

# Hydrogenation of Unsaturated Rubbers Using Diimide as a Reducing Agent

J. Samran,<sup>1</sup> P. Phinyocheep,<sup>1,2</sup> P. Daniel,<sup>3</sup> S. Kittipoom<sup>2</sup>

<sup>1</sup>Department of Chemistry, Faculty of Science, Mahidol University, Rama VI Road, Payathai, Bangkok 10400, Thailand

<sup>2</sup>Institute of Science and Technology for Research and Development, Mahidol University, Salaya Campus, Puthamonthon, Nakornpathom, 73170 Thailand

<sup>3</sup>Laboratoire de Physique de l'Etat Condensé LPEC (UMR CNRS no. 6087) Université du Maine, Avenue Olivier Messiaen, 72085 Le Mans Cedex 9, France

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**ABSTRACT:** The hydrogenation of natural rubber (NR) and various epoxidized natural rubbers (ENR) was investigated by using diimide generated *in situ* from the thermal decomposition of *p*-toluenesulfonylhydrazide (TSH) in *o*-xylene solution at 135°C. <sup>1</sup>H-NMR analysis indicated that approximately 85–95% of hydrogenation was performed with a twofold excess of TSH. FT-IR and Raman spectroscopy were employed to confirm the microstructure characteristics of the hydrogenated rubbers. The *cis*–*trans* isomerization was also observed by <sup>1</sup>H- and <sup>13</sup>C-NMR. The signal in <sup>1</sup>H-NMR of the epoxide group of the ENR disappears after hydrogenation while the signal of the opened epoxide

ring product was detected. This may be due to the epoxide ring opening reaction caused by the *p*-toluenesulfonic acid by-product. The high temperature of the reaction condition leads to chain degradation in both NR and ENR. Thermal behaviors of the hydrogenated rubbers characterized by differential scanning calorimetry showed that the glass transition temperatures of the hydrogenated rubbers were increased about 10–20°C compared with the starting rubbers. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 16–27, 2005

**Key words:** elastomers; hydrogenation; isomerization; modification; NMR

## INTRODUCTION

Chemical modification of existing polymers has been an active field of research as it leads to polymers with altered and improved properties or production of new materials. Unsaturated polymers, especially diene rubbers, are useful targets for chemical modification, because the double bonds in the polymer chains are prone to chemical reactions such as epoxidation, halogenation, and maleinization.<sup>1</sup> However, the polymers containing olefinic units have a tendency to be low-heat-resistant materials. Hydrogenation is a useful method for the reduction of unsaturation in diene rubbers.<sup>2,3</sup> It improves the thermal and oxidative stability of their parent polymers. For instance, hydrogenated nitrile butadiene rubber (HNBR) has been known to be a new oil-resistant elastomer with superior abrasion resistance at elevated temperatures. These properties provide more applications for HNBR in the automotive, military, and aerospace industries. Hydrogenated butadiene rubber (HBR) has good aging, heat and abrasion resistance, and improved dy-

amic properties, therefore HBR is part of the rubber formulation for tire treads.<sup>4</sup>

The hydrogenation of unsaturated polymers can be performed with elemental hydrogen in the presence of a transition metal catalyst or by a noncatalytic method, using an inorganic reagent such as diimide (N<sub>2</sub>H<sub>2</sub>).<sup>1,4</sup> Special equipment is normally required to perform catalytic hydrogenation because the reaction is carried out at a high temperature under high pressure. Additionally, various factors influence the catalytic hydrogenation, such as types of catalyst that affect the selectivity of hydrogenation and solvents that influence not only the solubility of reactants and resulting products but also the activity of catalysts.

Hydrogenation of polyisoprene is a rather complicated case of unsaturated polymers. The isopropenyl groups constituting the rubber chains are trisubstituted ethylene derivatives; they should be hydrogenated with a lower rate than mono- and disubstituted ethylenes. The process is even more complicated by virtue of the high molecular mass of polyisoprene obtained from natural rubber, due to its poor segmental mobility. Unfortunately, this condition has an adverse effect on product because increasing chain stiffness causes even greater restriction of chain mobility. Therefore, the use of catalytic hydrogenation of polyisoprene requires high temperatures and pressure, considerable amounts of catalyst, and longer reaction

Correspondence to: P. Phinyocheep (scppo@mahidol.ac.th)

times.<sup>5</sup> The severe conditions of catalytic hydrogenation, i.e., high pressure and high temperature, may cause degradation and difficulty in removing residual catalysts. Therefore, a moderate condition using other mild reducing agents has been explored and is preferred. Diimide used to hydrogenate the unsaturated rubbers can be conveniently prepared at atmospheric pressure with relatively simple apparatus and procedures. It is considered a noncatalytic hydrogenation process and has become increasingly popular. Diimide can be generated from various chemicals via the oxidation of hydrazine, the decarboxylation of potassium azodicarboxylate, and the thermal treatment of arenosulfonylhydrazides.<sup>5-7</sup> Among these reducing agents, the thermal decomposition of *p*-toluenesulfonylhydrazide has been widely used to hydrogenate the unsaturated unit in diene rubbers. Mango and Lenz employed noncatalytic hydrogenation to convert BR, IR, and SBR copolymers to high-heat-resistance polymers.<sup>6</sup> Hardwood *et al.*<sup>3</sup> reported the hydrogenation of unsaturated polymers, i.e., polybutadiene and polyisoprene by using diimide as a reducing agent. They found that the complete reduction could be obtained when five moles of TSH per mole of double bonds of butadiene or isoprene units was employed. Similar results were obtained in the case of isoprene-styrene diblock copolymers.<sup>8</sup>

Natural rubber (NR) and epoxidized natural rubber (ENR) are unsaturated rubbers with excellent elastic properties. The ENR also has good oil resistance upon epoxidation. However, both NR and ENR have primary drawbacks of poor thermal and oxidative resistances due to the unsaturated unit on the backbone. Singha *et al.*<sup>9</sup> reported that catalytic hydrogenation of NR using RhCl(PPh<sub>3</sub>) catalyst increased the thermal stability of the resulting product without affecting its glass transition temperature. The hydrogenation of NR using a homogeneous catalyst prepared from nickel 2-ethylhexanoate and triisobutylaluminum can lead to 100% hydrogenation under optimum reaction conditions.<sup>10</sup> For ENR, the presence of the epoxy group should influence the reaction condition of hydrogenation and properties of the resulting rubbers. A few studies have been conducted on catalytic hydrogenation of ENR. Bhattacharjee *et al.*<sup>11</sup> hydrogenated the NR and ENR by using a homogeneous palladium-macetate catalyst and found that the rate constant of hydrogenation decreases with an increase in the epoxide content of the rubber. This article describes the hydrogenation of NR and different epoxide levels of ENR by using the diimide reducing agent generated from the decomposition of *p*-toluenesulfonylhydrazide (TSH). The progress of the reaction determined by <sup>1</sup>H-NMR, IR, and Raman techniques is reported including the *cis-trans* isomerization evidence.

## EXPERIMENTAL

### Materials

Natural rubber latex was procured from Thai Rubber Latex Corporation (Thailand) Public Company Limited. The NR for hydrogenation was obtained from precipitation of the NR latex in methanol and it was then dried under vacuum at room temperature. Different types of ENR were prepared in latex form by using *in situ* performic acid generated from hydrogen peroxide and formic acid, according to the procedure outlined in the literature.<sup>12</sup> ENR22, ENR33, and ENR40 represent ENR containing 22, 33, and 40% epoxide levels, respectively, determined by <sup>1</sup>H-NMR. *p*-Toluenesulfonylhydrazide, which is a practical grade product from Fluka, and *o*-xylene, which is a product from JT Baker, were used as purchased.

### Hydrogenation procedure

Hydrogenation of unsaturated rubbers (NR or ENR) was carried out in a 250-ml three-necked round-bottomed flask, equipped with a magnetic stirring, a reflux condenser, and a nitrogen inlet tube. A solution of 1% (w/v) rubber in *o*-xylene was used with a molar ratio of TSH to unsaturated unit ([TSH]/[C=C]) equal to 2. The reaction took place at 135°C under nitrogen atmosphere. The solution was sampled at various reaction times and precipitated in methanol. The hydrogenated product was purified by dissolution in hexane and reprecipitation in methanol. Finally, the product was dried under vacuum at room temperature.

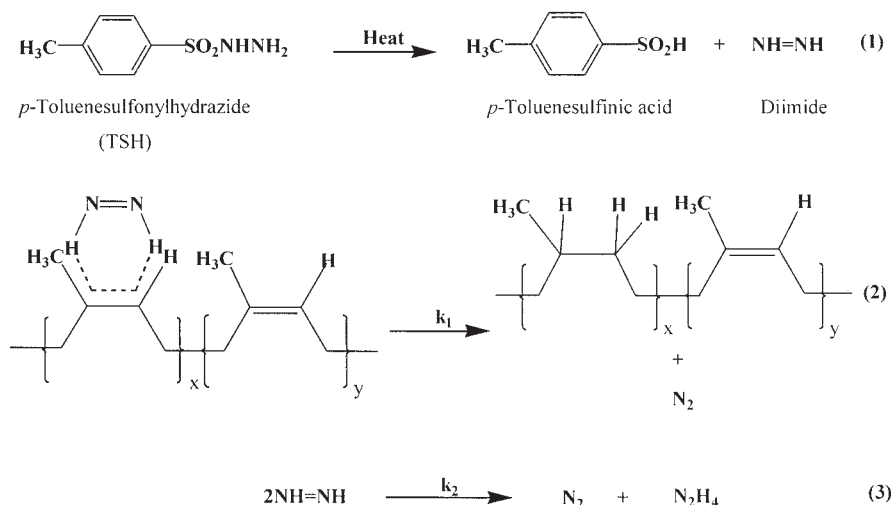
### Characterization of products

#### FT-IR spectroscopy

The chemical structure of the rubber samples was investigated by FT-IR (Perkin-Elmer System 2000 Fourier transform infrared spectrometer) spectroscopy. The samples were dissolved in distilled chloroform and then cast onto a NaCl cell. All samples were taken at 16 scans in the range of 4,000–600 cm<sup>-1</sup> with 4 cm<sup>-1</sup> resolution of spectra to obtain a good signal-to-noise ratio.

#### Raman spectroscopy

The Raman spectra of all samples were recorded on a T64000 Jobin-Yvon multichannel spectrometer adjusted to be a simple spectrograph configuration with a 600 line/nm grating. Samples were illuminated with a Coherent Argon-Krypton Ion Laser using the 647.1 nm line to avoid luminescence bands. To improve the ratio of signal/noise, each spectrum was accumulated 20 times during 30 s. The frequency range selected was 500–3,200 cm<sup>-1</sup>. Calibration of the spectrometer was



**Figure 1** Hydrogenation of polyisoprene unit by *p*-toluenesulfonylhydrazide (TSH): (1) decomposition of TSH by thermal treatment, (2) reaction of diimide and polyisoprene unit, and (3) disproportionation of diimide.

precisely checked on the  $520.2\text{ cm}^{-1}$  silicon band and the resolution of spectra can be estimated to be smaller than  $2\text{ cm}^{-1}$ .

#### Nuclear magnetic resonance spectroscopy

$^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  (Bruker DPX-300 NMR spectrometer) were used to identify the chemical structure of the rubbers before and after hydrogenation. NMR spectra were obtained from the samples dissolved in  $\text{CDCl}_3$  using tetramethylsilane (TMS) as an internal reference.

#### Determination of molecular weight by viscometry

The intrinsic viscosity,  $[\eta]$ , of samples was measured using an Ubbelohde viscometer at  $30^\circ\text{C}$ . The viscosity average molecular weight  $[M_v]$  was evaluated by the Mark–Houwink equation as shown below

$$[\eta] = KM_v^a$$

The Mark–Houwink constants,  $K = 33.1 \times 10^{-3}$  and  $a = 0.71$ , were used to estimate the  $M_v$  in toluene at  $30^\circ\text{C}$ .<sup>13</sup>

#### Differential scanning calorimeter (DSC)

The thermal behavior of the rubber sample was made on a DSC (Perkin Elmer DSC 7) under the scanning temperature from  $-100$  to  $150^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$  with the sample mass of 10 mg encapsulated in aluminium pans. The glass transition temperatures ( $T_g$ ) of hydrogenated products were measured from a DSC thermogram.

#### Thermogravimetric analysis (TGA)

The thermal stability of all samples was investigated by using TGA (Perkin–Elmer thermogravimetric analyzer 2000) in an atmosphere of nitrogen. The sample weight was 7–10 mg. The heating rate was  $10^\circ\text{C}/\text{min}$  and the temperature range was  $30$ – $500^\circ\text{C}$ .

## RESULTS AND DISCUSSION

Noncatalytic hydrogenation of NR and three types of epoxidized natural rubbers (ENR22, ENR33, and ENR40) was carried out by using 2 moles of TSH compared to the unsaturated unit. In principle, 1 mole of TSH generates 1 mole of diimide molecule under suitable condition [eq. (1) in Fig. 1]. The reduction could be conducted to highly specific hydrogen addition in a syn configuration [eq. (2) in Fig. 1]. Therefore, a 1 : 1 molar ratio should give complete hydrogenation. Several authors reported that 4 to 5 moles of hydrazide per mole of isoprene units are required for complete hydrogenation of homopolymers or copolymers containing a polyisoprene segment.<sup>6,8</sup> In our case, the molar ratio TSH/[C=C] of 2 : 1 was used to hydrogenate the unsaturated unit of NR and ENR. Partial hydrogenation is expected to occur in both cases. As described in the literature, the diimide could undergo disproportionation giving nitrogen and hydrazine as shown in eq. (3) of Figure 1. In addition, the rate of disproportionation ( $k_2$ ) was reported to be faster than that of the reaction between diimide and double bonds of diene polymers ( $k_1$ ).<sup>14</sup>

#### Hydrogenation of NR

The microstructure of HNR can be investigated by  $^1\text{H-NMR}$  as the signal of the proton adjacent to the

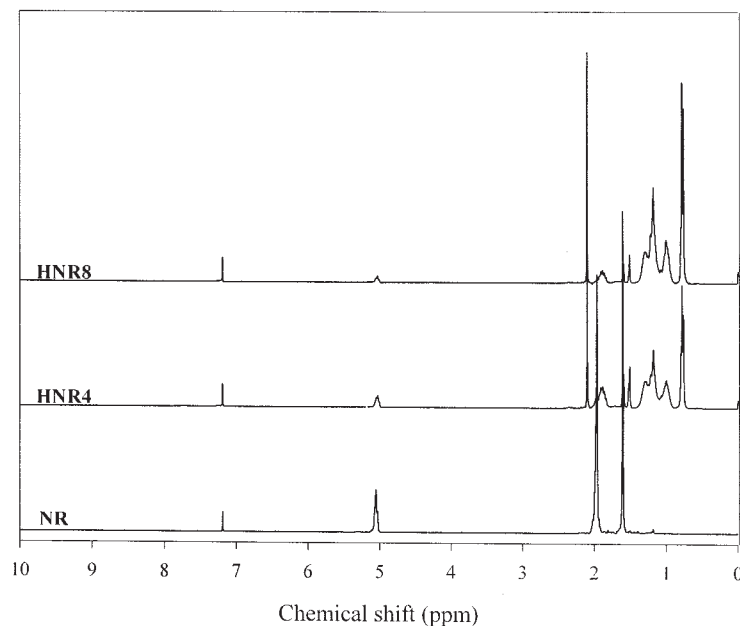


Figure 2  $^1\text{H-NMR}$  spectra of natural rubber (NR) and hydrogenated NR obtained at 4 (HNR4) and 8 h (HNR8).

double bond decreases as the hydrogenation proceeds. Figure 2 shows the  $^1\text{H-NMR}$  spectra of NR and the products of hydrogenation after 4 and 8 h of the reaction, symbolized as HNR4 and HNR8, respectively. It can be seen that the signal of the proton adjacent to the unsaturated unit of the hydrogenated NR at 5.12 ppm decreases with the increase of reaction time, as well as the decrease of signal at 1.67 ppm characteristic of the methyl proton of *cis*-1,4 polyisoprenic (PI) structure of NR. The appearance of the signals at 0.84 and 1.1–1.3 ppm, which represent methyl and methylene protons of the saturated unit, confirms the hydrogenation reaction.<sup>10</sup> The integrated areas of the signal at 5.12 and 0.84 ppm, corresponding to the olefinic unit and methyl proton of saturated unit, respectively, were used for the determination of the percentage of hydrogenation. The results of hydrogenation up to 8 h of reaction times are displayed in Table I. It can be seen that as the reaction time increased, the degree of hydrogenation increased. The  $^1\text{H-NMR}$  spectrum of the hydrogenated rubber also exhibits another extra signal at 1.60 ppm, which can be assigned to the methyl proton of *trans*-1,4-polyisoprenic unit. The percentage of the remaining double bonds in *cis* and *trans* structures of the hydrogenated samples at various reaction times is shown in Table I. The results demonstrate that, after 2 h of hydrogenation, *cis-trans* isomerization occurs and the concentration of the *trans* units increases at longer reaction times (4 h). However, at longer reaction times (6 h), the *trans* structure converts into the *cis* structure as the concentrations of the *cis* and *trans* units become equal. After a further increase in reaction time to 8 h, percent

hydrogenation increases and the *trans* unit obtained is slightly higher than the *cis* unit. It is proposed that in this system the *cis-trans* isomerization is reversible. The evidence of *cis-trans* isomerization is similar to polybutadiene and isoprene-styrene diblock copolymer, reported in the literature.<sup>8,15</sup> The formation of an unstable complex between the double bond and the *p*-toluenesulfonic acid by-product may cause the *cis-trans* isomerization reaction.<sup>8</sup> No fixation of the by-product on the rubber molecule was detected by  $^1\text{H-NMR}$ .

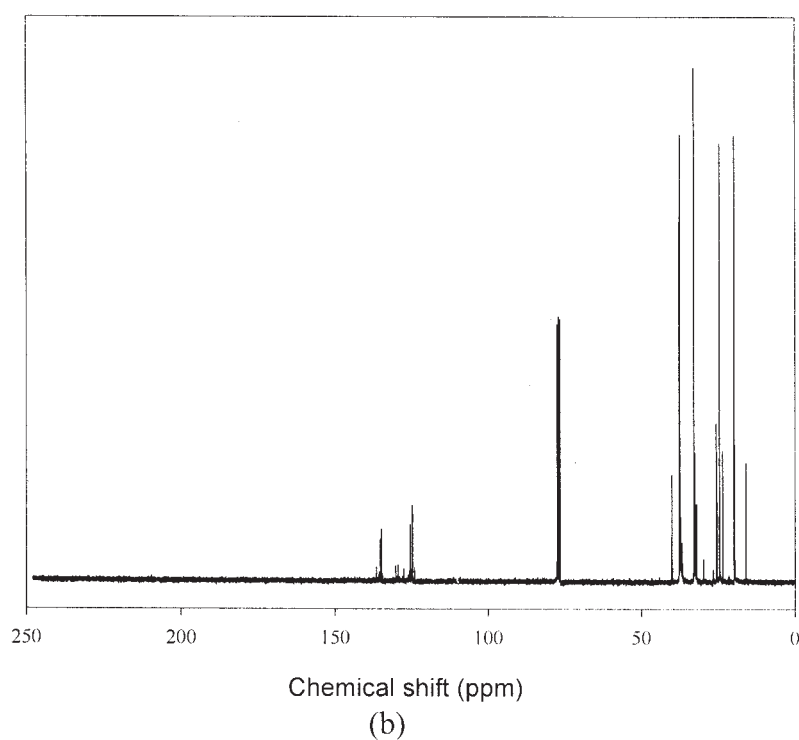
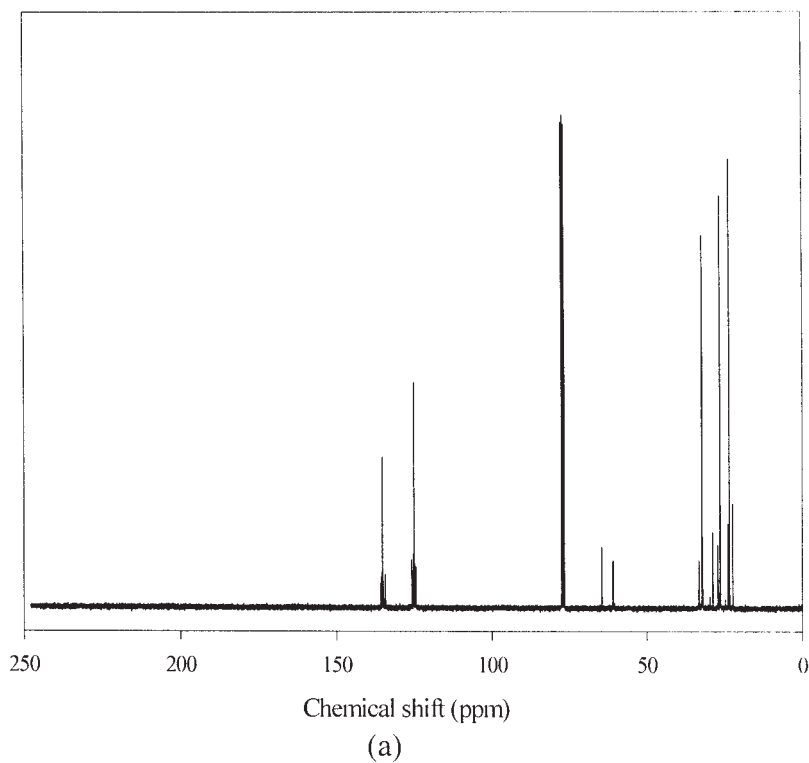
$^{13}\text{C-NMR}$  spectra of the HNR and NR are compared in Figure 3. The extra peaks at 19.5, 32.8, and 37.1 ppm are observed in the HNR sample. These signals correspond to the carbon of the methyl, methylene, and methine of the saturated unit. The observed chemical shifts are in good agreement with those reported in

TABLE I  
Results of % Hydrogenation and *cis* and *trans* Microstructures of Hydrogenated Rubbers at Various Reaction Times

Reaction time (h)	Hydrogenation <sup>a</sup> (%)	<i>Cis</i> structure <sup>b</sup> (%)	<i>Trans</i> structure <sup>b</sup> (%)
0	0	100	0
2	44.4	33.8	21.8
4	67.4	15	17.6
6	78.6	10.7	10.7
8	84.4	6.8	7.8
10	87.5	6.5	6.0

<sup>a</sup> Determined by  $^1\text{H-NMR}$ .

<sup>b</sup> Remaining double bonds in *cis* and *trans* configuration, i.e., % *cis* + % *trans* = 100 - % hydrogenation.



**Figure 3**  $^{13}\text{C}$ -NMR spectra of (a) natural rubber and (b) hydrogenated NR obtained at 8 h.

the literature.<sup>9,16</sup> The  $^{13}\text{C}$ -NMR spectrum of the partially hydrogenated product reveals evidence of the *cis-trans* isomerization of the isoprene unit in polymer chains. The carbon signals of the *cis* structure are positioned at 135.2 and 125.5 ppm while the signal at

134.9 and 124.7 ppm, corresponding to olefinic carbons of the *trans*-polyisoprenic structure, are also detected for HNR.

IR spectra of NR and HNR are depicted in Figure 4. The IR spectrum of NR exhibits two important char-



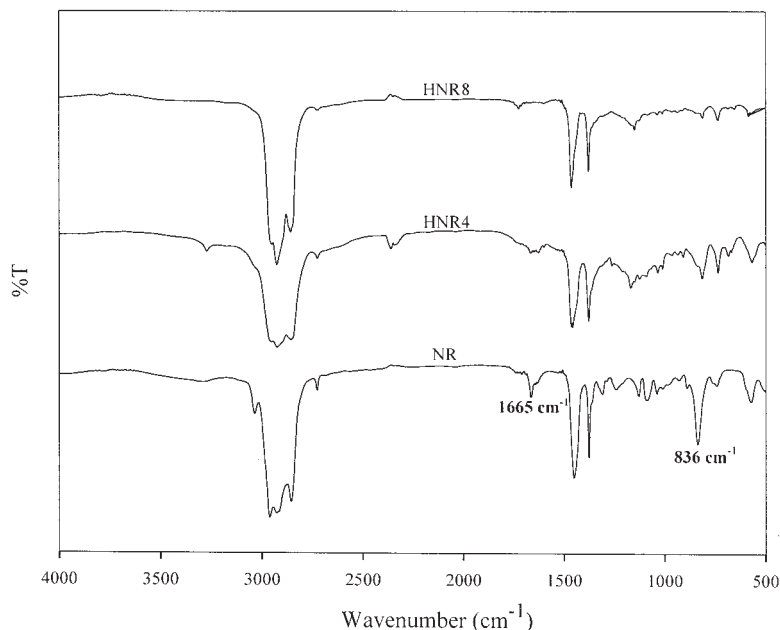


Figure 4 IR spectra of natural rubber and hydrogenated rubbers (HNR4 after 4 h and HNR8 after 8 h of reaction time).

acteristic peaks at  $1,665$  and  $836\text{ cm}^{-1}$ , attributing to the C=C stretching mode and the C-H out of plane deformation of the trisubstituted olefinic of polyisoprene, respectively. As the hydrogenation reaction proceeds, the intensity of the peaks at  $1,665$  and  $836\text{ cm}^{-1}$  are gradually decreased. Moreover, the appearance of peak at  $735\text{ cm}^{-1}$ , assigned to the  $-(\text{CH}_2)-$  groups of the hydrogenated products, is clearly observed.

Raman scattering technique can be used to follow the evolution of the hydrogenation reaction at various reaction times. The C=C stretching vibration is strongly active in Raman spectroscopy. The strong signal of C=C of NR is observed at  $1,663\text{ cm}^{-1}$  as shown in Figure 5. Upon hydrogenation, the decrease of this signal is clearly detected with the appearance of the signal at  $1,430\text{ cm}^{-1}$ , attributed to the  $-\text{CH}_2-$  deformation vibration. No alteration of the peak at  $1,452\text{ cm}^{-1}$  belonging to an asymmetric vibration of the  $-\text{CH}_3$  group in the Raman spectrum is illustrated after hydrogenation. Unfortunately, the *cis-trans* isomerization of the unsaturated unit of NR during hydrogenation cannot be detected, as the vibration frequency of the *cis* and *trans* structures of trisubstituted olefin in Raman spectrum is very close.<sup>17</sup>

### Hydrogenation of ENR

Figure 6 shows the typical  $^1\text{H-NMR}$  spectra before and after hydrogenation of ENR, containing 22 mol % of epoxidation level. Major peaks of ENR are observed in the aliphatic region at 1.6–2.03 ppm and the olefinic region at 5.12 ppm, while the oxirane group is ob-

served at 2.70 ppm. With the progress of hydrogenation, the area of the olefinic peak of hydrogenated ENR (HENR) decreases considerably compared with the starting rubber. Concurrently, a peak at 0.84 ppm assigned to the signal of the methyl proton of the saturated unit increases with the addition of reaction time. The results of hydrogenation of the three types of ENR at various reaction times are shown in Table II.

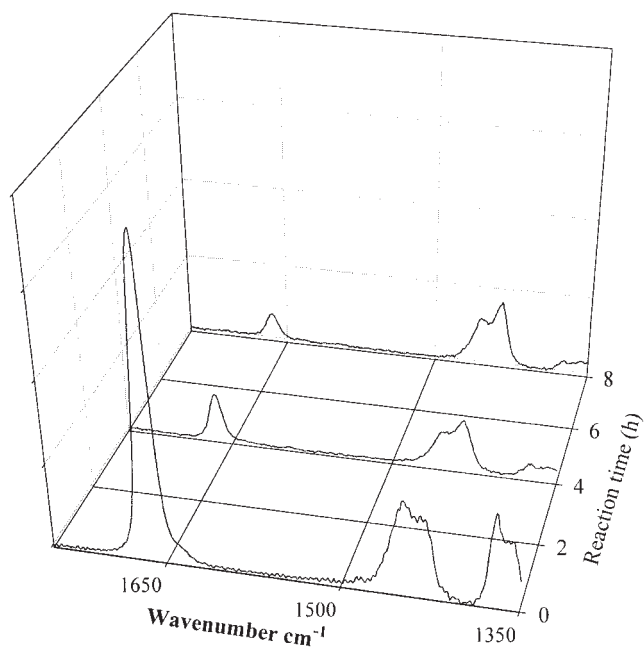
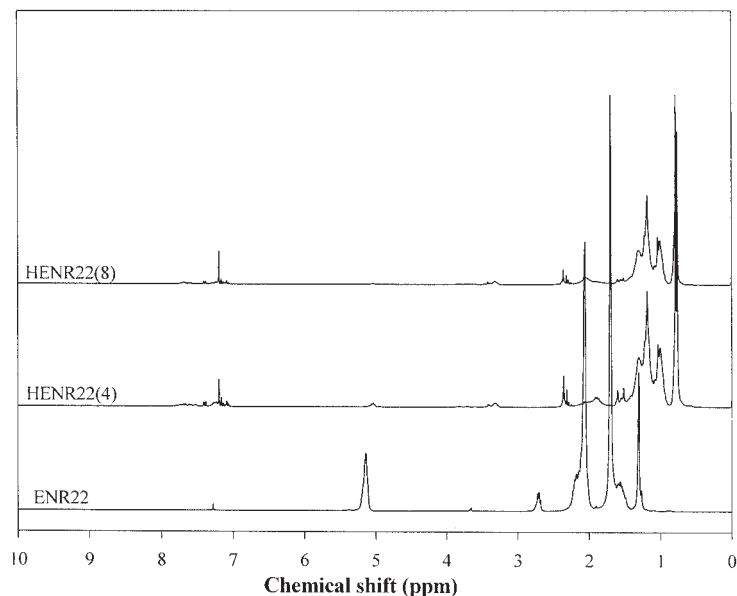


Figure 5 Raman spectra of natural rubber and hydrogenated rubbers obtained at 4 and 8 h.



**Figure 6**  $^1\text{H-NMR}$  spectra of ENR22 and hydrogenated ENR22 samples obtained at 4 and 8 h reaction times [HENR22(4) and HENR22(8)].

It can be observed that the hydrogenation of ENR is very fast at the early stage of the reaction. It seems likely that the rate of hydrogenation increases with increasing epoxide levels and much faster than the hydrogenation of NR. These results are in contrast to the work reported by Bhattacharjee *et al.*<sup>11</sup> using a homogeneous palladiumacetate catalyst for hydrogenation of ENR. In their case, they explained that the presence of the epoxide group might coordinate with the metal center, which competed with the coordination of the metal-hydride complex with the carbon-carbon double bond of the rubber, hence decreasing the rate of hydrogenation when the amount of the epoxide group increased. But in our case, the diimide generated from the decomposition of TSH directly react with the double bond of the polyisoprenic unit, which is preferably at the *cis* structure. In the case of NR, there was *cis-trans* isomerization, which might be due to the formation of an unstable complex between

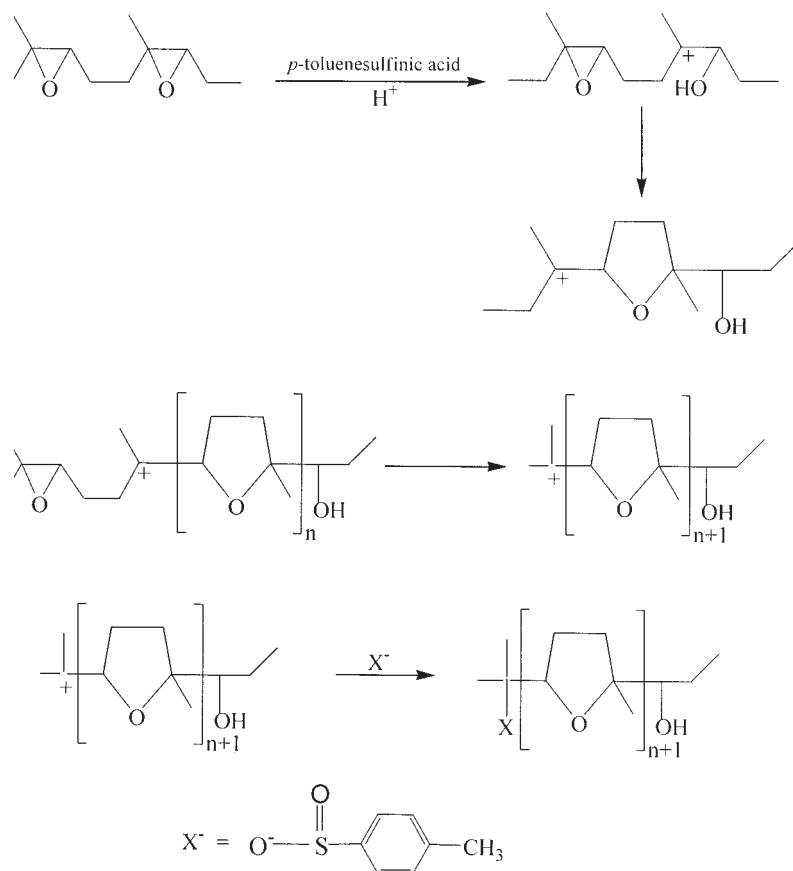
the double bond and *p*-toluenesulfinic acid by-product. But in the case of ENR, the formation of the epoxide ring-opened product and the addition of *p*-toluenesulfinic acid on the rubber chain were found, which will be discussed later in this section. Therefore, it can be proposed that the by-product might not interfere much at the double bond during hydrogenation reaction but rather it goes to the epoxide group on the molecular chain. Therefore, by increasing the epoxide content, the possibility that the *p*-toluenesulfinic acid encounters the epoxide unit increases, resulting in a decrease in the interference at the double bond of the rubber chain, therefore the hydrogenation reaction of ENR is much faster than that of NR. It was found that the signal of the proton at 5.12 ppm almost disappears at the 6-h reaction time in all cases of ENR. It may be postulated that the degree of hydrogenation is about 100% at this duration.

It is also noted in Figure 6 that the signal of the proton at 2.7 ppm disappears in all HENRs. The observation of extra signals in  $^1\text{H-NMR}$  at 1.83, 3.40, and 3.87 ppm can be assigned to signals of a methylene proton of a large membered ring, a proton at the  $\alpha$ -position of the hydroxyl group, and a methine proton. The epoxide ring-opened product may occur by the influence of *p*-toluenesulfinic acid by-product, followed by the furanization process as schematized in Figure 7. The epoxide ring is protonated, followed by the formation of the ring-opened product containing carbocationic intermediate. The epoxide ring at the adjacent unit then reacts with the carbocationic site, forming a furan unit. Propagation of furanization then proceeds with the other epoxide groups. A termina-

**TABLE II**  
Results of % Hydrogenation of Various Types of Epoxidized Natural Rubbers<sup>a</sup> at Various Reaction Times

Reaction time (h)	Hydrogenation (%)		
	ENR22 <sup>a</sup>	ENR33 <sup>a</sup>	ENR40 <sup>a</sup>
0	0	0	0
2	71.3	78.0	89.0
4	92.9	89.2	95.9
6	96.2	96.0	98.3
8	97.7	97.4	99.3

<sup>a</sup> Contain 22, 33, and 40 mole % epoxide groups, respectively.



**Figure 7** Schematic representation of the furanization of epoxidized 1,4-polyisoprene.

tion reaction can then occur by the fixation of the *p*-toluenesulfinate anionic group, resulting in the fixation of *p*-toluenesulfonic acid by-product onto the rubber chain. The formation of secondary epoxide ring-opened product so-called furanization also occurred on the preparation of epoxidized natural rubber when high concentrations of peroxyacid and elevated temperatures were employed.<sup>18,19</sup> The <sup>1</sup>H-NMR spectrum of the hydrogenated ENR reveals the signal at 7.70 ppm, corresponding to the signal of aromatic ring of *p*-toluenesulfonic group.<sup>3</sup> This signal is not observed in the case of HNR.

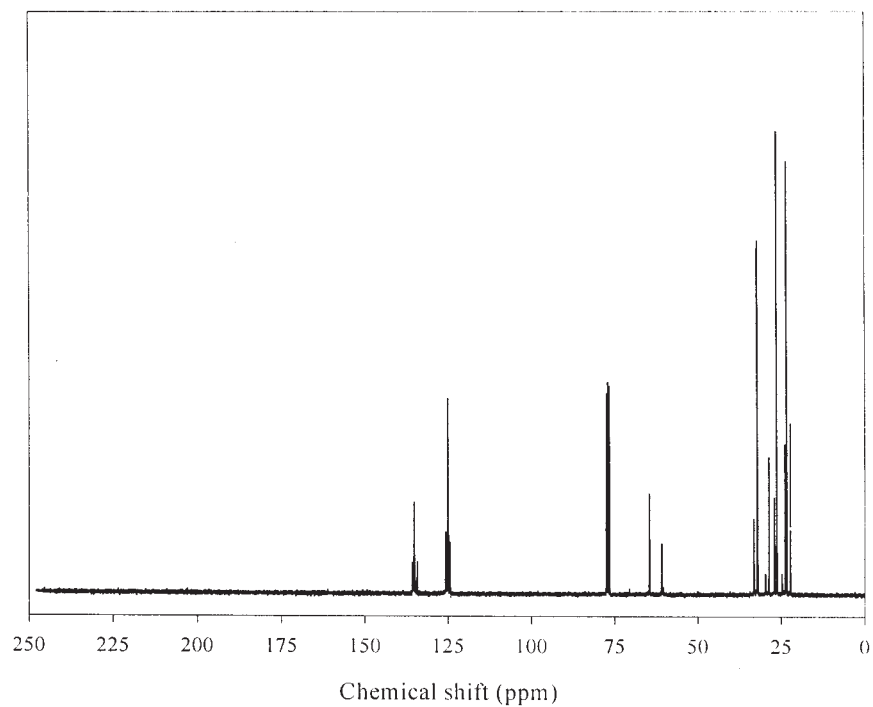
The <sup>13</sup>C-NMR spectrum of partially epoxidized natural rubber is shown in Figure 8(a). The characteristics of ENR are observed at 60.8 and 64.5 ppm, attributed to the methine carbon and the quaternary carbon resonances of the oxirane ring, respectively. The peaks at 126 and 135 ppm are the olefinic double-bond carbons in the unmodified polyisoprene units. Similar to HNR, the <sup>13</sup>C-NMR spectrum of HENR in Figure 8(b) exhibits signals at 37.5, 32.8, and 19.7 ppm. These results are assigned to the methine carbon of the saturated unit and carbons of methyl and methylene, respectively. The <sup>13</sup>C-NMR spectrum of HENR also supports evidence of furan ring formation at 82 ppm.<sup>20</sup>

Infrared spectra of ENR and HENR were recorded in the wavenumber range of 500–3,500 cm<sup>-1</sup>, as

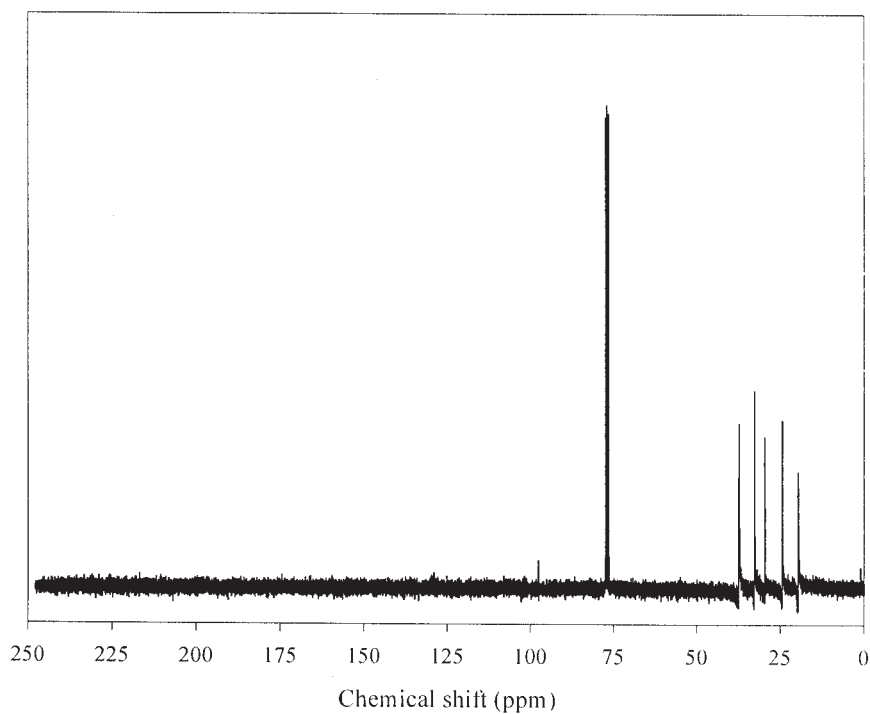
shown in Figure 9. The –CH<sub>2</sub> deformation vibration is exhibited in the region of 1,452 cm<sup>-1</sup>. A sharp peak appears at 1,377 cm<sup>-1</sup> due to the deformation vibration of the –CH<sub>3</sub> group. Two distinct peaks for the C–O–C of epoxy group are observed at 870 and 1,250 cm<sup>-1</sup> of ENR while the out of plane deformation of *cis* double bond is positioned at 836 cm<sup>-1</sup>. The IR spectrum of HENR reveals the decrease of signals at 1,665 and 836 cm<sup>-1</sup>, contributing to the C=C bond and the characteristic of *cis*-polyisoprene in the backbone. The characteristic of the oxirane ring in IR spectra also disappears after hydrogenation, as a result of ring opening during hydrogenation as proposed earlier. The strong absorption band at 3,450 cm<sup>-1</sup> is the O–H stretching of the hydroxy group. The IR spectrum of HENR also contains the signal contributing to SO<sub>2</sub> asymmetric and symmetric stretching at 1,334 and 1,145 cm<sup>-1</sup>, respectively. These signals are not eliminated after several precipitations in nonsolvent. This evidence supports the fixation of *p*-toluenesulfonic acid on the ENR backbone. The peaks at 811 and 1,035 cm<sup>-1</sup> correspond to the *p*-tolyl aromatic ring.<sup>21</sup>

The characterization of microstructures of ENR and HENR was also carried out by Raman spectroscopy as shown in Figure 10. This shows typical Raman spectra of ENR and HENR. Similar to hydrogenation of NR, it can be obviously seen that the peak at 1,663 cm<sup>-1</sup>





(a)



(b)

**Figure 8**  $^{13}\text{C}$ -NMR spectra of (a) ENR22 and (b) hydrogenated ENR22.

corresponding to the C=C bond of ENR decreases significantly after hydrogenation, while the peak at  $1,452\text{ cm}^{-1}$  belonging to an asymmetric vibration of

the  $\text{CH}_3$ -group did not alter after hydrogenation. From Raman scattering, the bands at  $1,330$  and  $1,152\text{ cm}^{-1}$  are depicted as asymmetric and symmetric -C-

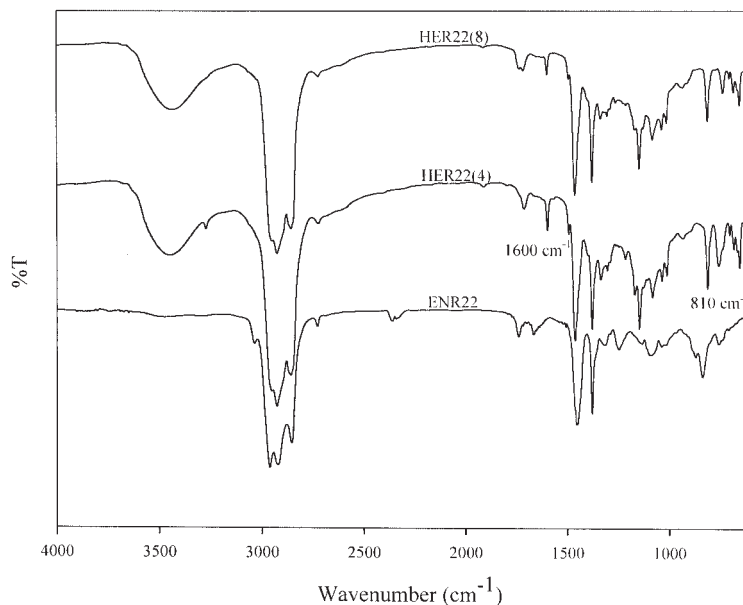


Figure 9 IR spectra of ENR22 and hydrogenated ENR22 samples obtained at 4 and 8 h.

SO<sub>2</sub>-C-vibration, respectively. The appearance of the band at 1,592 cm<sup>-1</sup>, assigned to the C=C stretching mode of aromatic ring, may confirm that *p*-toluenesulfonic acid attacks the rubber backbone of ENR.

#### Side reactions

Beside the *cis-trans* isomerization of C=C in the case of NR, the treatment of NR with TSH at 135°C causes the

chain cleavage as the percent hydrogenation increases. The decrease of viscosity average molecular weight of the HNR is observed as shown in Table III. Similar results of chain degradation are obtained in the case of hydrogenation of ENR by TSH. The *cis-trans* isomerization cannot be observed for HENR. The *p*-toluenesulfonic acid by-product of the decomposition of TSH induced the epoxide ring-opening reaction of ENR, leading to formation of furan and the fixation of the by-product on the rubber chain as described by IR, <sup>1</sup>H-NMR, and Raman spectroscopy.

#### Thermal behavior

TGA of NR, ENR, and the hydrogenated derivatives was measured under nitrogen atmosphere. TGA thermograms of NR and HNR are illustrated in Figure 11. The HNR begins to lose its weight starting from

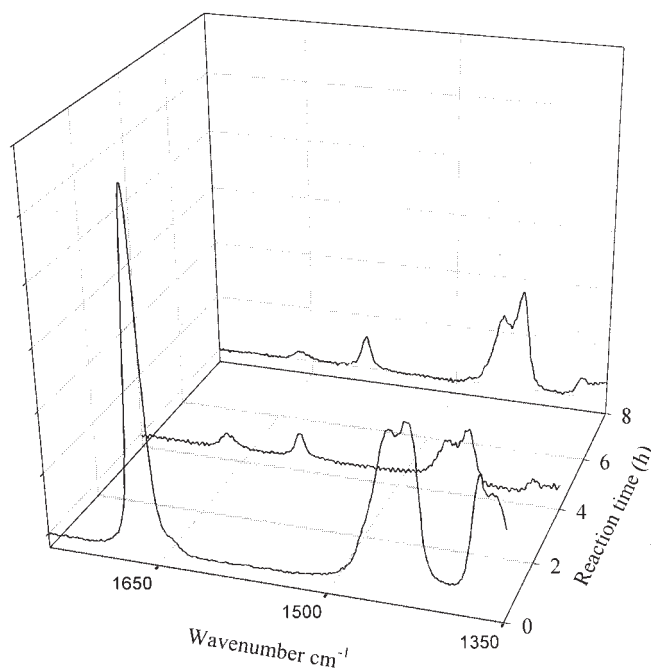
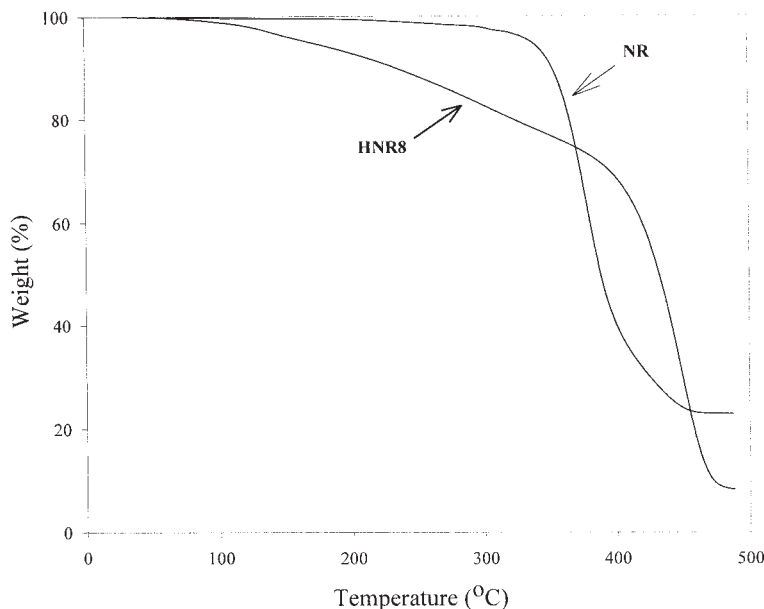


Figure 10 Raman spectra of ENR22 and hydrogenated ENR22 samples obtained at 4 and 8 h.

TABLE III  
Results of Glass Transition Temperature and Decomposition Temperature of NR, ENR, and Hydrogenated Rubbers

Sample	$M_v$	Hydrogenation (%)	$T_g$ (°C)	$T_d$ (°C)
NR	912,000	—	-66.1	377
HNR8	288,000	86.7	-42.7	449
ENR22	—	—	-40	381
HENR22(8) <sup>a</sup>	—	97.7	-31.1	450
ENR33	—	—	-37.6	390
HENR33(8) <sup>a</sup>	—	97.4	-14.4	449
ENR40	—	—	-36	388
HENR40(8) <sup>a</sup>	—	99.3	-1.5	446

<sup>a</sup> Hydrogenation was carried out during 8 h.



**Figure 11** TGA thermograms of natural rubber (NR) and hydrogenated natural rubber (HNR).

around 100°C at about 20%, the complete decomposition temperature of HNR is around 450°C, which is higher than that of the NR (about 350°C). One reason may be the  $M_v$  of the HNR ( $M_v = 288,000$ ) is much lower than that of the NR ( $M_v = 912,000$ ). For another reason, the HNR is the partial hydrogenation product of NR, therefore the residual unsaturated units that are located in a random manner in the molecular chain might be degraded in the first place, while the rigid part obtained after hydrogenation can resist the high temperature applied for a longer time. The decomposition temperatures ( $T_d$ ) of the hydrogenated products of ENR are higher than those of the starting rubbers by about 60–70°C (Table III).

The heat required for molecular deformation of polymers, i.e., glass transition temperature ( $T_g$ ), was recorded on DSC.  $T_g$  of the HNR and HENR are shown in Table III. It was found that the  $T_g$  of the rubber is increased by 20–30°C after hydrogenation. The increase in  $T_g$  results from the higher amount of saturated units, that is, the segmental mobility decreases. In addition, the *trans* microstructure obtained by *cis-trans* isomerization of residual double bonds may also result in the enhancement of  $T_g$  in the case of the hydrogenated NR. For HENR,  $T_g$  increases with higher epoxide contents in the starting sample. The result shows that  $T_g$  of HENR based on 40 mol % of epoxide content is higher than that of HENR (22 and 30 mol % of epoxide level). This might be because the rigid part in the rubber chains of HENR40 after hydrogenation contains a higher amount of the furan ring structure, which leads to less segmental mobility of the molecular chain.

## CONCLUSION

The hydrogenation of natural rubber and various epoxidized natural rubbers were investigated by using diimide generated *in situ* from the thermal decomposition of *p*-toluenesulfonylhydrazide in *o*-xylene solution at 135°C. The percentage hydrogenation was determined by  $^1\text{H-NMR}$  technique. The microstructure of the hydrogenated product was observed by IR,  $^1\text{H-}$ , and  $^{13}\text{C-NMR}$  as well as Raman techniques. The *cis-trans* isomerization was also observed from  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra in the case of hydrogenated NR, while furanization and addition of *p*-toluenesulfinic acid on the HENR were obviously detected. Thermal behaviors of the hydrogenated rubbers characterized by differential scanning calorimetry showed that the glass transition temperatures of the hydrogenated rubbers were increased about 10–20°C compared with the starting rubbers.

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