the percentage of hydrogenation degree, as shown in eq 7. Thus, the fast increment in the percentage of hydrogenation degree happened during the first period of the reaction. According to the layer model for diimide hydrogenation reported by Sakorn et al.,²⁵ the hydrogenation occurred from the outer layer and then into the inner particle. The gel content increased as the percentage of hydrogenation degree increased due to the linking between the rubbery chains. Unfortunately, gel formation was found during the progress of the reaction with time. It has been reported that two polymeric chains carrying epoxide groups can easily be crosslinked through the formation of ether linkage because the oxirane is easily ring-opened in alkali media, as shown in eqs 8 and 9.^{26,27} Referring to Figure 2, a new signal around 3.70 ppm during hydrogenation was attributed to the ether unit. This signal is not observed in the case of ENR. As a result, the gel content of the resultant rubber increased by increasing the percentage of hydrogenation degree. For reaction times above 8 h, the diffusion of the diimide species was retarded in the transformation of carbon–carbon double bonds to carbon–carbon single bonds due to a thicker saturated layer and the linking between the rubbery chains that acted as a barrier, thus resulting in a limited hydrogenation level.



4.4. Effect of Hydrazine Hydrate on the Hydrogenation of ENR. The influence of hydrazine (N₂H₄) used as the source for diimide production on the hydrogenation of ENR was studied over the range of 0.15–0.44 mol with a fixed amount of all other reagents under a reaction temperature of 40 °C for 6 h. With an increasing hydrazine hydrate, the percentage of hydrogenation degree was slightly increased. The main reaction is the N₂H₄/H₂O₂ reaction to produce the diimide species attached to the unsaturated ENR chains, as shown in eqs 6 and 7. Table 2 shows that more diimide molecules were

Table 2. Effect of Hydrazine Hydrate on the Hydrogenation of ENR^a

samples	N ₂ H ₄ (mol)	% HD _{residual double bond}	gel content (%)
HENR-06	0.15	67.61	40.11
HENR-07	0.18	68.35	44.91
HENR-03	0.22	73.52	45.65
HENR-08	0.29	74.27	43.07
HENR-09	0.44	77.69	40.44

^aConditions: H₂O₂, 0.22 mol; H₃BO₃, 11 mmol; gelatin, 0.22 g; T, 40 °C; time, 6 h.

generated from the redox system with an increasing hydrazine amount, thus leading to an increment in the percentage of hydrogenation degree. Above 0.22 mol of N₂H₄, the amounts of H₂O₂ were consumed to generate diimide molecules that were needed to hydrogenate the unsaturated units. Consequently, the amounts of H₂O₂ were insufficient to decompose more hydroxyl radicals. Thus, the gel content decreased with the presence of excess amounts of hydrazine hydrate.

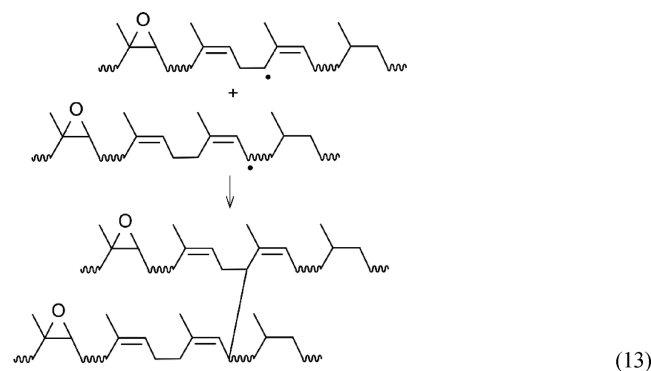
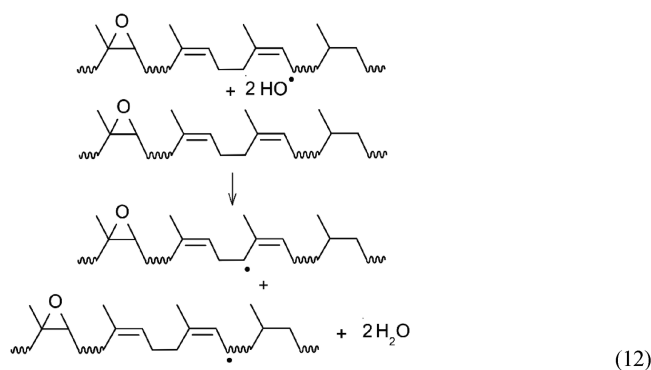
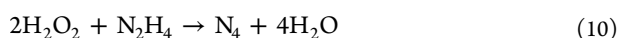
4.5. Effect of Hydrogen Peroxide on the Hydrogenation of ENR. The effect of hydrogen peroxide on the percentage of hydrogenation degree was determined over a range of 0.11–0.33 mol. The amount of H₂O₂ is a crucial factor in diimide generation. From Table 3, it can be seen that the percentage of hydrogenation degree increased as H₂O₂ increased. Both percentages of hydrogenation degree and gel content increased with an increase in the H₂O₂ amount up to 0.22 mol, and then the percentage of hydrogenation degree and gel content increased slightly. Therefore, the increasing trend may be due to the high amount of diimide generation and the high possibility of reacting with more carbon–carbon double bonds. When the amount of H₂O₂ was over 0.22 mol, the

Table 3. Effect of H₂O₂ on the Hydrogenation of ENR^a

samples	H ₂ O ₂ (mol)	% HD _{residual double bond}	gel content (%)
HENR-10	0.11	47.73	32.84
HENR-11	0.16	60.07	35.35
HENR-03	0.22	73.52	45.65
HENR-12	0.27	74.71	49.93
HENR-13	0.33	77.36	60.11

^aConditions: N₂H₄·H₂O, 0.22 mol; H₃BO₃, 11 mmol; gelatin, 0.22 g; T, 40 °C; time, 6 h.

percentage of hydrogenation degree increased slightly. It may be due to the side reaction of H₂O₂, as shown in eq 10. The gel content increased obviously with an increase in the amount of H₂O₂. The excessive H₂O₂ may be dissociated into hydroxyl radicals (HO•) that attacked the allylic proton of the *cis*-1,4-polyisoprene unit, forming a polymeric radical unit. The polymeric radicals can interact with each other to produce a crosslinking reaction, resulting in gel formation, as shown in eqs 11–13.^{20,28}



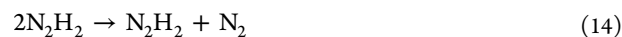
4.6. Effect of Boric Acid on the Hydrogenation of ENR.

The effect of boric acid on the percentage of hydrogenation degree was studied by varying the amount of H₃BO₃ over the range of 5.5–27.5 mmol, as shown in Table 4. So, the perusal of the results indicates that the percentage of hydrogenation degree and gel content increased rapidly with an increase in the H₃BO₃ amount up to 22.0 mmol. Then, the percentage of hydrogenation degree and gel content increased marginally. This may be due to the boric acid accelerating the diimide formation and activating the reaction of gel formation. The addition of boric acid as a catalyst could improve the disassociation of hydrazine and reduce the diimide side reactions [eqs 14 and 15].²⁹

Table 4. Effect of Boric Acid (H₃BO₃) on the Hydrogenation of ENR^a

samples	H ₃ BO ₃ (mmol)	% HD _{residual double bond}	gel content (%)
HENR-14	5.5	60.50	35.93
HENR-03	11.0	73.52	45.65
HENR-15	16.5	75.82	52.08
HENR-16	22.0	77.36	53.11
HENR-17	27.5	77.49	54.65

^aConditions: N₂H₄·H₂O, 0.22 mol; H₂O₂, 0.22 mol; gelatin, 0.22 g; T, 40 °C; time, 6 h.



4.7. Effect of Gelatin on the Hydrogenation of ENR.

The influence of the presence of gelatin was studied by using the variation in the gelatin amount over the range of 0.11–0.33 g, as shown in Table 5. The percentage of hydrogenation and gel

Table 5. Effect of Gelatin on the Hydrogenation of ENR^a

samples	gelatin (g)	% HD _{residual double bond}	gel content (%)
HENR-18	0.11	49.74	35.12
HENR-19	0.16	65.75	38.00
HENR-03	0.22	73.52	45.65
HENR-20	0.27	62.36	37.48
HENR-21	0.33	60.72	35.12

^aConditions: N₂H₄·H₂O, 0.22 mol; H₂O₂, 0.22 mol; H₃BO₃, 11 mmol; T, 40 °C; time, 6 h.

content increased with an increase in gelatin amount from 0.11 to 0.22 g. The addition of gelatin to the system can help to stabilize the catalyst on the rubber particle surface, thus increasing the percentage of hydrogenation degree. The percentage of hydrogenation degree and gel content decreased at a higher gelation amount. The presence of excess amounts of gelatin inhibited the diimide diffusion at the rubber particle surface, resulting in a decreasing percentage of hydrogenation degree.

4.8. Effect of Reaction Temperature on the Hydrogenation of ENR.

According to the Arrhenius equation, the reaction temperature usually plays an important role in hydrogenation. A series of experiments were carried out from 30 to 70 °C. Table 6 indicates the effect of the reaction temperature on the percentage of hydrogenation degree and gel content. The percentage of hydrogenation degree and gel content increased as the hydrogenation temperature increased up to 50 °C. As the reaction temperature elevated, both the

Table 6. Effect of Temperature on the Hydrogenation of ENR^a

samples	temperature (°C)	% HD _{residual double bond}	gel content (%)
HENR-22	30	43.28	30.99
HENR-03	40	73.52	45.65
HENR-23	50	86.34	62.62
HENR-24	60	88.48	63.63
HENR-25	70	89.19	63.64

^aConditions: N₂H₄·H₂O, 0.22 mol; H₂O₂, 0.22 mol; H₃BO₃, 11 mmol; gelatin, 0.22 g; time, 6 h.

activity of the reactant molecules and the probability of particle collision increased, increasing the percentage of hydrogenation degree. With an increase in temperature, H_2O_2 tended to decompose and produce hydroxyl radicals causing the cross-linking reaction triggered through hydroxyl radicals, resulting in gel formation, as shown in eqs 12 and 13. When the temperature was above 50 °C, the percentage of hydrogenation degree slightly increased because of the formation of gas bubbles during the addition of hydrogen peroxide. The gel content remained almost unchanged.

In this study, the percentage of gel content increased from 30.52 to 63.64 when the percentage of hydrogenation degree increased from 34.43 to 89.19. A similar observation was reported by Saengdee and co-workers²⁰ who also found that hydrogenated ENR samples (27 mol % degrees of hydrogenation and 17 mol % degrees of epoxidation and 25 mol % degrees of hydrogenation and 28 mol % degrees of epoxidation) were low in gel content (44.3% and 41.7%, respectively). Yusof et al.²⁸ suggested that materials with gels could be used differently as a lubricant (low gel content) or adhesive (high gel content).

4.9. Thermal Stability of the Hydrogenation of ENR.

The glass transition temperature is the temperature below which the amorphous domains of a polymer take on the characteristic properties of a glassy state: brittleness, stiffness, and rigidity. The result for the T_g is shown in Figure 4 and summarized in Table 7.

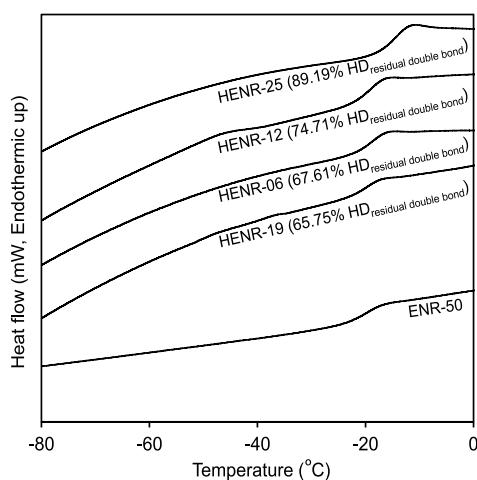


Figure 4. DSC thermograms of ENR-50, HENR-19, HENR-06, HENR-12, and HENR-25.

Table 7. Glass Transition (T_g) and Decomposition Temperature (T_{d5} , T_{d95} , and T_{max}) of ENR-50 and HENR with Varying % $HD_{residual\ double\ bond}$

samples	% $HD_{residual\ double\ bond}$	T_g (°C)	T_d (°C)		
			T_{d5}	T_{max}	T_{d95}
ENR-50		-19.6	347.0	399.0	446.7
HENR-19	65.75	-19.7	368.3	405.3	466.3
HENR-06	67.61	-18.2	370.0	421.7	469.3
HENR-12	74.71	-17.6	371.7	439.0	486.3
HENR-25	89.19	-14.3	396.7	442.0	488.3

The T_g of ENR with 50% epoxide group content was -19.6 °C. The T_g of HENR slightly increased with an increase in the percentage of hydrogenation degree. Thus, the increment in T_g of the hydrogenated product may result from a decrease in

unsaturated units (amorphous segments) by replacing the ethylene-propylene units (crystalline segments) in the polymer chain, which tends to decrease the mobility of the polymer. However, HENR still retains its rubbery behavior.

Figure 5 shows the TGA and DTG curves of ENR-50 and HENR at various % hydrogenations. The thermal degradation

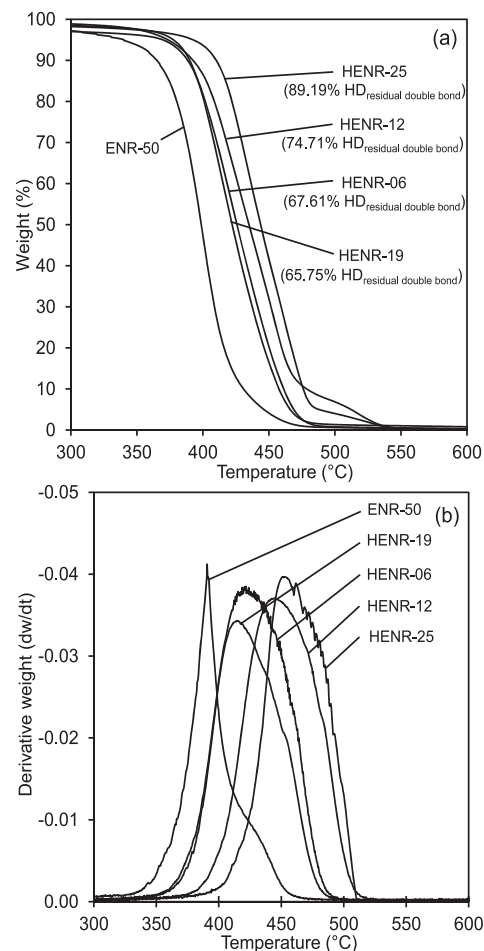


Figure 5. (a) TGA and (b) DTG thermogram of ENR-50, HENR-19, HENR-06, HENR-12, and HENR-25.

temperature of modified NR is listed in Table 7. The temperatures at 5% (T_{d5}) and 95% (T_{d95}) of its weight losses were obtained from the TGA curve, and the temperature at the maximum weight loss rate (T_{max}) was obtained from the peak of the DTG curves. It can be seen that the thermal degradation temperature of hydrogenated ENR samples increased with an increase in the percentage of hydrogenation or reduction of C=C bonds in ENR. The degradation of ENR and HENRs was similar and occurred via an overall one-step reaction and smooth weight loss curves. ENR has a T_{d5} , T_{max} , and T_{d95} of 347.0, 399.0, and 446.7 °C, respectively, while all HENRs exhibit higher degradation temperatures when compared with ENR. The T_{max} of HENRs increased from 405.3 to 442.0 °C when the percentage of hydrogenation degree increased from 65.75% (HENR-19) to 89.19% (HENR-25). The thermal degradation curves of HENRs, compared to ENR, shifted toward higher temperatures. It could be concluded that the hydrogenation of epoxidized natural rubber shows enhanced thermal stability and an increase in degradation temperature.

5. CONCLUSIONS

Hydrogenated ENR-50 with different hydrogenation degrees was prepared by the latex method. $^1\text{H-NMR}$ could determine the percentage of hydrogenation degree. TEM micrographs of the modified natural rubber particles confirmed the carbon double bond reduction. The analysis of the results showed that the increase in hydrazine hydrate, hydrogen peroxide, boric acid, and gelatin, the prolongation of reaction time, and the reaction temperature were favorable to the extent of hydrogenation. This can lead to either the formation of the ether linkage or the crosslinking reaction triggered through hydroxyl radicals. Thus, the gel content increased with an increasing degree of hydrogenation. The hydrogen peroxide amount and temperature appeared to be the main factors resulting in the gel formations. The ENR having 50% epoxide group content without hydrogenation contained around 27.54% of gel; when the percentage of hydrogenation reached 89.19%, the gel content was 63.64%. The thermal stability of the hydrogenated ENR-50, examined by TGA, was improved, and the glass transition temperature of hydrogenated ENR-50 kept increasing, which was higher than that of the original ENR-50. The hydrazine hydrate/hydrogen peroxide/boric acid as a catalyst system could result in the hydrogenation of ENR having 50% epoxide group content under a mild condition because it was carried out at atmospheric pressure and low temperatures.

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Notes

The authors declare no competing financial interest.

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