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New Approach on the Modification of Liquid Natural Rubber Production using Microwave Technique

(Pendekatan Baharu kepada Penghasilan Modifikasi Getah Asli Cecair menggunakan Teknik Gelombang Mikro)

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ABSTRACT

High-speed synthesis using microwave technique has attracted considerable intentions among researchers as it provides an efficient time of doing reactions. Modification of liquid natural rubber (LNR) via hydrogenation using of 2,4,6-trimethylbenzenesulfonylhydrazide (MSH) produced hydrogenated liquid natural rubber (HLNR). The results showed that microwave-assisted hydrogenation of LNR was experimentally found to give expected product in a short time (10–20 min). The structure of products was characterized by Fourier-transform infrared (FTIR) and the percentage of hydrogenation was determined from the $^1\text{H-NMR}$ spectrum. The highest hydrogenation percentage of HLNR for hydrogenation of LNR by microwave heating were obtained; an LNR hydrogenation percentage of 41.18% at a MSH:LNR weight ratio of 1.5:1, a microwave power of 600 W and a reaction time of 20 min. Diimide molecules have been generated more quickly at microwave frequencies and yield HLNR in a shorter time compared to reflux heating method.

Keywords: Diimide; hydrogenation; liquid natural rubber (LNR); microwave

ABSTRAK

Sintesis berkelajuan tinggi menggunakan teknik gelombang mikro telah menarik minat para penyelidik oleh kerana kecekapan masa untuk tindak balas. Modifikasi getah asli cecair (LNR) melalui penghidrogenan menggunakan 2,4,6-trimetilbenzenasulfonilhidrazid (MSH) telah menghasilkan getah asli cecair terhidrogen (HLNR). Hasil kajian menunjukkan penghidrogenan LNR berbantu gelombang mikro mampu menghasilkan produk yang dijangka dalam masa yang singkat (10-20 min). Struktur produk telah dicirikan oleh transformasi Fourier inframerah (FTIR) dan peratus penghidrogenan telah ditentukan daripada spektrum $^1\text{H-NMR}$. Peratusan penghidrogenan tertinggi HLNR untuk penghidrogenan LNR melalui pemanasan gelombang mikro telah diperolehi; peratus penghidrogenan LNR sebanyak 41.18% pada nisbah berat MSH:LNR 1.5:1, kuasa gelombang mikro 600 W dan masa tindak balas ialah 20 min. Molekul diimida dijana lebih cepat pada frekuensi gelombang mikro dan menghasilkan HLNR dalam masa yang lebih singkat berbanding kaedah pemanasan refluks.

Kata kunci: Diimida; gelombang mikro; getah asli cecair (LNR); penghidrogenan

INTRODUCTION

Over the last few decades, depolymerization of natural rubber (NR) to liquid natural rubber (LNR) has been developed and studied extensively. NR is known as a renewable green resource and has attracted more attention due to environmental protection and resource-saving requirements (Ning et al. 2015). Although NR possesses many advantages, the presence of unsaturated bonds makes NR easy to degrade when exposes to sunlight, ozone, air, and especially, at elevated temperatures (Wongthong et al. 2013). Therefore, chemical modifications to NR are preferable to overcome these weaknesses. The conversion of the solid phase of the NR to the liquid due to the reduction of molecular weight expands its applicability in many fields. Hydrogenation, epoxidation, hydroxylation, and fluorination reactions to LNR are some of the chemical modifications that have been carried out. Among them, the hydrogenation reaction of LNR is easier-route to perform

because of the easy or simple mixing of LNR properties (Nur Hanis Adila et al. 2015).

The use of high pressure and high temperature during catalytic hydrogenation may cause degradation and difficulty in separating catalysts that absorbed on polymer molecules. For that reason, a mild reducing agents such as diimide was used to hydrogenate the polymer. Hydrogenated polymer can be appropriately prepared at atmospheric pressure with relatively simple procedures compare to catalytic hydrogenation (Samran et al. 2004). Some studies have used diimide molecules as a hydrogen source in saturation of LNR chain (Nur Hanis Adila et al. 2015; Muhammad Jefri et al. 2017; Nur Aidasyakirah et al. 2017). Thermal decomposition of *p*-toluenesulfonyl hydrazide (TSH) and 2,4,6-trimethylbenzenesulfonylhydrazide (MSH) generated diimide molecules (Scheme 1). Hydrogenated liquid natural rubber (HLNR) with a hydrogenation percentage of 95.9% was successfully produced with

TSH:LNR weight ratio of 3:1 and the reaction was refluxed at 130°C for 4 h in the *o*-xylene solvent (Nur Hanis Adila et al. 2015). Cusack et al. (1976) reported that the heat decomposition for MSH is 24 times higher than TSH. Meanwhile, the studies conducted by Hamizah et al. (2016) showed that MSH gave a high percentage of HLNR with short response time and low reaction temperature.

Synthesis or heating methods using microwave have also experienced considerable growth over the past decade, particularly in organic reactions (Gedye et al. 1986; Giguere et al. 1986; Galletti et al. 2008). In short, microwave radiation is located between infrared and radio wave in the electromagnetic spectrum with wavelength between 0.001 and 1 m, and frequency range between 0.3 and 300 GHz. Hydrogenation of the polymer is usually performed in the reactor or using reflux methods, but requires longer time and larger amount of heat energy. Hence, the replacement of reflux method by microwave-assisted in the production of hydrogenated polymer is demanded. The ability of the microwave to penetrate the material without damaging or ionizing makes it useful in detecting the composition and structure and in energy transport (Cross et al. 1982). The rapid heating process based on energy consumption at microwave frequencies is capable of producing hydrogenated polymer and replace other heating techniques.

In the present work, we report on the hydrogenation of LNR using domestic microwave. Rapid heating of MSH at microwave frequencies is expected to produce diimide molecules more quickly and yield HLNR in a shorter time compare to reflux heating method.

MATERIALS AND METHODS

MATERIALS

Natural rubber (NR) was supplied by the Rubber Research Institute of Malaysia (RRIM). Reagent grade ethanol, methanol and toluene were obtained from R&M Chemicals. Reagent grade 2,4,6-trimethylbenzenesulfonylhydrazide

(MSH), rose bengal and methylene blue were purchased from Sigma Aldrich. Microwave heating process was performed using Samsung GE71M Microwave Oven.

HYDROGENATION OF LNR BY MICROWAVE HEATING

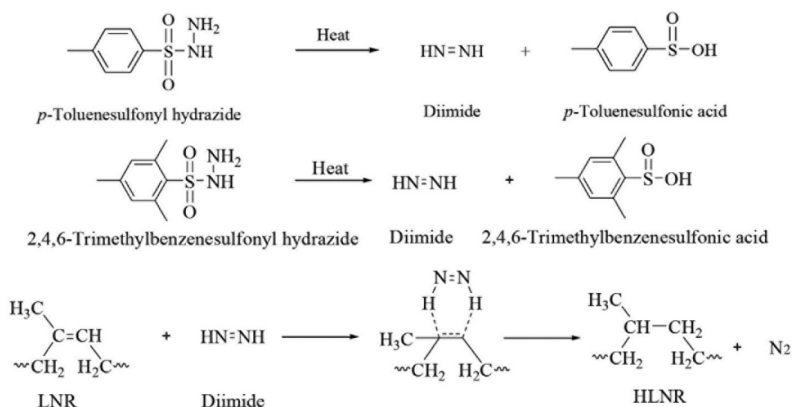
In this work, LNR with 25% of dry rubber content was prepared via photo-oxidative degradation method (Ibrahim 1996). LNR (0.5 g) was diluted with 10 mL of toluene. Different amounts of MSH was added into LNR solution at different MSH:LNR weight ratios (0.5:1, 1:1 and 1.5:1). The mixture was then placed and heated in a microwave oven with different power (300 W, 450 W and 600 W) for various reaction times (10, 15 and 20 min) according to the specified parameters in order to study the effects of parameter changes on the percentage of hydrogenation. The resulting product was filtered and coagulated with ethanol. Finally, the precipitate from coagulation process was dried in vacuum oven to remove any remaining solvent.

CHARACTERIZATION OF PRODUCT

The microstructure of products was determined by attenuated total reflectance-Fourier-transform infrared (ATR-FTIR) spectroscopy (Agilent Cary 630 FTIR) and Nuclear Magnetic Resonance (NMR) spectroscopy (Bruker AVANCE III HD). The changes in the main LNR spectral bands were observed upon hydrogenation. The value of integration on the ¹H-NMR signals were used to determine the hydrogenation percentage (Naharullah et al. 2016). The hydrogenation percentage was calculated using (1).

$$\text{Degree of olefin conversion (\%)} = \frac{100(A-7B)}{A+3B} \quad (1)$$

where A is the peak area of paraffin proton (0.8-2.1 ppm); and B is the peak area of olefinic protons (5.1 ppm). The equation was derived based on Kongparakul et al. (2011).



SCHEME 1. Production of diimide molecule and its effect on the hydrogenation of LNR

RESULTS AND DISCUSSION

STRUCTURE OF LNR AND HLNR

The structures of LNR and HLNR at 41.18% hydrogenation were characterized using FTIR within the range of 4000–600 cm^{-1} , and the spectra are shown in Figure 1. There are two important absorption bands, which are located at 834 and 1664 cm^{-1} corresponding to the olefinic C–H bending and C=C stretching, respectively. After hydrogenation, the intensity of these two absorption bands were reduced. It was due to the decreasing amount of olefinic C–H group and C=C group. However, absorption band at 3000–2800 cm^{-1} , which corresponded to the stretching of sp^3 C–H, was increased upon hydrogenation due to the increasing amount of alkane group.

Figure 2 shows the ^1H NMR spectra of LNR and HLNR at 41.18% hydrogenation. Based on the ^1H NMR of HLNR, signals at 5.12, 2.02 and 1.73 ppm, which corresponded to olefinic proton, unsaturated methylene and unsaturated methyl groups were reduced. Meanwhile, new proton signal appeared in the range of 0.8–1.4 ppm, indicating the existence of saturated methylene and saturated methyl groups. The value of hydrogenation percentage was

obtained by comparing the ratio between the integration of the olefinic proton signal and integration of the signals in the range of 0.8–2.1 ppm (Naharullah et al. 2016).

EFFECT OF REACTION PARAMETERS

Heating process using microwave ovens are not appropriate for TSH. Although the purpose of the study was to accelerate the reaction time, the TSH thermolysis rate was relatively low would make the reaction in the microwave oven to be long. The use of domestic microwave ovens for a long time will cause some problems such as being burned due to uncontrolled temperature and pressure. Therefore, MSH was used as the diimide source is that saturation process due to its high rate of thermolysis (Cusack et al. 1976).

Experimental data for microwave heating hydrogenation of LNR using MSH are given in Table 1. MSH was partially dissolved at room temperature in toluene. The solubility of MSH was increased at higher temperature. After a few minutes of exposure to the microwave radiation, deep yellowish solution formed. This observation indicated that the formation of diimide (N_2H_2) molecules that served as the source of hydrogen for

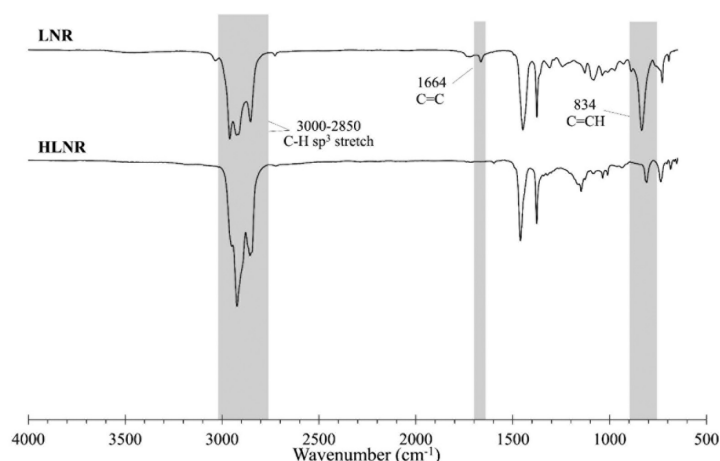


FIGURE 1. FTIR spectra of LNR and HLNR at 41.18% hydrogenation

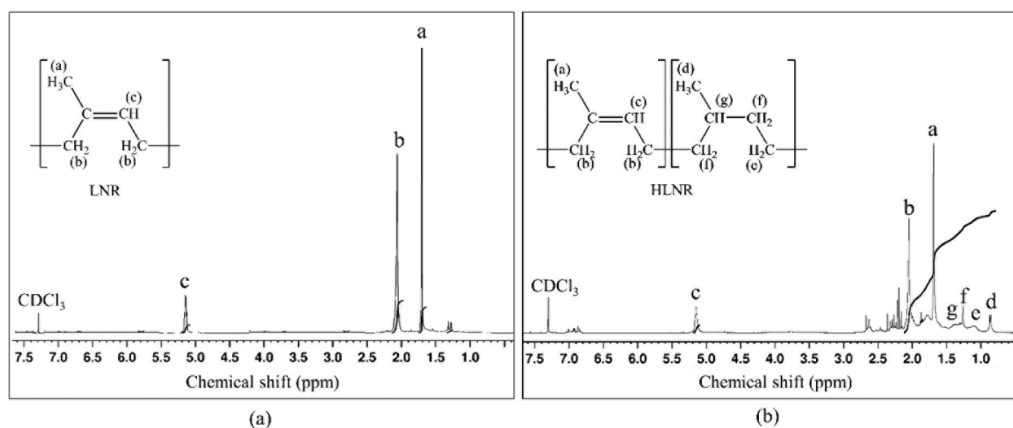


FIGURE 2. NMR spectra of (a) LNR and (b) HLNR at 41.18% hydrogenation

saturation of LNR chain. In this work, the effect of different MSH:LNR weight ratios (0.5:1, 1:1 and 1.5:1), microwave power (300 W, 450 W and 600 W) and reaction times (10, 15 and 20 min) were investigated.

Table 2 shows that as the MSH:LNR ratio increased from 0.5:1 to 1.5:1, the hydrogenation percentage increased from 26.14 % to 32.16 %. In theory, 1 mol of MSH will produce 1 mol of diimide molecule. In a study conducted by Hamizah et al. (2016), the use of MSH:LNR weight ratio of 2:2 for hydrogenation using reflux heating has decreased the percentage of hydrogenation. This is because, Miller (1965) stated that excessive diimide can cause more disproportionation in the reaction. Therefore, MSH:LNR weight ratio of 1.5:1 is sufficient for this work.

The study on the effect of the microwave power on LNR hydrogenation showed that a deep yellowish mixture was obtained after around 4 min of reaction at 300 and 450 W. However, the same occurrence was obtained only after about 2 min of reaction at 600 W. As shown in Table 3, increasing the microwave power would increase the hydrogenation percentage of HLNR. This may be due to the higher reaction rate that generated the diimide molecule faster. The rapid heating at microwave frequencies will lead to maximum production of HLNR in a short time. In addition, the reaction mixture was not heated at higher than 600 W because of the limitation of domestic microwave. Other than that, the non-stirred mixture in microwave oven was found to be a critical factor on the

mass transfer, influencing the percentage of hydrogenation compare to reflux heating experiments. That is why the percentage of hydrogenation was low when conducted an experiment using microwave heating technique.

Basically, the hydrogenation process cannot take place if the diimide molecule was not generated continuously. Besides, the extension of reaction time would increase the chances of LNR to react with the diimide molecule. Based on Table 4, it can be clearly seen that the reaction time had significantly increased the percentage of hydrogenation. In this work, HLNR with 41.18% of hydrogenation was obtained with MSH:LNR weight ratio of 1.5:1, microwave power of 600 W and reaction time at 20 min. LNR hydrogenation using MSH by reflux heating gave the highest hydrogenation percentage of 47.60% with a MSH:LNR weight ratio of 0.75:1 at 100°C for 60 min (Idris et al. 2018). Whereas, the hydrogenation of LNR by heating in microwaves has given the highest hydrogenation percentage of 41.18% with a MSH:LNR weight ratio of 1.5:1 at 600 W for 20 min.

Thus, the application of microwave frequencies as heating tool was capable of replacing the reflux methods and reactor in order to produce hydrogenated polymer in a short time. For future scale-up process, optimization of this method through Response Surface Methodology (RSM) is needed. The optimum conditions determined by RSM can be used to scale-up the process and also minimize production costs.

TABLE 1. Hydrogenation percentage of LNR at different parameter conditions

MSH:LNR weight ratio	Microwave power (W)	Reaction time (min)	Hydrogenation (%)
0.5:1	300	10	17.15
1:1	300	10	20.45
1.5:1	300	10	22.90
0.5:1	300	15	21.26
1:1	300	15	23.25
1.5:1	300	15	26.79
0.5:1	300	20	23.49
1:1	300	20	25.37
1.5:1	300	20	29.43
0.5:1	450	10	19.14
1:1	450	10	22.44
1.5:1	450	10	25.37
0.5:1	450	15	23.02
1:1	450	15	28.93
1.5:1	450	15	31.18
0.5:1	450	20	26.14
1:1	450	20	30.75
1.5:1	450	20	32.16
0.5:1	600	10	22.24
1:1	600	10	26.47
1.5:1	600	10	29.43
0.5:1	600	15	29.87
1:1	600	15	31.69
1.5:1	600	15	33.91
0.5:1	600	20	31.46
1:1	600	20	37.97
1.5:1	600	20	41.18

TABLE 2. Hydrogenation percentage of LNR calculated at different MSH:LNR weight ratio

MSH:LNR Weight Ratio	Hydrogenation (%)
0.5:1	26.14
1:1	30.75
1.5:1	32.16

Conditions: Microwave power = 450 W; reaction time = 20 min

TABLE 3. Hydrogenation percentage of LNR calculated at different microwave power

Microwave Power (W)	Hydrogenation (%)
300	25.37
450	30.75
600	37.97

Conditions: MSH:LNR weight ratio = 1:1; reaction time = 20 min

TABLE 4. Hydrogenation percentage of LNR calculated at different reaction time

Reaction Time (min)	Hydrogenation (%)
10	29.43
15	33.91
20	41.18

Conditions: MSH:LNR weight ratio = 1.5:1; microwave power = 600 W

CONCLUSION

In summary, thermolysis process of MSH by microwave heating is found to be suitable for hydrogenation of LNR. Analysis of FTIR and NMR spectra showed the same basic changes of the main peak as reflux heating technique. A MSH:LNR weight ratio of 1.5:1 yielded a hydrogenation percentage of 41.18 % after 20 min of reaction at 600 W. This method can produce HLNR at short reaction times.

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