


2,4,6-Trimethylbenzenesulfonylhydrazide를 이용한 액상 천연고무의 수소화: 반응표면분석법을 이용한 반응 매개변수 최적화

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Hydrogenation of Liquid Natural Rubber Using 2,4,6-Trimethylbenzenesulfonylhydrazide: Optimisation of Reaction Parameters via Response Surface Methodology

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Abstract: Hydrogenation of liquid natural rubber (LNR) using 2,4,6-trimethylbenzenesulfonylhydrazide (MSH) in toluene was studied. HLNR structure was characterized by nuclear magnetic resonance (NMR) and Fourier transform infrared spectroscopy (FTIR). Response surface methodology (RSM) based on 5-level-2-factor central composite rotatable design (CCRD) was used to analyze the correlative effects of reaction, MSH:LNR weight ratio (0.5-1.0) and reaction time (20-60 min) with a fixed reaction temperature of 100 °C. Multivariate statistical analysis was developed in a form of quadratic model in order to correlate the reaction parameter to the response received. The optimum conditions derived via RSM were the MSH:LNR weight ratio of 0.7 and a reaction time of 25.86 min. The R^2 value of 0.9557 showed that the model was well-fitted with the experimental data, whereby the model was almost ideal while the lack-of-fit considered rather unseemly (i.e. insignificant).

Keywords: response surface methodology (RSM), central composite rotatable design (CCRD), optimization, liquid natural rubber, hydrogenation.

Introduction

Natural rubber (NR) is a valuable material originated from the rubber trees *Hevea brasiliensis*, and its major component is polyisoprene.¹ NR is a cheap and versatile elastomer, thus being widely used in adhesive and automobile industries because of its elasticity and high mechanical strength properties. Nowadays, NR is being recognized as a renewable resource and this has attracted more attention to itself because of the requirement of environmental protection and resource

saving.² However, the NR possessed low resistance to heat, ozone and chemical reagents of NR because of its unsaturated chain structure. Through the production of highly saturated NR, these drawbacks can be improved. Therefore, researchers have focused on chemical modification of NR to reduce the unsaturation in the main chain. The desired product must restrain high temperature conditions so that it could be used in a variety of practical applications, such as rubber blending and vulcanization.³ A simple modification of NR is liquid natural rubber (LNR). LNR can be produced via depolymerization that converts solid-phase NR to liquid-phase NR.⁴⁻⁶ After depolymerization, LNR will have an active group in the isoprene chain such as -OH, -OOH and -C=O.^{7,8} Seng *et al.* stated LNR offers as a good dispersing and toughening agent

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into epoxy matrix in order to improve the toughness of cured epoxy due to the presence of active groups.⁹ Hisham *et al.* also reported the mechanical properties of the unsaturated polyester resin can be improved by introducing the LNR.¹⁰ The short polymeric chain of LNR expands its applicability in many fields compared to dried rubber due to the possible chemical modifications made.¹¹

Hydrogenation is an effective method in lowering the level of C=C unsaturation in the polymeric chain. Generally, hydrogenation involves the addition of hydrogen atom in the unsaturated bond of alkenes/alkynes. Saturated moiety in the polymer chain has led to the improvement in its physical properties, such as its stability against thermal, oxidative and radiation-induced.¹²⁻¹⁴ Basically, saturation of NR through hydrogenation process can be divided into two methods, which are catalytic and non-catalytic hydrogenation. Catalytic hydrogenation is the reaction of catalyst that will activate the hydrogen molecules and the carbon-carbon double bond species.¹⁵ However, catalytic hydrogenation is costly because the reaction uses expensive catalyst such as ruthenium,¹⁶ iridium¹⁷ or rhodium¹⁸ complexes and it has to be carried out at high pressure and temperature in the presence of hydrogen gas.

Meanwhile, non-catalytic hydrogenation is a method using diimide molecule that supplies hydrogen to the C=C bond. Non-catalytic hydrogenation uses a cheaper reagent and requires milder conditions compared to catalytic hydrogenation. This hydrogenation method has two major advantages, which are avoiding handling of hydrogen gas and removal of reaction catalyst. Mahittikul *et al.* reported the hydrogenation of natural rubber latex uses *p*-toluenesulfonyl hydrazide (TSH) as diimide source.¹⁹ Recently, hydrogenation of LNR using TSH as diimide sources has also been reported.^{20,21} Rasid *et al.* successfully reported the hydrogenation of LNR using 2,4,6-trimethylbenzenesulfonylhydrazide (MSH) with slightly milder conditions compared to using TSH.²² Basically, they have studied the main reaction parameters such as weight ratio of diimide source to LNR, reaction temperature and reaction time.

Response surface methodology (RSM) has been widely used for designation and optimization of experiments by combining statistical techniques and mathematical modeling.^{23,24} The main advantage of RSM is the reduced number of experimental runs needed to provide sufficient information for the statistically acceptable result.²⁵ RSM based on CCRD was used in this study to correlate the relationship between the reaction parameters and response with a smaller number of experimental runs. RSM comprising a five-level-two-factor central composite

rotatable design (CCRD) was used in our work to evaluate the interactive effect and obtain the optimum conditions for the hydrogenation process. In this work, optimization of hydrogenation of LNR using MSH by RSM has been reported. The parameters in this study were selected based on the previous work.²²

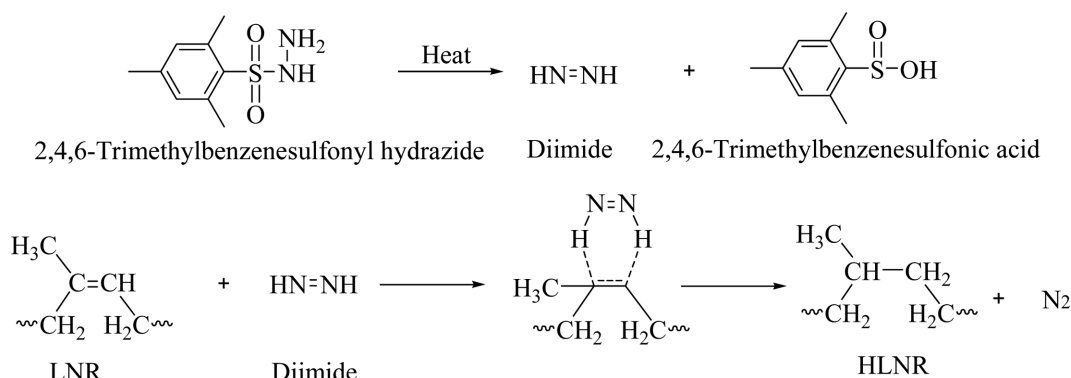
Experimental

Materials. In this work, natural rubber was provided by the Rubber Research Institute of Malaysia (RRIM). Reagent grade toluene (>99%), methanol (>99.8%) and ethanol (95%) were purchased from R&M Chemicals (Himachal Pradesh, India). Reagent grade methylene blue ($\geq 95\%$), rose bengal (95%) and 2,4,6-trimethylbenzenesulfonylhydrazide (97%) were purchased from Sigma Aldrich (Missouri, USA).

Attenuated total reflectance-Fourier-transform infrared (ATR-FTIR) spectroscopy (Agilent Cary 630 FTIR) was used to monitor any changes in the main LNR spectral bands upon hydrogenation. Nuclear magnetic resonance (NMR) spectroscopy was performed in CDCl_3 at 400 MHz on a Bruker AVANCE III HD instrument. The ^1H NMR signals were integrated in order to determine the hydrogenation percentage. Gel permeation chromatography (GPC) was employed to investigate 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).

Preparation of LNR. LNR, in this study, was prepared via photo-oxidative degradation method.²⁶ Firstly, NR was soaked in toluene until it was completely swollen. The swollen NR was added with methanol (10 mL), rose bengal (0.100 g) and methylene blue (0.066 g). The mixture of NR was stirred for 12 days using a mechanical stirrer at 10-30 rpm under visible light at room temperature. The product was then centrifuged at 6000 rpm for 30 min to separate the gel formed during photodegradation.

Hydrogenation of LNR. A dried LNR was prepared in a vacuum oven for 24 h. MSH with different amounts were added to a fixed weight of dried LNR (0.5 g) with ratio 0.5:1 to 1:1 of MSH:LNR. 10 mL of toluene was added and each mixture was stirred at 650 rpm. The reaction was refluxed at 100 °C with different reaction time (20-60 min). After hydrogenation, hydrogenated rubber was filtered and precipitated in ethanol and finally dried in a vacuum oven to remove any remaining solvent. The reaction scheme of hydrogenation of



Scheme 1. Thermolysis of MSH and hydrogenation of LNR by diimide.

LNR using MSH is shown in Scheme 1.

Experimental Design and Statistical Analysis. RSM comprising a five-level-two-factor CCRD was used in this study, requiring 13 experiments. The fractional factorial design in this study consisted of 4 factorial points, 4 axial points and 5 center points. The generalized response surface model is shown below.

$$Y = \beta_0 + \sum_{i=1}^2 \beta_i x_i + \sum_{i=1}^2 \beta_{ii} x_i^2 + \sum_{i=1}^2 \sum_{j=i+1}^2 \beta_{ij} x_i x_j \quad (1)$$

where, Y (hydrogenation %) represents the response variable, β_0 is constant term, β_i represents the coefficients of the linear parameters, x_i represents the variables, β_{ii} represents the coefficients of the quadratic parameters, and β_{ij} represents the coefficients of the interaction parameters.

The reaction undergoes with different amount of MSH to a fixed volume of LNR. The weight ratios of 0.5:1 to 1:1 for MSH:LNR were used in order to determine the effect of MSH:LNR ratio on the percentage of hydrogenation. The reaction also undergoes at different reaction time (20–60 min). However, reaction temperature was fixed at 100 °C. Increasing the reaction temperature was less contributive for the increment of hydrogenation percentage. In addition, Rasid *et al.* (2016) found that 100 °C was the optimum reaction temperature in order to achieve a high percentage of hydrogenation.²² During the experiments, the mixing speed was fixed at 650 rpm. Based on the studies that have been done, the range of each parameter was selected.²² Table 1 shows the variables based on the range of parameters that have been selected in terms of coded actual values.

Determination of significant variances between the independent variables was carried out using analysis of variance

Table 1. Levels of Variables for the CCRD

Variable	Levels				
	-2	-1	0	+1	+2
MSH:LNR weight ratio, A (g)	0.50	0.57	0.75	0.93	1.00
Reaction time, B (min)	20.00	25.86	40.00	54.14	60.00

(ANOVA). Multiple regressions were performed in analyzing the data to predict the coefficients of the fitted second-order polynomial model. Unsatisfactory of the final reduced model was checked through the comparison made between the experimental values obtained and the predicted values. The validation process for the suggested model was performed to verify the final model.

Results and Discussion

Model Fitting and ANOVA. Experimental data for hydrogenation of LNR using MSH as diimide source are given in Table 2. The predicted values were obtained from model-fitting technique using the software Design Expert version 7.1.5. It can be seen that the actual value satisfactorily correlated to the observed values.

The ANOVA for the model is shown in Table 3. The calculated F -value of the model (30.15) indicates that the model is significant and the lack-of-fit F -value of 4.17 shows that it is not significant relative to pure error. The model of P -value (0.0001) that was less than 0.05 indicated that the model of F -value was recognized as significant. The model is considered well-fitted to the experiment if there are significant regressions and non-significant lack-of-fit.²⁷ A and B are referred as the main linear term effects, while AB is the interaction terms, and A^2 and B^2 are the quadratic terms in the responses. In this

Table 2. Central Composite Quadratic Polynomial of HLNR

Run no.	MSH:LNR weight ratio, <i>A</i> (g)	Reaction time, <i>B</i> (min)	Hydrogenation (%)	
			Actual	Predicted
1	0.75 (0)	40.00 (0)	26.04	24.72
2	0.93 (+1)	25.86 (-1)	21.38	23.36
3	0.57 (-1)	25.86 (-1)	16.18	17.59
4	0.75 (0)	60.00 (+2)	47.60	45.49
5	0.75 (0)	40.00 (0)	22.54	24.72
6	1.00 (+2)	40.00 (0)	31.13	28.86
7	0.93 (+1)	54.14 (+1)	39.35	41.67
8	0.50 (-2)	40.00 (0)	19.42	17.96
9	0.57 (-1)	54.14 (+1)	30.27	32.02
10	0.75 (0)	40.00 (0)	24.81	24.72
11	0.75 (0)	40.00 (0)	26.20	24.72
12	0.75 (0)	40.00 (0)	24.02	24.72
13	0.75 (0)	20.00 (-2)	23.96	22.34

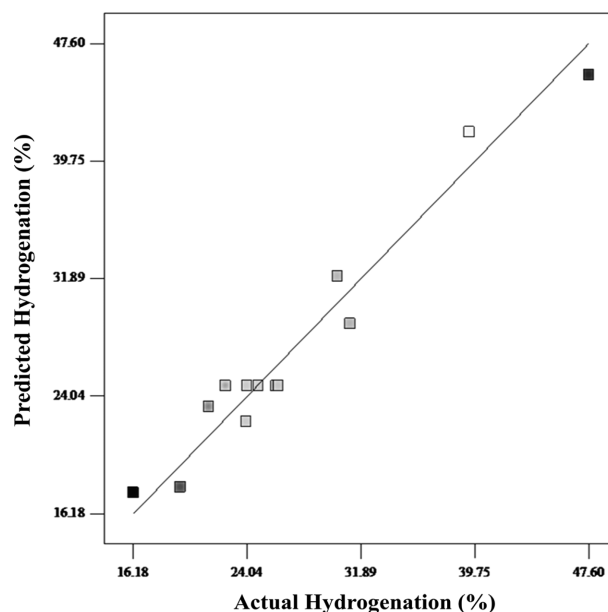
study, *A* and *B* were significant ($p < 0.05$). Figure 1 shows good correlation between the actual and predicted hydrogenation percentage of the product. The well-fitted model can be seen through linear distribution. The generated quadratic models were employed to study the effect of variables and their interactions on the hydrogenation percentage of HLNR.

The ANOVA showed that hydrogenation of LNR using MSH was most suitably described with quadratic polynomial model. From the design expert, the quadratic polynomial as shown is given below:

$$\text{Hydrogenation (\%)} = +24.72 + 3.86A + 8.19B + 0.97AB - 0.66A^2 + 4.60B^2 \quad (2)$$

Table 3. ANOVA for Hydrogenation of LNR Using MSH

Source	Sum of squares	Degree of freedom	Mean square	<i>F</i> -value	<i>P</i> -value
Model	816.91	5	163.38	30.15	0.0001
MSH:LNR weight ratio, <i>A</i>	118.89	1	118.89	21.94	0.0023
Reaction time, <i>B</i>	536.15	1	536.15	98.94	<0.0001
<i>AB</i>	3.76	1	3.76	0.69	0.4321
<i>A</i> ²	3.00	1	3.00	0.55	0.4811
<i>B</i> ²	146.94	1	146.94	27.12	0.0012
Residual	37.93	7	5.42	-	-
Lack-of-fit	28.75	3	9.58	4.17	0.1006
Pure error	9.18	4	2.30	-	-
Corrected total	854.84	12	-	-	-

**Figure 1.** Comparison of predicted and actual value of hydrogenation percentage by the response surface model.

where, *A* is the MSH:LNR weight ratio and *B* is the reaction time. The positive sign and negative sign in front of the terms indicate synergistic effect and antagonistic effect, respectively. The quadratic model was discovered to have a suitable coefficient of determination ($R^2 = 0.9556$), indicating that 95.56% of the total variation in the observed responses was assigned to the independent variables. The quadratic polynomial model was highly sufficient to represent the actual relationship between the response (hydrogenation %) and the significant parameters. In general, a regression model is considered having high correlation with above 0.9 for R^2 value.²⁸ Furthermore, Hamzaoui *et al.* had stated that the closer the R^2 value

to 1, the better the regression model that fits the actual data can be obtained.²⁹ Therefore, the higher value of R^2 gained in this empirical model indicates a good correlation between the predicted and actual HLNR percentage of hydrogenation.

Effect of Parameters. The correspondence among all variables and response can be known by reviewing the three-dimensional (3D) response surface plots created from the predicted quadratic polynomial model. The 3D response surface plot can also recognize each parameter of optimum level for the production of HLNR. As shown in Figure 2, the MSH:LNR weight ratio and the reaction time were clarified in the range of 0.57-0.93 and 25.86-54.14 min, respectively, with the reaction temperature fixed at 100 °C. It was shown that the maximum hydrogenation percentage (over 41%) was obtained when 0.93 MSH:LNR weight ratio was used to react at 54.14 min. Based on this result, increasing the weight ratio of MSH:LNR would increase the hydrogenation percentage. Meanwhile, prolonging the reaction time would become more significant in increasing the hydrogenation percentage. It was shown that the reaction time was more important in comparison to MSH:LNR weight ratio for the hydrogenation percentage of HLNR.

Hydrogenation cannot occur if the diimide was not gen-

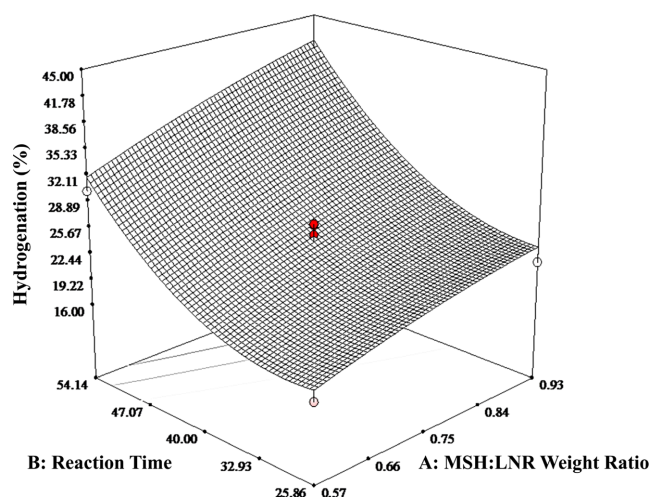


Figure 2. Three-dimensional response surface plots for the MSH:LNR weight ratio *versus* reaction time (min).

erated by thermolysis of MSH. In addition, extension of reaction time will lead to a higher percentage of hydrogenation as long as the diimide source remains in reaction. Once all MSH are decomposed by thermolysis, hydrogenation cannot be continued due to deficiency of diimide. MSH:LNR weight ratio also plays an important role in the hydrogenation of LNR. Rasid *et al.* had achieved the ratio of 1:1 for optimum MSH:LNR weight ratio.²² Rasid *et al.* also conducted an experiment with weight ratio of 2:1. It was revealed that the hydrogenation percentage had decreased.²² Excessive of diimide in the reaction can probably cause bigger disproportionation.³⁰ As mentioned previously, the reaction temperature was fixed at 100 °C. Increasing the reaction temperature proved to be less contributive for the increment of the hydrogenation percentage. It has less effect on the hydrogenation percentage because the reaction temperature had already exceeded 100 °C.

Optimum Conditions. The optimum conditions for the hydrogenation of LNR using MSH were predicted using the optimization function of the design expert software. The software demonstrates the most desirable (optimum) conditions for the hydrogenation of LNR, as shown in Table 4. The greatest percentage of hydrogenation of LNR was 20.30%. The optimum reaction parameters were at 25.86 min, MSH:LNR weight ratio at 0.70 and reaction temperature of 100 °C. The response surface can designate the optimal combination of parameters to obtain the highest percentage with minimum reaction conditions. All parameters were assigned for minimum value to get maximum HLNR percentage of hydrogenation. Validation for the quadratic model to optimize the hydrogenation of LNR using MSH has been studied, as shown in Table 5. It was revealed that with different reaction conditions, the hydrogenation percentage was still acceptable. Relationship between the parameters and the response on the hydrogenation of LNR revealed good correspondence based on small differences of predicted and actual values.

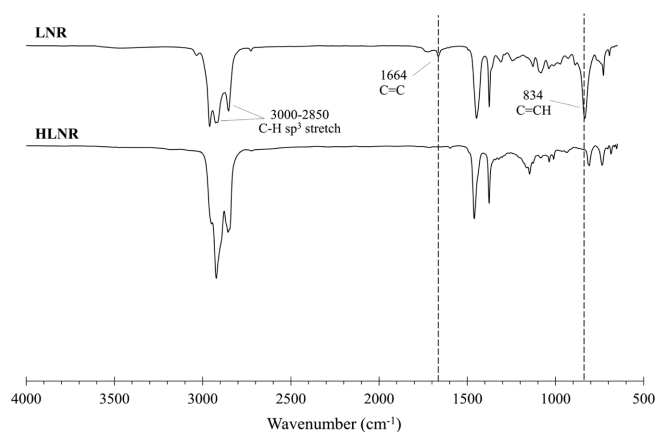
Structural Analysis of HLNR. The microstructures of LNR and HLNR were characterized using FTIR and the FTIR spectra are shown in Figure 3. The main absorption bands are located at 834, 1664, and 3000-2850 cm^{-1} , which correspond to olefinic C-H bending, C=C stretching and sp^3 C-H stretching,

Table 4. Optimum Conditions for the Hydrogenation of LNR Using MSH as Diimide Source

Run no.	MSH:LNR weight ratio, A (g)	Reaction time, B (min)	Hydrogenation (%)		Deviation
			Actual	Predicted	
1	0.70	25.86	22.24	20.30	1.94

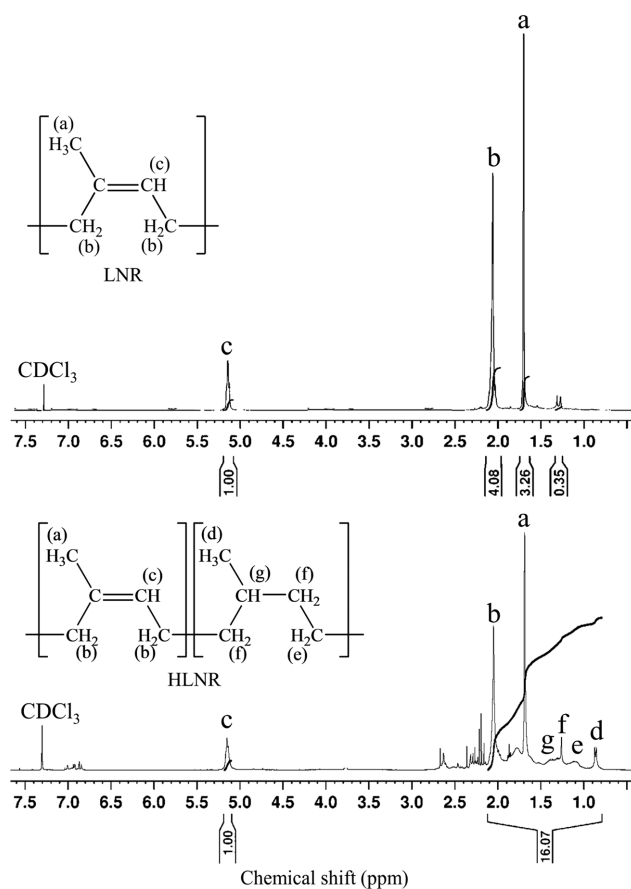
Table 5. Validation of the Quadratic Model for Optimisation of HLNR Using MSH via Response Surface Methodology

MSH:LNR weight ratio, A (g)	Reaction time, B (min)	Hydrogenation (%)		Difference
		Actual	Predicted	
0.95	57	46.35	46.04	0.31
0.85	45	30.56	30.36	0.20
0.80	50	33.20	34.04	0.84
0.85	22	23.78	23.02	0.76
0.70	50	31.32	31.47	0.15

**Figure 3.** FTIR spectra of LNR and HLNR at 47.60% hydrogenation.

respectively. The formation of HLNR was confirmed using FTIR by comparing it to LNR. The most obvious change is the intensity of the sp^3 C–H stretching in the range of 3000–2850 cm^{-1} , which is due to the increasing number of alkane groups upon hydrogenation. However, the intensity of the other two peaks is decreased due to the reduced amount of C=C stretching (1664 cm^{-1}) and olefinic C–H bending (834 cm^{-1}).

The ^1H NMR spectra of LNR and HLNR at 47.60% hydrogenation are shown in Figure 4. Integrated peak area of the olefinic proton (5.12 ppm), unsaturated methylene (2.02 ppm) and methyl groups (1.73 ppm) decrease upon hydrogenation. Based on the spectrum of HLNR, those three signals were slightly reduced. New proton signals appeared in the range of 0.85–1.39 ppm, which corresponded to the methylene ($-\text{CH}_2-$), and methyl ($-\text{CH}_3$) groups. However, the new peak intensities are quite low since LNR is not fully hydrogenated. The percentage of hydrogenation was calculated from the integration done on NMR spectrum. The ratio between the integration of the olefinic proton signal and integration of the signals in the range of 0.8–2.1 ppm was used in the calculation.²¹ The signals

**Figure 4.** ^1H NMR spectra of LNR and HLNR at 47.60% hydrogenation.

around 2.3–2.5 ppm corresponded to benzylic proton from toluene and MSH.

Based on Abdullah, small peak around 1.25–1.35 ppm may corresponded to alcohol.³¹ It can also be seen from the low absorption band around 3300–3600 cm^{-1} due to the presence of $-\text{OH}$ active terminal in LNR. Other than that, small absorption band around 1720 cm^{-1} may possibly the $-\text{C}=\text{O}$ active terminal in LNR. After hydrogenation, the intensity of those two absorption bands is decreased. This may be due to the reduction of $-\text{OH}$ and $-\text{C}=\text{O}$ by diimide molecule as a side reaction.³²

In conclusion, the FTIR and NMR spectra showed that the microstructural changes had occurred during the hydrogenation process.

Molecular Weight of HLNR. Gel permeation chromatography (GPC) is used to determine the molecular weight and PDI of rubber samples. The number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index (PDI) of NR, LNR and HLNR are listed in

Table 6. Molecular Weight and PDI of NR, LNR and HLNR

Sample	M_n	M_w	PDI
NR	475536	2747729	5.77
LNR	19474	45588	2.34
HLNR	2272	3766	1.66

Table 6. The M_w of natural rubber is 2747729. The M_w and PDI of LNR were 45588 and 2.34, respectively. After hydrogenation, the M_w and PDI of HLNR reduced due to the high reaction temperature (100 °C).

Conclusions

Comparison of predicted and experimental values discovered good correspondence between the two with R^2 value of 0.9557, indicating that regression models derived from RSM could be used to effectively describe the relationship between the variables and response in hydrogenation of liquid natural rubber using 2,4,6-trimethylbenzenesulfonylhydrazide (MSH). The ANOVA indicated that the model demonstrated the real correlation between the two factors and response in the hydrogenation of liquid natural rubber. These models can be used to predict hydrogenation percentage of HLNR under any given conditions within the experimental range. We have proven that the optimum hydrogenation percentage of HLNR can be satisfactorily predicted via RSM.

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