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Hydrogenation of Liquid Natural Rubber via Diimide Reduction in Hydrazine Hydrate/Hydrogen Peroxide System

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ABSTRACT

Abstract. Liquid natural rubber (LNR) with molecular weight of lower than 10^5 and shorter polymeric chain than natural rubber was prepared. LNR was then hydrogenated via diimide reduction by oxidation of hydrazine hydrate with hydrogen peroxide. The unsaturated units of the rubber were converted into saturated hydrocarbon to strengthen the backbone of the polymer so it was able to resist thermal degradation. The results indicated that hydrogenation degree of the product (HLNR) could be extended to 91.2% conversion under appropriate conditions. The hydrogenated LNR (HLNR) was characterized using Fourier-Transform Infrared (FTIR) and Nuclear Magnetic Resonance (NMR) spectroscopy. The physical characteristics of HLNR were analyzed with Thermogravimetric Analysis (TGA).

Keywords: *hydrogenation, diimide reduction, liquid natural rubber, NMR, TGA*

PACS: 83.80.Va

INTRODUCTION

Natural rubber (NR) obtained from *Hevea brasiliensis* is a versatile elastomer that can be used in a variety of products. An extensive amount of research has been performed with the enhancement of the properties of natural rubber due to an increased awareness about green conservation and an increased prominence on the usage of renewable resources. Chemical alteration of polymers has been broadly investigated to yield new materials or highly improved properties polymers [1].

Unsaturated polymers are commonly targeted for the modification as the double bonds in the chains are susceptible to be manipulated into new structures through series of chemical reactions such as halogenation, epoxidation, and hydrogenation. The modified polymers are expected to be resistant towards thermal and oxidative degradation [2]. The reduction of double bond units of rubber provides weather resistance of the rubber as the unsaturated components of the rubber were replaced with the saturated unit after hydrogenation process. Arayapranee & Rempel in 2009 reported that 48% hydrogenated natural rubber vulcanizate had higher heat and ozone resistance than natural rubber vulcanizate. Therefore, it could be used as rubber materials for outdoor purpose [3].

Liquid natural rubber (LNR) is widely used in automotive industries. It can be prepared from the depolymerisation of natural rubber. Its microstructure is similar with shorter polymeric chains of natural rubber with molecular weight that is generally lower than 10^5 [4]. Due to its high cis 1,4-polyisoprene units, LNR has low thermal and oxidative stability. In this project, LNR was hydrogenated to improve its degradation resistance. The addition of hydrogen into the unsaturated units of LNR came from hydrazine hydrate/hydrogen peroxide system. The system produced diimide species that responsible for the reduction of LNR. This method is introduced by Wideman in 1984 and lots of optimisations have been done to achieve better results [5]. FIGURE 1 shows the production of diimide species and its action on the unsaturated units of polyisoprene.

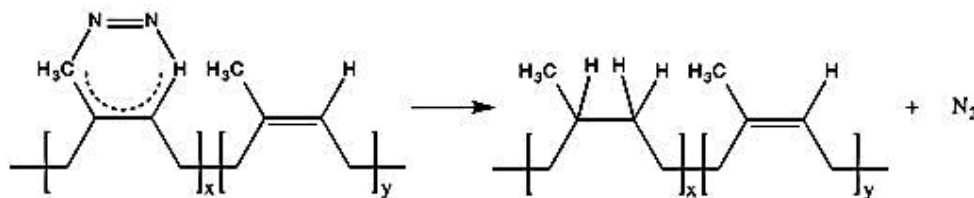


FIGURE 1. Production of diimide species and its action on the hydrogenation of polyisoprene [6].

In the present work, we report the work on the hydrogenation of LNR. It has been demonstrated that the hydrogenation of LNR can yield modified rubbers with improved physical and thermal properties.

EXPERIMENTAL

Material and Characterization

Natural rubber was supplied by Rubber Research Institute of Malaysia (RRIM). Toluene and methanol were purchased from RM Chemical and used as received. Methylene blue, Rose Bengal, hydrazine hydrate and hydrogen peroxide were purchased from Sigma Aldrich. The FTIR and NMR spectroscopy of the samples were analyzed by Perkin Elmer/ BX spectrometer, USA and JEOL JNM-ECP 300 MHz spectrometer, Japan respectively while the decomposition temperature of the samples were measured by thermogravimetric analyser (TGA/SDTA 851e, Mettler Toledo, Switzerland).

Preparation of LNR

LNR was prepared by chemical degradation of natural rubber. About 500 g of NR was dissolved in 1 liter of toluene for overnight. Photosensitizer of Rose Bengal, methylene blue and 10 ml of methanol were added into the solution. Mechanical stirrer was used to stir the solution for 10 days with exposing it to visible light. The LNR was collected and then centrifuged. Two layers of rubber were formed. The top layer was used as it has the minimum gel formation.

Diimide reduction of LNR

The emulsion of 5 g LNR, 0.1 g sodium dodecyl sulphate as a surfactant, few drops of silicone oil, and water were added and stirred for 30 minutes in the three-neck round-bottom flask. Hydrazine hydrate was added for 30 minutes. The system was being heated to 60°C while stirring. The solution of hydrogen peroxide and boric acid was prepared by dissolving 1.5 g of boric acid in 40 ml of hydrogen peroxide. It was then added drop wise for 8 hours. The product obtained was coagulated in ethanol. It was then dried in vacuum oven for at least 12 hours.

RESULTS AND DISCUSSION

Structure Characterization of LNR and HLNR

Fourier-Transform Infrared (FTIR) and Nuclear Magnetic Resonance (NMR) spectroscopy were used to confirm the HLNR.

FTIR was used to define the functional groups in a molecule. The intense peaks at 1663 cm^{-1} and 837 cm^{-1} assigned to C=C stretching vibration and C-H bending vibration in the $-\text{CH}=\text{CH}$ group of polyisoprene respectively. Any changes on the area should indicate that hydrogenation had happened [7]. FIGURE 2 shows the IR spectra of LNR and HLNR. The reduced intensity at 1664 cm^{-1} and 834 cm^{-1} peak recognized to double bond stretching and olefin bending of C-H in the LNR respectively.

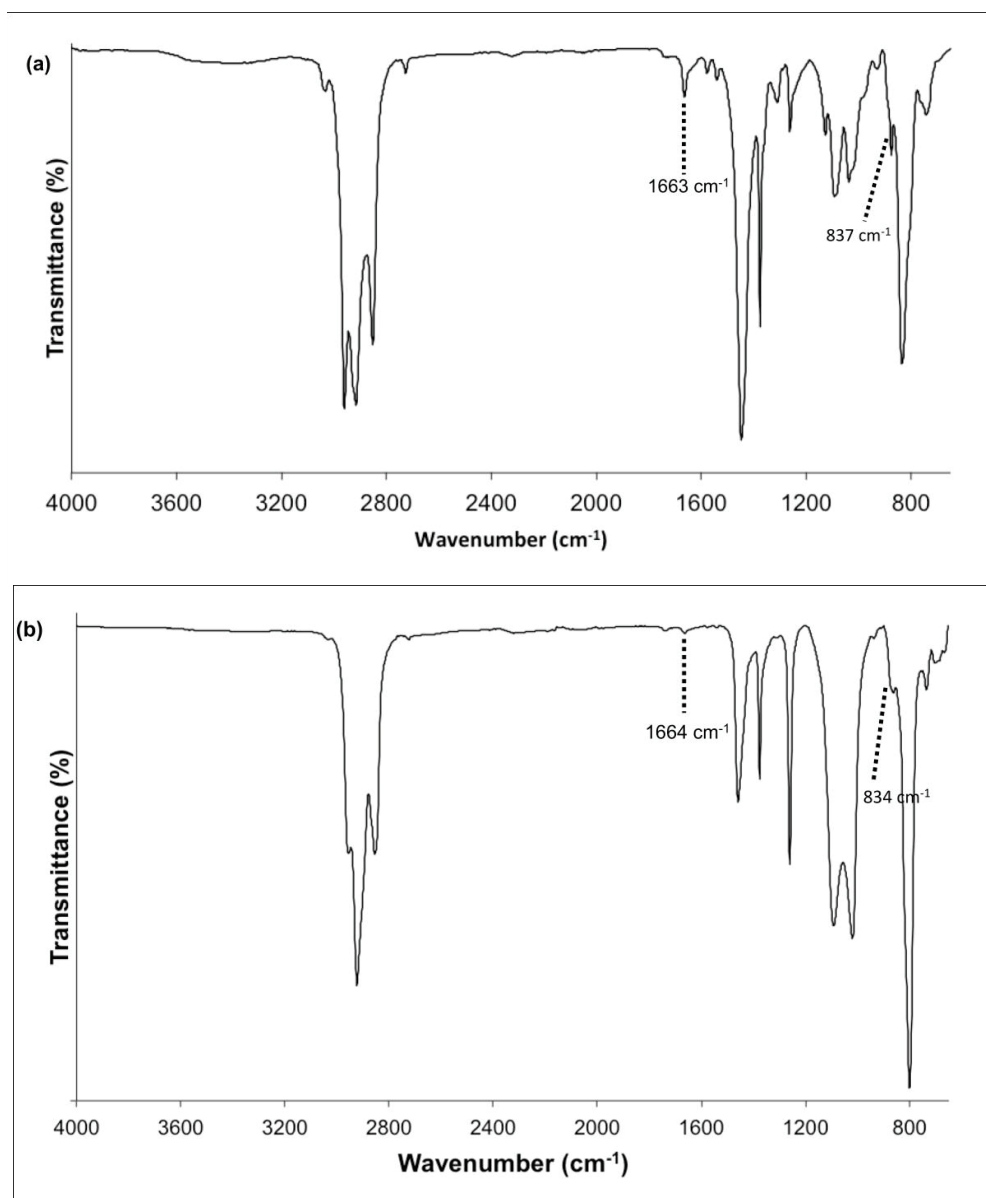


FIGURE 2. IR spectrum of (a) LNR (b) HLNR

The hydrogenated LNR (HLNR) was confirmed by the characterization of ¹HNMR spectroscopy. Indicating that hydrogenation had arisen, the integrated peak area of 5.3 ppm decreased when the degree of hydrogenation increased. New peaks appeared at 0.8 ppm and 1.0-1.3 ppm attributed to the CH₃ group of saturated carbon CH₂ and CH of saturated LNR respectively [8]. FIGURE 3 shows ¹HNMR spectrum of LNR and HLNR while Table 1 shows each peaks assignment. The reduced peak of olefinic area at 5.3 ppm and new signals appearing in the range of 0.8-2.2 ppm indicated that hydrogenation had taken place.

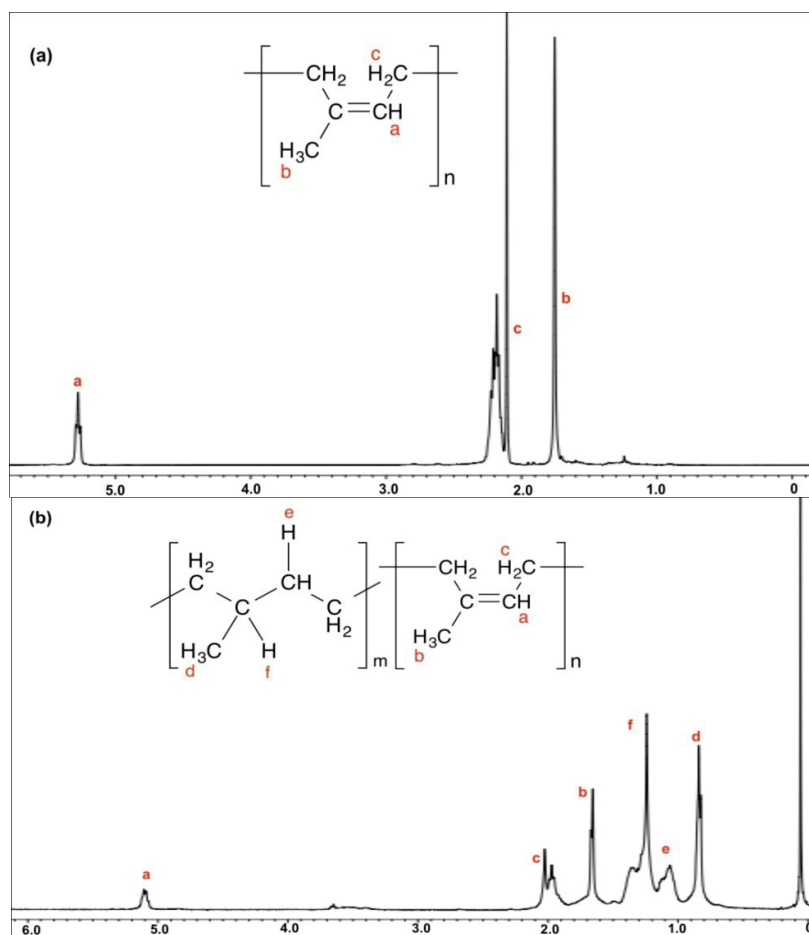


FIGURE 3. ¹H NMR spectrum of (a) LNR (b) HLNR.

TABLE (1) Peak assignment of ¹H NMR spectra

Spectrum	Label	Chemical (ppm)	Shift	Theoretical Shift (ppm)	Chemical	Number of Proton	Inference
A (LNR)	a	5.29		5.15	R-CH=C-R	1	R-CH=C-R
	b	1.75		1.65	R-CH ₃	3	R-CH ₃
	c	2.12		2.05	R-CH ₂ -R	4	R-CH ₂ -R
	a	5.12		5.15	R-CH=C-R	1	R-CH=C-R
B (LNR)	b	1.65		0.8-2.2	R-C=C-CH ₃	3	R-C=C-CH ₃
	c	2.05		0.8-2.2	R-CH ₂ -R	4	R-CH ₂ -R
	d	0.82		0.8-2.2	R-CH ₃	3	R-CH ₃
	e	1.08		0.8-2.2	R-CH ₂	1	R-CH ₂
	f	1.25		0.8-2.2	R-CH	1	R-CH

Both ¹³C NMR spectra for LNR and HLNR are compared as shown in FIGURE 4. There are extra peaks observed at 19.5, 23.5, 32.6, and 37.2 ppm in the HLNR spectrum which attribute to the carbon of the methyl, methylene, and methane of the saturated unit respectively. The decreases in peaks at 125.0 and 136.0 which corresponds to olefinic carbons specifies that the hydrogenation has taken place as the olefinic carbons became saturated.

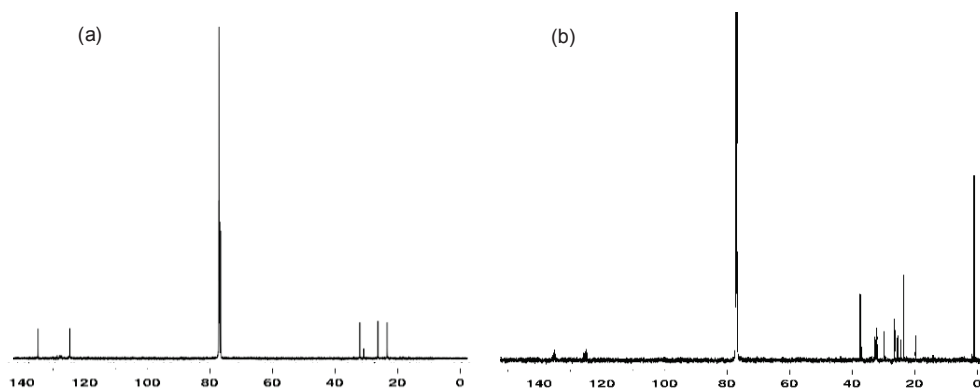


FIGURE 4 ^{13}C NMR of (a) LNR and (b) HLNR

Thermal Decomposition of LNR and HLNR

TGA was carried out to study the degradation temperature of LNR and HLNR. Two sub-levels of the decomposition temperature were obtained to give the information of the initial decomposition temperature (T_{initial}), in which can be calculated by the tangent on the thermogram (TG) curve and the maximum decomposition temperature (T_{max}), which is the maximum peak of the derivative of the TG curve. The range of decomposition temperature of the samples is based on the T_{initial} and T_{max} . The thermograms and of the samples are as shown in FIGURE 5. Table 2 shows a comparison of the decomposition temperatures of LNR and HLNR. It is found that the decomposition temperature for HLNR is higher than LNR. This indicates that the thermal and stability of the HLNR products were improved by hydrogenation.

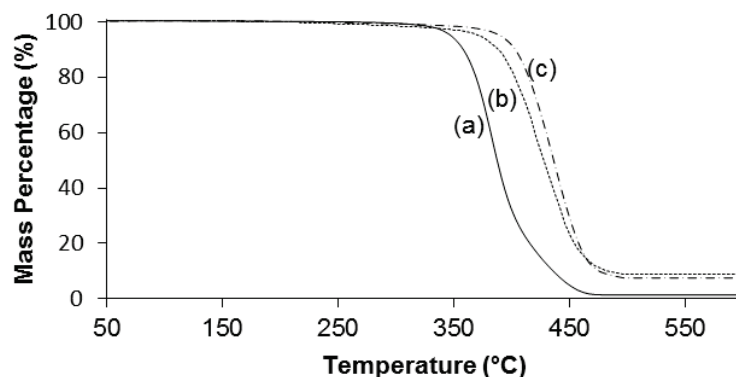


FIGURE 5 Thermogram of (a) LNR (b) 50% HLNR and (c) 60% HLNR.

TABLE (2). Decomposition temperatures of samples

Sample	% Hydrogenation	T_{initial} (°C)	T_{max} (°C)
LNR	-	340	381
HLNR 1	50%	380	422
HLNR 2	60%	390	435

CONCLUSION

The hydrazine hydrate/hydrogen peroxide system can be used to convert the unsaturated units of LNR into hydrogenated units of HLNR. The thermal properties of products are improved as the unsaturated backbone has been saturated that resists to thermal degradation.

ACKNOWLEDGEMENT

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