

IN SITU HYDROGENATION OF LIQUID EPOXIDIZED NATURAL RUBBER USING DIIMIDE

(Penghidrogenan *In Situ* Getah Asli Cecair Terepokside Menggunakan Diimida)

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Abstract

A low-molecular-weight liquid epoxidized natural rubber (LENR) was prepared through photosensitized degradation of epoxidized natural rubber with 50 mol percent of epoxy content (ENR-50). LENR was modified into hydrogenated liquid epoxidized natural rubber (HLENR) via *in situ* thermal degradation of arylsulfonyl hydrazide as a hydrogenating agent. The chemical structures of LENR and HLENR were characterized using Fourier transform infrared (FTIR) and ¹H nuclear magnetic resonance (NMR) spectroscopies. The thermal behaviour of LENR and HLENR were analysed using thermogravimetric analysis (TGA). The molecular weight and polydispersity index (PDI) of LENR and HLENR were determined using gel permeation chromatography (GPC). The parameter studies on the hydrogenation of LENR were investigated based on the source of diimide, weight ratios of LENR: *p*-toluenesulfonyl hydrazide (TSH), temperature, reaction time and solvent of the reaction. The highest conversion of hydrogenation was achieved at 130 °C for 4 hours reaction time, with 1:1 weight ratio of LENR: TSH using *o*-xylene as a solvent.

Keywords: hydrogenation, liquid natural rubber, epoxidized, hydroxylated

Abstrak

Getah asli cecair terepokside (LENR) dihasilkan melalui penguraian fotopemeka yang dijalankan ke atas getah asli terepokside yang mempunyai 50 mol% kandungan epoksi (ENR-50). LENR dihidrogenkan kepada LENR terhidrogen (HLENR) melalui penguraian terma *in situ* dengan menggunakan agen penghidrogenan iaitu arilsulfonil hidrazida. Struktur kimia LENR dan HLENR dicirikan menggunakan spektroskopi inframerah transformasi Fourier (FTIR) dan resonans magnet nukleus ¹H. Sifat terma LENR dan HLENR dikaji menggunakan analisis termogravimetri (TGA). Berat molekul dan indeks kepoliserakan (PDI) dikaji menggunakan kromatografi penelapan gel (GPC). Kajian mengenai penghidrogenan LENR dikaji berdasarkan beberapa parameter tindak balas seperti sumber diimida, nisbah berat LENR: *p*-toluenasulfonil hidrazida (TSH), suhu, masa dan pelarut tindak balas. Penukaran penghidrogenan yang tertinggi diperolehi apabila tindak balas dijalankan pada suhu 130 °C selama 4 jam, dengan nisbah berat LENR:TSH sebanyak 1:1 serta menggunakan *o*-xilena sebagai pelarut.

Kata kunci: penghidrogenan, getah asli cecair, terepokside, terhidroksil

Introduction

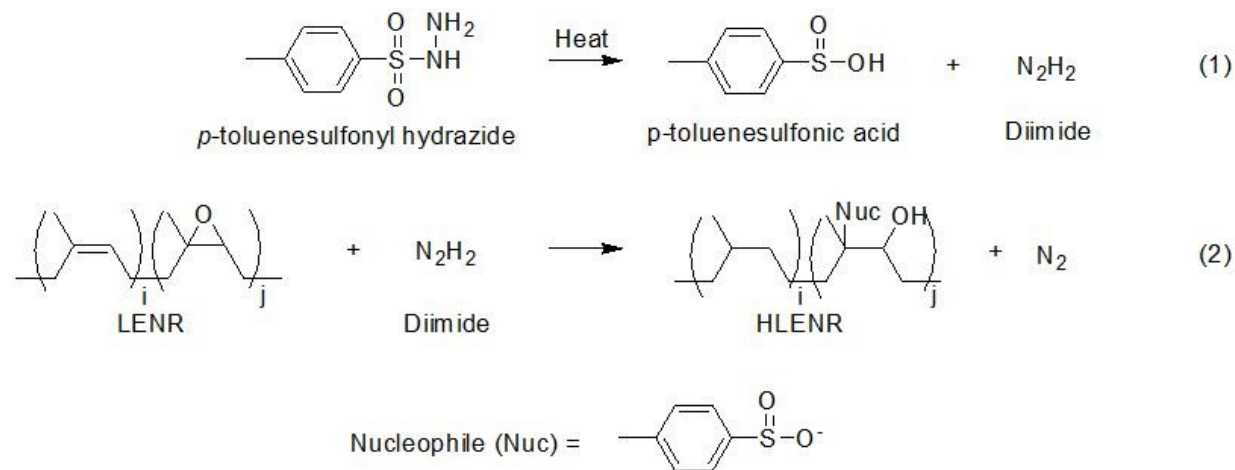
Natural rubber (NR) produced from *Hevea brasiliensis* trees is a crucial raw material for the production of industrial products such as tyres, gloves, adhesives, sealants, medical devices and consumer products [1-3]. NR had been used in various fields of applications due to its high elasticity and flexibility, resilience, abrasion resistance, efficient heat

dispersion, impact resistance and tear strength [4, 5]. However, NR deteriorates against ozone, sunlight, and weathering due to the unsaturated in its polymeric chains [4, 6]. Thus, chemical modifications of NR are very important in order to enhance the chemical, physical and mechanical properties of NR.

Previously, there are many chemical modifications that had been done to NR such as, hydrogenation, epoxidation, halogenation, grafting, metathesis and cyclization [1]. Among these modifications, hydrogenation of NR is significance to improve the properties in terms of its thermal stability, weather resistance and oxidative [7]. There are two types of hydrogenation that had been done to NR, which are catalytic and non-catalytic. Catalytic hydrogenation requires high pressure autoclave and the presence of transition metal catalyst systems such as nickel, titanium, rhodium, ruthenium or palladium [8 – 11]. On the other hand, non-catalytic hydrogenation method is more convenient because it only requires a simple apparatus preparation at atmospheric pressure and employed diimide intermediate from thermal decomposition of arylsulfonyl hydrazide [12]. Mahittikul et al. reported an *in situ* hydrogenated natural rubber latex via thermolysis of *p*-toluenesulfonyl hydrazide (TSH) [13].

Epoxidized natural rubber (ENR) is a chemically modified form of NR, having epoxy functional group and also showed slightly similar drawbacks as NR due to its remaining unsaturated double bonds in polymeric backbones. Hence, hydrogenation of ENR will overcome the drawbacks by saturating the remaining double bonds and ring opened the epoxy groups into hydroxyl groups. Research on the hydrogenation of ENR conducted in latex form requires a deproteinization process to remove the protein in the rubber [11]. Although, chemical reactions conducted in latex form often encountered with problems of latex stability, uneven particle size distribution and contamination due to non-rubber components of natural rubber latex [14]. To overcome the problems encountered by latex, liquid form of ENR is the best solution. The liquid form of ENR which is liquid epoxidized natural rubber (LENR), a partially depolymerized ENR can be produced via mechanical milling, chemical degradation initiated by potassium peroxodisulfate and photooxidation initiated by ultraviolet irradiation [15].

In the present work, we made an attempt to hydrogenate liquid epoxidized natural rubber through the thermal degradation of TSH. The diimide (N_2H_2) generated from thermolysis of TSH gives hydrogen molecules (H_2) to the $C=C$ and $C-O-C$ of the LENR (Scheme 1) [13, 16, 17]. We also optimize the effect of TSH concentration, temperature, solvent and reaction time. The analysis of the hydrogenated products have been performed using FTIR, 1H NMR, TGA and GPC.



Scheme 1. Hydrogenation of LENR using TSH

Materials and Methods

Materials

Epoxidized natural rubber-50 (ENR-50) was supplied from Malaysian Rubber Board. Toluene, *o*-xylene, hexane and methanol were supplied by R&M Chemicals. Methylene blue, rose Bengal, *p*-toluenesulfonyl hydrazide (TSH) and 2,4,6-trimethylbenzenesulfonyl hydrazide (MSH) were purchased from Sigma Aldrich.

Synthesis of LENR

LENR was prepared by photosensitized degradation of ENR-50 [18]. 1 kg of ENR-50 was cut into smaller cube and soaked in 2 L of toluene overnight. Methylene blue (0.10 g) and Rose Bengal (0.15 g) were dissolved in methanol before added into rubber mixture. The mixture was stirred continuously using a mechanical stirrer in the presence of visible light at 70 °C for 10 to 14 days. The mixture was centrifuged to separate the gel formation.

Hydrogenation of LENR

TSH was used as a diimide source in the hydrogenation reaction. Different amounts of TSH were added to a fixed volume of LENR solution at TSH/LENR weight ratios of 1:1 to 3:1 to determine the effect of TSH concentration on the percentage of hydrogenation. Each mixture was heated to temperature ranging from 90 °C until 150 °C and stirred for 1–5 hours to study the effect of reaction time on the percentage of hydrogenation. The products were filtered and coagulated with hexane to remove the residual TSH. Finally, it was dried in a vacuum oven to remove any remaining solvent. In this work, we also studied the effect of solvent by using *o*-xylene and toluene on the percentage of hydrogenation LENR.

Characterization

Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy (Perkin Elmer) was used to determine any changes in the functional groups that might have been induced by the hydrogenation reaction. The samples were analysed in the wavenumber range of 4000 – 600 cm⁻¹. NMR spectroscopy was used to examine the microstructure of the product. Samples were dissolved in deuterated chloroform (CDCl₃) for measurements with the Fourier Transform Nuclear Magnetic Resonance 400MHz Cryoprobe (FT-NMR 400MHz Cryo). Integration of signals from proton NMR (¹H NMR) was used to estimate the percentage of conversion of the hydrogenation, content of the epoxy group, content of the residual double bonds and content of the hydroxyl group of HLENR as shown in equation 1 – 4 below:

$$W_{\text{conversion}} [\text{mol}\%] = \frac{I_{1.25/2}}{I_{1.25/2} + I_{2.71} + I_{3.35} + I_{5.14}} \times 100 \quad (1)$$

$$X_{\text{epoxy}} [\text{mol}\%] = \frac{I_{2.71}}{I_{1.25/2} + I_{2.71} + I_{3.35} + I_{5.14}} \times 100 \quad (2)$$

$$Y_{\text{double bond}} [\text{mol}\%] = \frac{I_{3.35}}{I_{1.25/2} + I_{2.71} + I_{3.35} + I_{5.14}} \times 100 \quad (3)$$

$$Z_{\text{hydroxyl}} [\text{mol}\%] = \frac{I_{5.14}}{I_{1.25/2} + I_{2.71} + I_{3.35} + I_{5.14}} \times 100 \quad (4)$$

where *I* is the integration at chemical shifts 1.25, 2.71, 3.35 and 5.14 ppm that correspond to methylene of hydrogenated isoprene units, epoxy methine of epoxidized-*cis*-1,4-isoprene units, hydroxylated methine and olefinic methine of unsaturated *cis*-1,4-isoprene units, respectively, in ¹H NMR spectrum [11].

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed on TGA/SDTA 851°, Mettler Toledo. Gel permeation chromatography (GPC) was employed to determine the molecular weight (*M_w*) and polydispersity index (PDI) of LENR and HLENR (Waters 1515 Isocratic HPLC Pump equipped with a Waters 2414 Refractive Index detector, Waters Corporation, USA).

Results and Discussion

Hydrogenated liquid epoxidized natural rubber (HLENR) was produced via non-catalytic hydrogenation of LENR using diimide intermediate from arylsulfonyl hydrazide such as *p*-toluenesulfonyl hydrazide (TSH) and 2,4,6-trimethylbenzenesulfonyl hydrazide (MSH).

Microstructure of LENR and HLENR

Figure 1 depicts the FTIR spectra of LENR and HLENR. The main features of LENR appears at 1251 and 870 cm^{-1} are attributed to the symmetric and asymmetric stretching of the epoxide ring, respectively. The absorption at 1664 and 828 cm^{-1} in LENR spectrum correspond to C=C stretching and olefinic C-H bending, respectively. Both LENR and HLENR spectra show broad absorption bands at 3600-3100 cm^{-1} due to O-H stretching, and the intensities of the absorption bands for HLENR are intense than LENR [19]. The increment of HLENR intensity at 3600-3100 cm^{-1} arised due to the ring opening of epoxy groups into hydroxyl groups.

^1H NMR spectra of LENR and HLENR were shown in Figure 2. In LENR spectrum, six major signals appeared at 1.30, 1.68, 2.10, 2.20, 2.71 and 5.14 ppm were assigned to methyl of unsaturated *cis*-1,4-isoprene units (*b*), methyl of epoxidized-*cis*-1,4-isoprene units (*e*), methylene of *cis*-1,4-isoprene units (*c*), methylene of epoxidized-*cis*-1,4-isoprene units (*f*), epoxy methine (*d*) and olefinic methine (*a*), respectively. HLENR spectrum showed the appearance of hydrogenated methylene (*a'*) hydroxylated methine (*h*) and hydroxyl proton (*i*) at chemical shifts 1.25, 3.35 and 3.90 ppm, respectively. The signals appeared at 2.30-2.50 ppm on HLENR spectrum correspond to benzylic protons of the remaining TSH and the nucleophile ($\text{CH}_3\text{C}_6\text{H}_5\text{SO}_2^-$) [12, 17, 20].

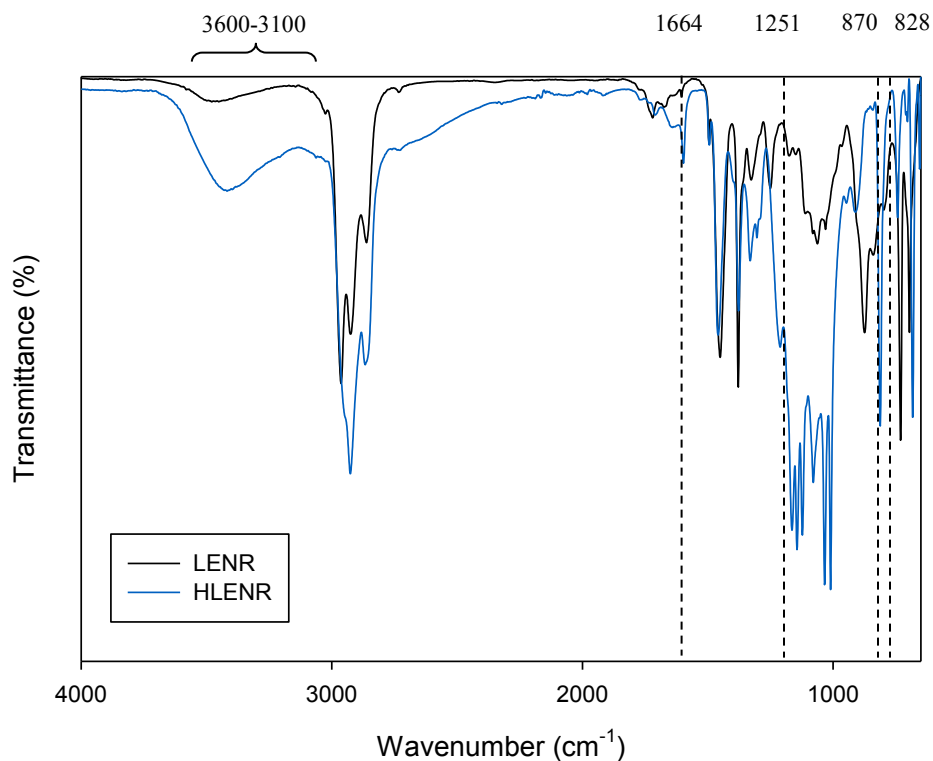


Figure 1. FTIR spectra of LENR and HLENR

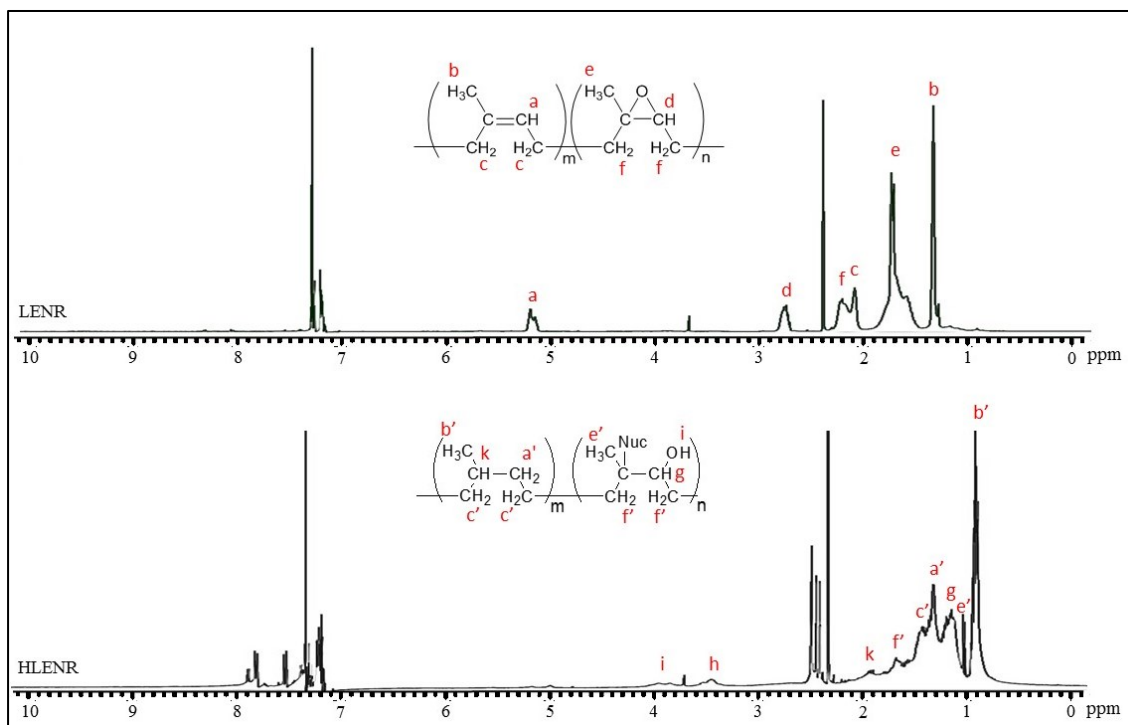


Figure 2. ¹H NMR spectra of LENR and HLENR

Parameter Studies on Hydrogenation of LENR: Effect of diimide source

p-toluenesulfonyl hydrazide (TSH) and 2,4,6-trimethylbenzenesulfonyl hydrazide (MSH) had been study to produce diimide for the non-catalytic hydrogenation of LENR (Table 1). TSH showed a higher conversion of hydrogenation which is 90.29%. The hydrogenation of LENR using MSH produced more hydroxyl content caused by the stronger nucleophilic attack in the epoxide ring compare to TSH. The content of epoxy group and residual double bonds decreased as the conversion of hydrogenation increased. However, the content of hydroxyl for hydrogenation LENR using MSH was higher compared to TSH because, MSH was quite unstable to undergo hydrogenation.

Table 1. Effect of diimide source on hydrogenation of LENR

Experiment	Diimide Source	Conversion of Hydrogenation (mol%)	Content of Epoxy Group (mol %)	Content of Residual Double Bonds (mol %)	Content of Hydroxyl Group (mol %)
1	TSH	90.29	0.81	0.45	8.46
2	MSH	40.80	7.94	3.80	47.47

Condition: weight ratio of TSH: LENR = 1:1, temperature = 130 °C, reaction time = 4 hours, solvent = *o*-xylene

Effect of LENR: TSH weight ratio

The weight ratio of LENR: TSH was varied for 1:1, 1:2 and 1:3. Table 2 showed the increase in the amount of TSH, resulted to reduce the conversion of hydrogenation of LENR. Higher amount of TSH was expected to undergo side reaction which interrupt the hydrogenation of LENR and reduced the hydroxyl content. The epoxy content increased as the conversion of hydrogenation decreased.

Table 2. Effect of LENR: TSH weight ratio on hydrogenation of LENR

Experiment	Weight Ratio of LENR:TSH	Conversion of Hydrogenation (mol%)	Content of Epoxy Group (mol%)	Content of Residual Double Bonds (mol%)	Content of Hydroxyl Group (mol%)
3	1:1	90.29	0.81	0.45	8.46
4	1:2	56.27	40.00	0.95	2.77
5	1:3	56.27	42.16	0.16	1.40

Condition: temperature = 130 °C, reaction time = 4 hours, solvent = *o*-xylene

Effect of temperature

The effect of temperature was investigated from 90 °C until 150 °C (Table 3). From 90 °C until 130 °C, the conversion of hydrogenation gradually increase to the highest conversion of hydrogenation. TSH solubility with *o*-xylene increased with the increasing temperature because rate decomposition of TSH increased. However, when the temperature was increased to 150 °C, the conversion of hydrogenation slightly dropped due to the occurrence of unduly wasteful side reaction [13]. The content of epoxy group and residual double bonds decreased while content of hydroxyl increased as the conversion of hydrogenation increased.

Table 3. Effect of temperature on hydrogenation of LENR

Experiment	Temperature (°C)	Conversion of Hydrogenation (mol%)	Content of Epoxy Group (mol%)	Content of Residual Double Bonds (mol%)	Content of Hydroxyl Group (mol%)
6	90	46.78	37.27	11.42	4.53
7	110	53.44	35.74	5.49	5.33
8	130	90.29	0.81	0.45	8.46
9	150	86.6	0.18	0.77	12.45

Condition: weight ratio of TSH: LENR = 1:1, reaction time = 4 hours, solvent = *o*-xylene

Effect of reaction time

Table 4 showed the increasing trend of reaction time has increased the conversion of hydrogenation. At the reaction of 5 hours, the conversion of hydrogenation almost the same with the conversion of hydrogenation for 4 hours because the reaction already completed at 4 hours reaction time. The content of epoxy group and residual double bonds decreased while content of hydroxyl increased when the conversion of hydrogenation increased.

Table 4. Effect of reaction time on hydrogenation of LENR

Experiment	Reaction Time (hours)	Conversion of Hydrogenation (mol%)	Content of Epoxy Group (mol%)	Content of Residual Double Bonds (mol%)	Content of Hydroxyl Group (mol%)
10	1	33.71	56.78	5.87	3.64
11	2	53.94	42.95	1.26	1.85
12	3	78.99	15.75	2.15	8.70
13	4	90.29	0.81	0.45	8.46
14	5	90.11	0.01	1.29	8.59

Condition: weight ratio of TSH: LENR = 1:1, temperature = 130 °C, solvent = *o*-xylene

Effect of solvent

There were two types of solvent had been studied on the hydrogenation of LENR. Based from Table 5, *o*-xylene resulted in higher conversion of hydrogenation due to *o*-xylene is more likely to dissolve TSH and easily produced diimide. However, the hydrogenation of LENR using toluene produced a lower conversion of hydrogenation but higher in hydroxyl group.

Table 5. Effect of solvent on hydrogenation of LENR

Experiment	Solvent	Conversion of Hydrogenation (mol%)	Content of Epoxy Group (mol%)	Content of Residual Double Bonds (mol%)	Content of Hydroxyl Group (mol%)
15	Toluene	46.45	~0	2.24	51.31
16	<i>o</i> -xylene	90.29	0.81	0.45	8.46

Condition: weight ratio of TSH: LENR = 1:1, temperature = 130 °C, reaction time = 4 hours

Thermal analysis of LENR and LNR-OH

TGA and DTG thermograms of LENR and HLENR were shown on Figure 3 and 4, respectively. LENR and HLENR thermograms showed multi step changes. The first step changes (30 °C – 310 °C) of LENR and HLENR were due to the loss of solvent, moisture and low-molecular-weight oligomers [21]. After 310 °C to 400 °C, the weight loss were due to the unstable intermediates in hydrogenation of LENR. The Figure 4 clearly showed the maximum degradation temperature of LENR and HLENR at 413 °C and 445 °C, respectively. The maximum degradation temperature of HLENR showed a higher temperature compared to LENR because of the hydrogenation reaction had proven to saturate the unsaturated part of LENR.

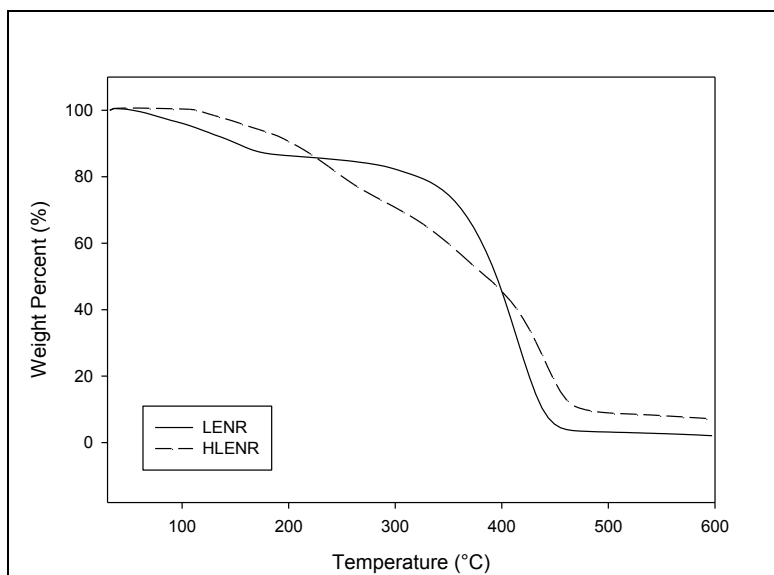


Figure 3. TGA thermograms of LENR and HLENR

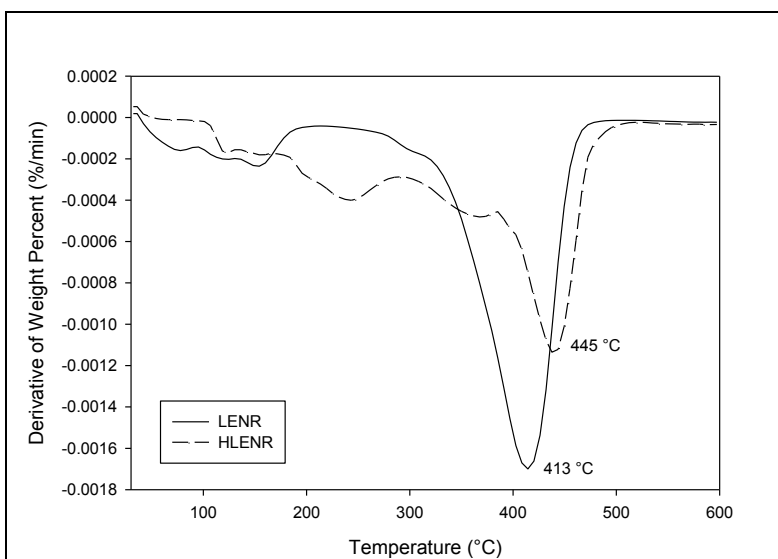


Figure 4. DTG thermograms of LENR and HLENR

Molecular Weight of LENR and LNR-OH

Table 6 showed the number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) of LENR and HLENR. M_w of LENR and HLENR were reduced from 47900 g/mol to 17000 g/mol due to the high reaction temperature in the hydrogenation of LENR. The high reaction temperature depolymerized the polymeric chains of HLENR.

Table 6. Molecular weight of LENR and HLENR

Sample	M_n	M_w	PDI
LENR	18200	47900	2.63
HLENR	4600	17000	3.69

Conclusion

Non-catalytic hydrogenation of LENR using diimide was efficiently conducted to produce hydrogenated rubber containing hydroxyl group. The optimum reaction condition was achieved using TSH as diimide source with 1:1 of LENR: TSH weight ratio at 130 °C for 4 hours of reaction time using *o*-xylene as solvent.

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