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# Mild Approach for Non-Catalytic Hydrogenation of Liquid Natural Rubber Using 2,4,6-Trimethylbenzenesulfonyl Hydrazide as the Diimide Source

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This article reports an efficient, mild-temperature method for the hydrogenation of liquid natural rubber (LNR). The hydrogenation of LNR was studied using diimide generated *in situ* from the thermolysis of 2,4,6-trimethylbenzenesulfonyl hydrazide (MSH) in *o*-xylene at 100°C. The effects of reaction temperature, reaction time, solvent, and MSH/LNR weight ratio on the percentage of hydrogenation were evaluated. ^{1}H NMR analysis revealed that ~80% hydrogenation was achieved with a weight ratio of MSH: LNR = 1:1 at 100°C in *o*-xylene within 60 min.

## Introduction

Natural rubber (NR) is a renewable material harvested from the sap of rubber trees, *Hevea brasiliensis*, and contains polyisoprene as its major component.[1] NR has been widely used in automobile and adhesive industries, due to its superior tensile strength, excellent elasticity, high tear resistance, low permanent set, and waterproof nature. However, due to the large amount of double bonds in its chain structure, NR is susceptible to oxidative and thermal degradation, ozonolysis, and extreme weathering. In order to improve the thermal stability of NR, chemical modification *via* hydrogenation can be performed to produce highly saturated NR. The desired product of the hydrogenation reaction should withstand high temperature conditions and therefore could be used in various applications, such as rubber blending and vulcanization.[2]

Typically, NR has an average weight molecular weight ($M_w$) of ~$2.5 \times 10^6$ that must be reduced during manufacturing processes. Low-molecular-weight NR can be easily modified into various useful products. One example is liquid natural rubber (LNR), which is a reduced form of NR with short polymeric chains and molecular weight lower than $10^5$.[3] The short polymeric chain of LNR is more advantageous than that of NR because it makes chemical modifications possible and thus expands the applicability of LNR in various fields.

In general, hydrogenation involves the reaction of molecular hydrogen with alkenes/alkynes to reduce unsaturated organic compounds, normally in the presence of a catalyst.

Considerable efforts have been made to hydrogenate NR using homogeneous catalysts that comprise transition metal complexes such as nickel, rhodium, iridium, or ruthenium complexes.[4–7] The catalytic hydrogenation of NR has the advantages of being highly selective toward the desired products and not being prone to macroscopic diffusion problems. However, the classical catalytic hydrogenation reaction involving transition metal complexes is expensive. Moreover, the catalytic hydrogenation has to be conducted at high temperature and pressure, which requires special equipment.[8]

On the other hand, non-catalytic hydrogenation methods use hydrogenation reagents, such as diimide ($N_2H_2$), that convert unsaturated organic compounds into reduced alkane products. Diimide can be generated in a number of ways, but the widely used method is the thermolysis of *p*-toluenesulfonyl hydrazide (TSH).[8–12] Non-catalytic hydrogenation offers two major advantages: avoiding unnecessary handling of hydrogen gas and removal of the catalyst. However, this method takes place only at very high temperatures. Mahittikul *et al.*[9] studied the hydrogenation of NR using TSH in an *in situ* system at 135°C, and obtained hydrogenated NR in the form of an alternating ethylene–propylene copolymer. Azhar *et al.*[13] studied the hydrogenation of LNR using the same diimide source at 130°C and managed to achieve >90% hydrogenation yield.

Even though NR and LNR can be successfully reduced, chain scission can also be promoted and often results in low-molecular-weight products due to the high reaction temperatures used.[14] In order to prevent these problems, it

is necessary to perform hydrogenation reactions under a relatively low temperature. 2,4,6-Trimethylbenzenesulfonyl hydrazide (MSH) is a hydrogenation agent that releases diimide intermediates through a thermolysis reaction. Cusack *et al.* discovered that the thermolysis rate for MSH is 24 times higher than that of TSH.[15] Therefore, it is reasonable to expect that MSH may be effective in the hydrogenation of NR and LNR, because diimide can be generated at lower temperatures.

In this article, we report LNR hydrogenation under a relatively low temperature using MSH as the diimide source. We have also studied the effect of the reaction temperature, reaction time, solvent, and MSH/LNR weight ratio against the percentage of hydrogenation. The thermal behavior of LNR and hydrogenated LNR (HLNR) is also discussed.

## Experimental

**Materials.** In this study, we used NR from the Malaysian Rubber Board (Kuala Lumpur, Malaysia). Toluene (>99%), *o*-xylene (>99%), hexane (85%), and methanol (>99.8%) were supplied by R&M Chemicals (Himachal Pradesh, India). Methylene blue (≥95%), rose Bengal (95%), TSH, and MSH (97%) were supplied by Sigma Aldrich (Missouri, USA). Cyclohexane (99.5%) was purchased from Merck (Darmstadt, Germany).

**Preparation of LNR.** Liquid natural rubber was synthesized by photosensitized degradation, according to the method described by Kargarzadeh *et al.*[16] Dried NR was cut into small pieces and dissolved in toluene with catalytic amounts of methylene blue and rose Bengal. The solution was stirred frequently using a mechanical stirrer in the presence of visible light at a storage temperature of 80°C for 2 weeks, until the rubber mixture turned into a golden-yellow viscous liquid. Purification of LNR was carried out by centrifugation for 4 min at 3000 rpm. The dry rubber content was determined using a standard laboratory method.[17]

**Preparation of HLNR.** Hydrogenation of LNR was carried out in a 250-mL round bottom flask, equipped with a reflux condenser and a magnetic stirrer. A solution of LNR and MSH in an organic solvent was refluxed at different temperatures (80–110°C) for various reaction times (30–90 min) in order to study the effect of the reaction temperature and time on the percentage of hydrogenation. A control experiment was carried out using TSH as the diimide source and the percentage of hydrogenation was compared to the results obtained using MSH. *o*-Xylene, toluene, cyclohexane, and hexane were used to determine the effect of the solvent on the percentage of hydrogenation. Different amounts of MSH were added to a fixed volume of the LNR solution at MSH/LNR weight ratios of 1:1 and 2:1 to determine the effect of MSH concentration on the percentage of hydrogenation. The products were filtered and coagulated with methanol to remove any residual

MSH. Finally, they were dried in a vacuum oven to remove any remaining solvent.

**Characterization of Products.** Fourier-transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopies were used to determine the structure of the products. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy (Perkin Elmer, Massachusetts, USA) was used to determine any changes in the functional groups that may have been induced during the hydrogenation reaction. The samples were analyzed in transmittance mode ranging between 4000 and 600 cm$^{-1}$. NMR spectroscopy was used to analyze the chemical structure of the product. Integration of proton NMR ($^1$H NMR) signals was used to estimate the percentage of conversion from LNR to HLNR. The samples were dissolved in CDCl$_3$ for the measurements with a Fourier-transform nuclear magnetic resonance 600-MHz Cryoprobe (FT-NMR 600 MHz Cryo). The degradation temperature of the samples was determined using differential thermal analysis (DTA) (TGA/SDTA 851$^e$, Mettler Toledo, Greifensee, Switzerland).

## Results and Discussion

**Structure of LNR and HLNR.** The chemical structures of LNR and HLNR at 80% hydrogenation were characterized using FTIR, and the spectra are shown in Figure 1. The main peaks are located at 3050, 3000–2850, 1660, and 834 cm$^{-1}$, which correspond to sp$^2$ C–H stretching, sp$^3$ C–H stretching, C=C stretching, and sp$^2$ C–H bending, respectively. The most obvious change is the intensity of the sp$^3$ C–H stretching band, which increases upon hydrogenation of LNR due to the increasing number of alkane groups. Meanwhile, the intensity of the other three peaks decreases, which can be attributed to the reduced amount of olefinic C–H and C=C groups in the structure of HLNR.

$^1$H NMR spectra of LNR and HLNR after 60 min of reaction are shown in Figure 2. It can be seen that the signal for the protons attached to the double bonds of LNR at 5.12 ppm, as well as those of the protons at unsaturated methylene (2.20 ppm) and methyl (1.67 ppm) groups
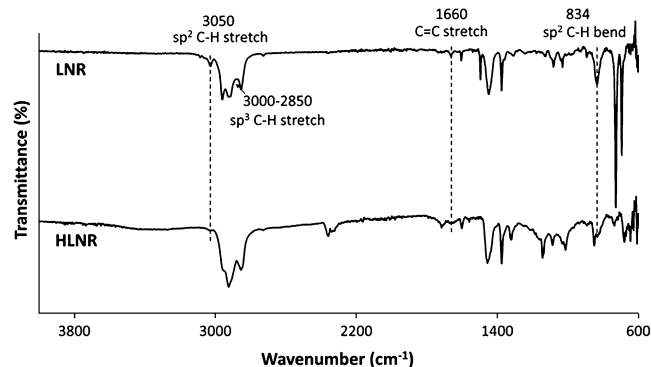


**Figure 1.** FTIR spectra of LNR and HLNR at 80% hydrogenation.

decrease upon hydrogenation. New signals appear between 0.8 and 1.39 ppm, indicating the existence of methyl, methylene, and methine protons in the saturated unit. The percentage of hydrogenation was calculated from the integrated areas of the olefinic unit signal at 5.12 ppm and the methyl proton of the saturated unit in the range of 0.8–2.2 ppm. The signals at 2.3–2.5 ppm correspond to benzylic protons from *o*-xylene and MSH.

**Effect of Reaction Temperature.** MSH was partially dissolved in *o*-xylene at room temperature. The solubility of MSH in the solvent increased with increasing temperature. After a few minutes, the resulting colorless solution changed to a deep yellow saturated mixture, indicating the liberation of diimide intermediates. Diimide (HN=NH) is a labile hydrogen donor that transfers hydrogen molecules to the C=C bonds of the LNR structure, liberating nitrogen gas.

Several experiments were conducted at different reaction temperatures, as shown in Table 1. No changes in the reaction mixture were observed at 80 and 90°C, which indicate that diimide intermediates are not generated at temperatures below 90°C. This may be due to the inactivation of MSH decomposition, unless sufficient heat is provided to initiate the reaction. At 100°C, a deep yellowish saturated mixture was obtained after 30 min of reaction, which then resulted in an 80% yield of hydrogenation in a short reaction time (60 min). When the temperature was increased to 110°C, the reaction rate increased, but the percentage of hydrogenation decreased to 34.1%. This may be due to a degradation
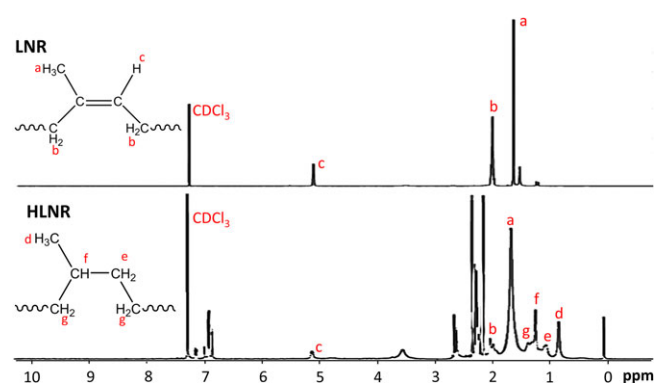
reaction that forms radicals at the allylic positions of the double bonds at high temperatures.[18] Another factor can be the chain scission reactions that lead to the formation of side products.[14] Hence, the optimum reaction temperature to afford a high percentage of hydrogenation (80%) was found to be 100°C.

**Effect of Reaction Time.** The effect of the reaction time on LNR hydrogenation was investigated by varying the reaction time, from 30 to 90 min, as depicted in Figure 3. The temperature, solvent, and weight ratio of MSH/LNR were kept constant at 100°C, *o*-xylene, and 1:1, respectively. Based on Figure 3, the percentage of hydrogenation was significantly increased between 30 and 60 min reaction time. However, when the reaction exceeded 60 min, the percentage of hydrogenation decreased. Clearly, the reaction time has a significant influence on the percentage of hydrogenation of LNR. The major advantage of using MSH as the diimide source is that hydrogenation is completed within a short period of time (60 min) while the same reaction has to be carried out for 6–8 h to obtain >80% of hydrogenation when using TSH as the diimide source.[11,13] The use of MSH results in a faster hydrogenation reaction compared to TSH due to its higher thermolysis rate, as reported by Cusack *et al.*[15]

**Effect of Diimide Source.** A control reaction was carried out using another source of diimide, TSH. The results of the hydrogenation reaction using the two sources (MSH and TSH) are listed in Table 2. The results show that no changes in the reaction mixture are observed when TSH is used as the diimide source at 100°C. At the elevated temperature of 130°C (required to activate TSH), the use of TSH results in a lower percentage of hydrogenation (41.4%) compared to that using MSH, even after 4 h of reaction time. Thus, it can be concluded that MSH is a better diimide source for the hydrogenation of LNR at mild temperatures.

**Effect of Solvent.** A series of reactions were performed to study the effect of the solvent on the percentage of LNR hydrogenation. The choice of solvents was based on a previous study by Mahittikul *et al.*[9] Four different solvents
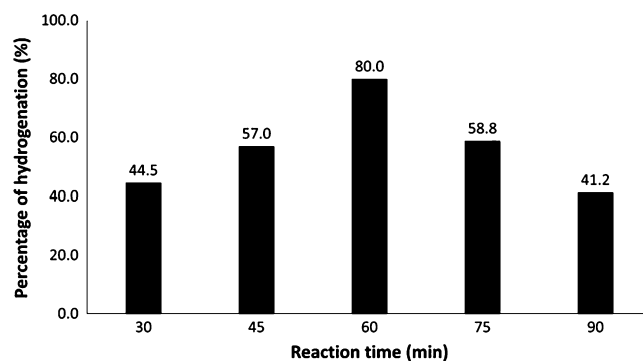
**Figure 2.** $^{1}$H NMR spectra of LNR and HLNR at 80% hydrogenation.

**Table 1.** Hydrogenation percentage of LNR calculated from $^{1}$H NMR spectra at different reaction temperatures.

| Reaction temperature (°C) | Percentage of hydrogenation (%) |
|---|---|
| 80 | — |
| 90 | — |
| 100 | 80.0 |
| 110 | 34.1 |

*Conditions*: time = 60 min; solvent = *o*-xylene; MSH/LNR ratio = 1:1.

**Figure 3.** Percentage of hydrogenation of LNR calculated from $^{1}$H NMR spectra at different reaction times at 100°C, using *o*-xylene as the solvent, and a MSH/LNR ratio of 1:1.

**Table 2.** Percentage of hydrogenation of LNR calculated from ^{1}H NMR spectra using different diimide sources.

| Diimide source | Reaction temperature (°C) | Reaction time | Percentage of hydrogenation (%) |
|---|---|---|---|
| MSH | 100 | 60 min | 80.0 |
| TSH | 100 | 60 min | No reaction |
| TSH | 130 | 4 h | 41.4 |

*Conditions*: solvent = *o*-xylene; MSH/LNR ratio = 1:1.

**Table 3.** Percentage of hydrogenation of LNR calculated from ^{1}H NMR spectra using different solvents.

| Solvent | Polarity index[19] | Percentage of hydrogenation (%) |
|---|---|---|
| *o*-Xylene | 2.5 | 80.0 |
| Toluene | 2.4 | 30.7 |
| Cyclohexane | 0.2 | 18.2 |
| Hexane | 0.0 | 4.5 |

*Conditions*: $T = 100°C$; time = 60 min; MSH/LNR ratio = 1:1.

**Table 4.** Percentage of hydrogenation of LNR calculated from ^{1}H NMR spectra using different MSH/LNR ratios.

| MSH/LNR ratio | Percentage of hydrogenation (%) |
|---|---|
| 1:1 | 80.0 |
| 2:1 | 50.8 |

*Conditions*: $T = 100°C$; time = 60 min; solvent = *o*-xylene.

with different polarity indexes were used: *o*-xylene, toluene, cyclohexane, and hexane, as shown in Table 3. The results show that the percentages of LNR hydrogenation differ greatly when different solvents are used in the system. The highest percentage of hydrogenation was achieved with *o*-xylene as the solvent in the MSH diimide-generated system. Thus, it can be concluded that MSH dissolves better in a solvent with a high polarity index and, therefore, it can easily produce diimide intermediates that can react with the C=C groups to afford high hydrogenation yields.

**Effect of MSH/LNR Ratio.** In this article, two weight ratios of MSH to LNR were used, 1:1 and 2:1, in order to study the influence of MSH concentration on the percentage of hydrogenation, while the other parameters were kept constant. Table 4 shows that, by increasing the weight ratio of MSH:LNR from 1:1 to 2:1, the percentage of hydrogenation decreases. An excess of diimide source in the reaction mixture can possibly cause greater disproportionation, which is the main side reaction that the liberated diimide can undergo.[20] Theoretically, 1 mol of MSH would generate 1 mol of diimide under the appropriate conditions. Therefore, a 1:1 molar ratio is sufficient for complete hydrogenation. In conclusion, the percentage of hydrogenation is inversely proportional to the weight ratio of MSH/LNR.

**Thermal Behavior of LNR and HLNR.** Thermal behavior analysis was used to investigate the thermal stability of HLNR. Thermogravimetric analysis (TGA) was carried out to determine the degradation temperature of LNR and HLNR (Figure 4). The thermogravimetric curves of both LNR and HLNR have a similar shape, except for small differences in the decomposition zone and in the kinetics of the process. The thermogram of LNR shows a single-step decomposition, while the thermogram of HLNR at 80% hydrogenation shows a two-step decomposition. For HLNR, the first stage of the decomposition is due to the
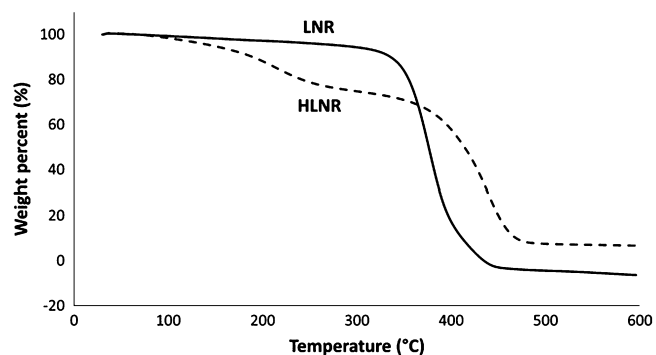


**Figure 4.** TGA thermograms of LNR and HLNR at 80% hydrogenation.
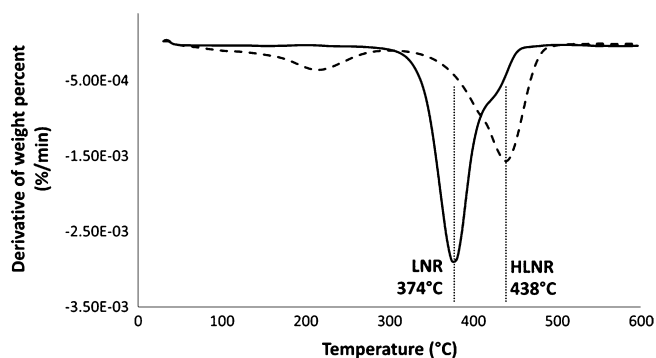


**Figure 5.** DTG thermograms of LNR and HLNR at 80% hydrogenation.

side product of MSH thermolysis at around 211°C. The degradation temperatures of LNR (374°C) and HLNR (438°C) can be seen more clearly from the maximum peaks of the DTG curves of the samples (Figure 5). Based on these results, the hydrogenation reaction has proven to increase the thermal stability of LNR: an increased hydrogenation percentage results in a higher degradation temperature. The enhanced stability of HLNR is achieved because the weak π–bonds in the unsaturated units are converted to stronger C—H sigma (σ) bonds in the saturated HLNR.[21] A

similar behavior in the thermal properties of hydrogenated products has been observed by Tangthongkul *et al*.

## Conclusion

In summary, this article reports a highly efficient work-up procedure for the hydrogenation of LNR. The attractive features of this method include a high percentage of hydrogenation at short reaction times and low temperatures. Furthermore, the thermal stability of HLNR was improved from 374 to 438°C, as a result of the high hydrogenation percentage (80%).

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