

Research Article

Studies on Hydrogenation of Liquid Natural Rubber Using Diimide

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Liquid natural rubber (LNR) is a depolymerized natural rubber (NR) which consists of shorter polymeric chains and lower molecular weight ($M_w < 10^5$). Hydrogenated LNR (HLNR) was synthesized via the thermal decomposition of *p*-toluenesulfonyl hydrazide (TSH) or 2,4,6-trimethylbenzenesulfonyl hydrazide (MSH). The LNR and HLNR structures were characterized by Fourier-transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopies. The percentage of hydrogenation was calculated from NMR spectrum. The optimum percentage of hydrogenation (>90%) was achieved by manipulating the reaction parameters such as sources of diimide, TSH concentration, solvent, and reaction time. The optimum condition was 3 : 1 weight ratio of TSH/LNR in *o*-xylene at 130°C in 4-hour reaction period.

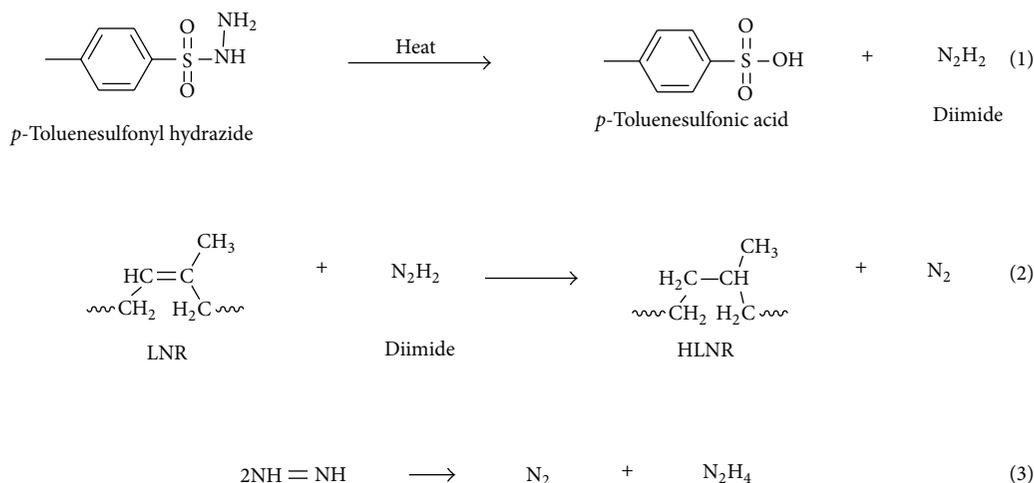
1. Introduction

Natural rubber (NR) is one of the most valuable renewable resources extracted from the rubber tree, *Hevea brasiliensis*. The main components in NR are rubber particles (30–40%), water (55–65%), protein (2–3%), sterol glycosides (0.1–0.5%), resin (1.5–3.5%), ash (0.5–1.0%), and carbohydrate (1.0–2.0%) [1, 2]. NR is well known for its outstanding elastic property and high mechanical strength. It has attracted great interest in various fields and is used extensively in many applications and products. However, NR has poor heat resistance and low resistance to weather and chemical reagents due to its unsaturated C=C bonds, thus limiting its use in outdoor application. To increase the level of saturation, hydrogenation, a simple chemical modification, can enhance the stability against thermal and oxidative degradation of NR.

Liquid natural rubber (LNR) is defined as a modified natural rubber having similar microstructure as NR but with shorter polymeric chains and lower molecular weights ($M_w < 10^5$). The presence of a reactive and unsaturated bond in

LNR offers many possibilities for chemical modifications. In contrast to dried rubber, the use of LNR is advantageous for the production of various products because it can be processed easily and requires less energy [3]. LNR has two major advantages over the synthetic rubbers. Firstly, the synthetic route for the preparation of LNR is more green/renewable and more energy efficient than other technologies such as metathesis degradation and cleavage by periodic acid/lead tetra acetate [4–6]. Secondly, NR can be obtained from natural resources (green route).

Hydrogenation is one of the most efficient methods to transform the unsaturated part of natural rubber (NR) into saturated moiety and alter and improve physical properties of unsaturated polymers. The hydrogenation of NR can be carried out by two main methods such as catalytic (homogeneous and heterogeneous) and noncatalytic hydrogenation. Catalytic hydrogenation is the reaction of catalyst that will activate hydrogen molecules and the carbon-carbon double bond species [7]. In the presence of catalysts, hydrogenation of polymers is difficult and generally unsatisfactory. This



SCHEME 1: Hydrogenation of LNR using TSH.

is due to the high tendency of polymer molecules to be absorbed on catalysts, thus rendering the catalysts inefficient or ineffective. Double bonds in the polymers can be reduced successfully when high temperatures, large amounts of catalyst, and high hydrogen pressures are employed, but chain cleavage is also promoted by severe hydrogenation conditions and low molecular weight products [8–10].

A noncatalytic hydrogenation is a method using diimide molecule that releases hydrogen molecules to the carbon-carbon double bond of the unsaturated polymers. The reaction is carried out under milder conditions compared to catalytic hydrogenation, such as low pressure and requiring simple apparatus [11, 12]. The diimide molecule can be generated by methods such as the oxidation of hydrazine, the thermal decomposition of arenesulfonylhydrazides, and the photochemical irradiation of 1-thia-3,4-diazolidine-2,5-dione [13]. *p*-Toluenesulfonyl hydrazide (TSH) and 2,4,6-trimethylbenzenesulfonyl hydrazide (MSH) have been used to hydrogenate the carbon-carbon double bond of unsaturated polymer [14].

The objectives of this work were to study the noncatalytic hydrogenation of liquid natural rubber via the thermolysis of TSH and MSH. The diimide generated from thermal decomposition of TSH releases hydrogen molecule to the C=C of the LNR (Scheme 1) [15, 16]. We also studied the effect of diimide source, TSH concentration, solvent, and reaction time against the percentage of hydrogenation. The reaction scheme of this reaction was shown in Scheme 1.

2. Materials and Methods

2.1. Materials. In this work, we used natural rubber from Rubber Research Institute of Malaysia (RRIM). Toluene (>99%), *o*-xylene (>99%), ethanol (95%), and methanol (>99.8%) were supplied by R&M Chemicals (Himachal Pradesh, India). Methylene blue ($\geq 95\%$), rose Bengal (95%), *p*-toluenesulfonyl hydrazide (TSH) (97%), and 2,4,6-trimethylbenzenesulfonyl hydrazide (MSH) (97%) were purchased from Sigma Aldrich (Missouri, USA).

2.2. Hydrogenation of LNR. LNR with 10% of dry rubber content was prepared [17]. TSH was used as a diimide source in the hydrogenation reaction. Different amounts of TSH were added to a fixed volume of LNR solution at TSH/LNR 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 a temperature 130°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 ethanol 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 diimide source by using MSH. *o*-Xylene and toluene were used to identify the effect of solvent on the percentage of hydrogenation LNR.

2.3. Characterization. Fourier-transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopies were used to determine the structure of the products formed. Attenuated total reflectance-Fourier-transform infrared (ATR-FTIR) spectroscopy (Perkin Elmer) was used to determine any change in the functional groups that might have been induced by the hydrogenation reaction. The samples were analyzed in transmittance mode within the range 4000–600 cm^{-1} . NMR spectroscopy was used to examine the microstructure of the product. Integration of signals from proton NMR (^1H NMR) was used to estimate the percentage of conversion from LNR to HLNR. Samples were dissolved in CDCl_3 for measurements with the Fourier-Transform Nuclear Magnetic Resonance 600 MHz Cryoprobe (FT-NMR 600 MHz Cryo). The degradation temperatures of samples were determined by using thermogravimetric analysis (TGA) and differential thermal analysis (DTA) (TGA/SDTA 851^e, Mettler Toledo, Switzerland). Gel permeation chromatography (GPC) was used to investigate the molecular weight (M_w) and polydispersity index (PDI) of LNR and HLNR (Waters 1515 Isocratic HPLC Pump equipped with a Waters 2414 Refractive Index detector, Waters Corporation, USA).

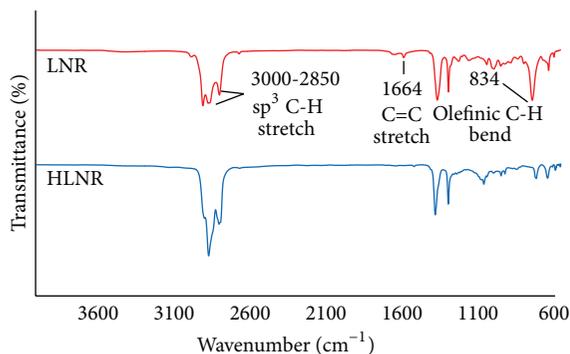


FIGURE 1: FTIR spectra of LNR and HLNR (95.9%).

3. Results and Discussion

3.1. Structure of LNR and HLNR. The microstructures of LNR and HLNR at 95.9% hydrogenation were characterized by FTIR, and the spectra are shown in Figure 1. The main peaks are located at 3000–2850, 1664, and 834 cm^{-1} corresponding to sp^3 C–H stretching, C=C stretching, and olefinic C–H bending, respectively. The intensity of sp^3 C–H stretching is increased as a result of hydrogenation of LNR whereby the intensity of the other two peaks is decreased due to the reduced amount of C=C and olefinic C–H. Several peaks between 1500 and 900 cm^{-1} are more intense than they appear in the LNR spectrum, and the stronger signals in that range originated from the paraffin C–H bending vibrations owing to the increasing number of alkane groups after hydrogenation.

The ^1H NMR spectra of LNR and HLNR are shown in Figure 2. The spectrum of LNR shows signals at 1.73, 2.02, and 5.12 ppm, which are assigned to the protons of unsaturated methyl ($\text{R}-\text{CH}_3$), unsaturated methylene ($\text{R}-\text{CH}_2-\text{R}$), and olefinic ($\text{R}-\text{CH}=\text{C}-\text{R}_2$), respectively. After hydrogenation, these signals are reduced and new signals appear in the range of 0.85–1.39 ppm, corresponding to the methane (CH_4), methylene ($-\text{CH}_2-$), and methyl ($-\text{CH}_3$) groups. The percentage of hydrogenation was calculated from the ratio between the integration of the olefinic proton signal and integration of the signals in the range of 0.8–2.2 ppm. The signals around 2.3–2.5 ppm correspond to benzylic proton from *o*-xylene, toluene, and TSH. Meanwhile, the signal at 3.7 ppm corresponds to the ethanol used for coagulation. In conclusion, the FTIR and NMR spectra show the microstructural changes that occurred during hydrogenation.

3.2. Thermal Analysis of LNR and HLNR. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out to determine the degradation temperature of LNR and HLNR. According to Figure 3, below 316°C, LNR thermogram slightly decreased at the early stage because of the evaporation of toluene in LNR. HLNR is quite stable below 398°C. Thermograms of TGA and DTA showed that the degradation of LNR occurred in two stages, while HLNR occurred in one stage. The first stage degradation of LNR

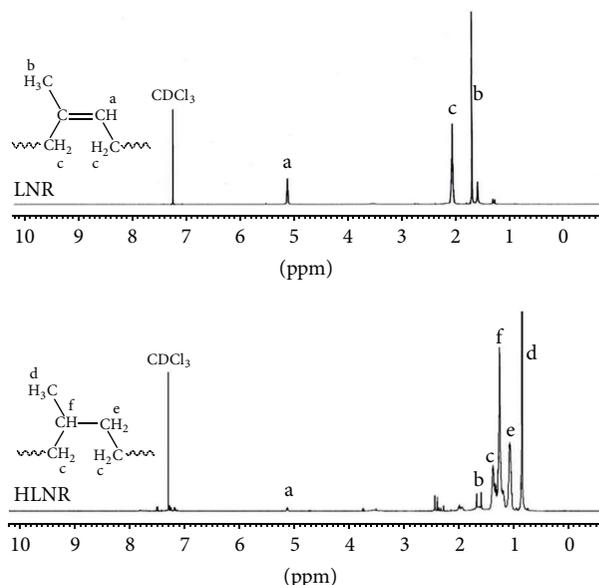


FIGURE 2: ^1H NMR spectra of LNR and HLNR (95.9%).

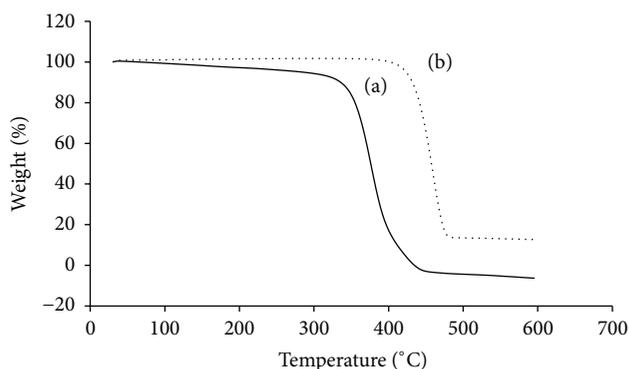


FIGURE 3: TGA thermograms of (a) LNR and (b) HLNR at 95.9% of hydrogenation.

started at 316°C and ended at 403°C. In this stage, a weight loss of 78.37% was observed. The second stage degradation of LNR started at temperature above 403°C until 444°C. During this stage, the weight loss was 17.16%. Beyond 444°C, the weight loss during this stage was 4.04% that corresponded to the cyclized rubber [18].

Meanwhile, the degradation of 95.9% HLNR started at 398°C and ended at 473°C. From the thermograms of DTA (Figure 4), the degradation temperatures of LNR (374°C) and HLNR at 95.9% (462°C) can be seen more clearly by the maximum peaks in the thermograms. Based from the result obtained, hydrogenation reaction had been proven to increase the thermal stability of LNR with increasing percentage of hydrogenation having higher degradation temperature.

3.3. Molecular Weight of LNR and HLNR. Gel permeation chromatography (GPC) is a separation method based on relative size for polymers. GPC is used to determine the

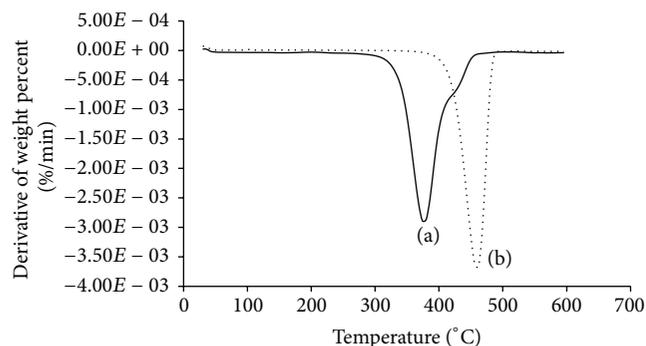


FIGURE 4: DTA thermograms of (a) LNR and (b) HLNR at 95.9% hydrogenation.

molecular weight and PDI of LNR and HLNR. The number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index (PDI) of LNR and HLNRs are listed in Table 1. The M_w of natural rubber is more than 10^7 [19]. The M_w and PDI of LNR were 88 400 u and 8.11, respectively. After hydrogenation, the M_w and PDI of HLNRs reduced due to the high reaction temperature (130°C) and long reaction time (4 hours) [16]. However, the percentage of hydrogenation did not give significant difference in M_w and PDI, since the reactions were done in the same reaction temperature and time.

3.4. Effect of Diimide Source. Several experiments were conducted by using different sources of diimide (TSH and MSH). According to Cusack et al., the thermal decomposition of MSH is 24 times that of TSH. MSH is a better diimide source for the hydrogenation of LNR compared to TSH due to its decomposition rate. Besides that, MSH also produces a more stable system [20]. In this work, we used TSH and MSH to study the effect of diimide sources on the percentage of hydrogenation. Table 2 shows the data of this study. By the weight ratio of 1:1 between LNR and sources of diimide, MSH gives a higher percentage of hydrogenation, 68.4%, in a shorter reaction time which is only 50 minutes. Otherwise, TSH only gives 41.4% of hydrogenation even after 4 hours of reaction time. It indicated that MSH can perform faster hydrogenation reaction compared to TSH due to its higher rate of decomposition. The other factor that can attribute to the result is the amount of reactants used to conduct the experiment.

3.5. Effect of TSH Concentration. The weight ratio of TSH to LNR was varied from 1:1 until 3:1 in order to study the influence of TSH concentration on percent of hydrogenation, while the other parameters are kept constant. Table 3 shows that increasing weight ratio of TSH to LNR will gradually increase the percentage of hydrogenation. From the analysis of NMR spectroscopy, the optimum weight ratio was achieved at 3:1 since the hydrogenation level exceeded 90%. Higher amount of TSH provides more source of hydrogen, hence increasing its hydrogenation percentage. In conclusion,

TABLE 1: Molecular weight and PDI of LNR and HLNR.

Sample	M_n	M_w	PDI
LNR	10 900	88 400	8.11
HLNR (41.4%)	28 400	67 000	2.36
HLNR (72.5%)	26 900	55 600	2.07
HLNR (95.9%)	25 900	58 800	2.27

TABLE 2: Effect of diimide source on the hydrogenation of LNR.

Experiment	Source of diimide	Percentage of hydrogenation (%)	Reaction time
1	TSH	41.4	4 hours
2	MSH	68.4	50 minutes

Condition: weight ratio of (TSH/MSH)/LNR = 1:1, $T = 130^\circ\text{C}$, and solvent = *o*-xylene.

TABLE 3: Effect of TSH concentration on the hydrogenation of LNR.

Experiment	Weight ratio of TSH/LNR	Percentage of hydrogenation (%)
3	1:1	41.4
4	2:1	72.5
5	3:1	95.9

Condition: source of diimide = TSH, $T = 130^\circ\text{C}$, solvent = *o*-xylene, and time = 4 hours.

TABLE 4: Effect of solvent on the hydrogenation of LNR.

Experiment	Solvent	Percentage of hydrogenation (%)
6	Toluene	72.6
7	<i>o</i> -Xylene	95.9

Condition: source of diimide = TSH, weight ratio of TSH/LNR = 3:1, $T = 130^\circ\text{C}$, and time = 4 hours.

the percentage of hydrogenation is directly proportional to weight ratio of TSH/LNR.

3.6. Effect of Solvent. A few of reactions were carried out to study the effect of solvent used on the degree of hydrogenation of LNR. Whilst the other parameters are being fixed, the solvent used is swapped from toluene to *o*-xylene to investigate the effect of solvent used. Based on TSH/LNR ratio of 3:1 at 130°C in 4-hour reaction period, *o*-xylene is more effective as a solvent (95.9% hydrogenation) compared to toluene (72.6% hydrogenation) with the same reaction parameters. By using toluene, hydrogenation above 90% only can be achieved after 6-hour reaction time. Table 4 illustrates the comparison of the hydrogenation percentage between toluene and *o*-xylene. TSH is likely to dissolve in *o*-xylene to a greater extent than toluene and easily produces diimide that reacts with carbon-carbon double bonds to achieve a higher percentage of hydrogenation [16]. For the conclusion, *o*-xylene is a better solvent to use compared to toluene for

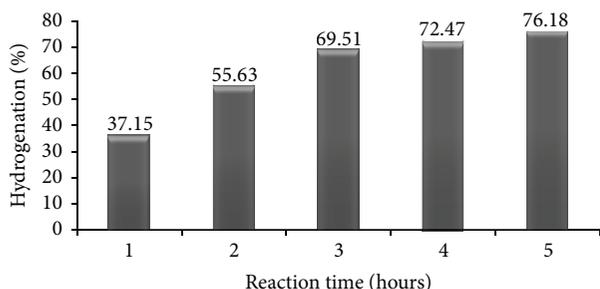


FIGURE 5: Effect of reaction time on the hydrogenation of LNR. Condition: source of diimide = TSH, weight ratio of TSH/LNR = 2 : 1, $T = 130^{\circ}\text{C}$, and solvent = *o*-xylene.

getting hydrogenation above 90% in this study because the reaction time needed is shorter.

3.7. Effect of Reaction Time. The effect of reaction time on LNR hydrogenation was investigated by varying the reaction time from 1 to 5 hours. Weight ratio TSH/LNR, temperature, and solvent used were kept constant at 2 : 1, 130°C and *o*-xylene, respectively. From 1 to 3 hours of reaction time, the increments are significantly increased, but on the 4th and 5th hours, there are only small increments recorded (Figure 5). In 1 to 3 hours, degree of hydrogenation is increased rapidly as the time increased. At 4 hours of reaction time, the hydrogenation increases slightly since the diimide source is insufficient to obtain the optimum hydrogenation followed by the 5th hour. On the bright side, the increase trend of degree of hydrogenation still can be seen, which concludes that the percentage of hydrogenation is directly proportional to the reaction time.

4. Conclusions

In summary, a TSH/LNR weight ratio of 3 : 1 yielded a hydrogenation percentage of 95.9% after 4 hours of reaction at 130°C with *o*-xylene as solvent. LNR's thermal stability had been proven to increase from 374°C to 462°C after 95.9% conversion of hydrogenation.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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