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Thermal Properties of Hydrogenated Liquid Natural Rubber

Naharullah Jamaluddin, Ibrahim Abdullah, and Siti Fairus M. Yusoff

School of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

Abstract. Natural rubber (NR) was modified to form liquid natural rubber (LNR) via photooxidative degradation. Hydrogenated liquid natural rubber (HLNR) was synthesized by using diimide as source of hydrogen which the diimide is produced by thermolysis of *p*-toluenesulfonyl hydrazide (TSH). The structure of HLNR was characterized by determining the changes of main peaks in Fourier Transform infrared and nuclear magnetic resonance spectra after hydrogenation. Thermogravimetric analysis showed that the HLNR had higher decomposition temperature compared to LNR and the decomposition temperature is directly proportional to the percentage of conversion.

Keywords: liquid natural rubber, hydrogenation, diimide, thermolysis.

INTRODUCTION

Natural rubber (NR) is a polymer consists of isoprene repeating units with a molecular weight of higher than 10^7 u. Natures of NR like highly elastic, resistant to shear, and has desirable dynamic properties appoint NR as one of the important natural resources. These properties are expected to be influenced by non-rubber parts in the composition of NR such as proteins and phospholipids [1]. Other materials can be found in NR up to 5% of dry mass. Besides that, NR is a really big molecule that can have several side reactions naturally like back-biting, cyclisation, agglomeration or coagulation. Therefore, depolymerisation of NR producing liquid natural rubber (LNR) can remove these unwanted species.

Based from Institut de Recherches sur le Caoutchouc [2], LNR has shorter polymeric chains compared to NR with the same microstructure and its molecular weight is lower than 10^5 u. Basically, LNR is the modified NR of liquid phase. However, the application of LNR is still limited due to NR properties of easily degraded after exposure to light and oxidation. Therefore, the interest of modifying NR grows among researchers to improve the physical and chemical properties of NR. Hydrogenation is the most SUITABLE modification to counter the drawback of NR or LNR because of the active site for hydrogenation in polyisoprene chains are the double bonds [3]. Addition of H atom to unsaturated bond of polyisoprene will reduce the site for oxidation to occur [4].

Both catalytic and non-catalytic hydrogenation of NR have been developed with the most of it are catalytic hydrogenation. Catalytic hydrogenation can produce higher percentage of conversion in a short time. However, the costs are really high and usually requires a specific reactor like parr reactor or glass reactor that specially built for insertion and removal of metals as catalyst. On the other hand, non-catalytic hydrogenation is much lower cost and carried out easily by the reaction between NR and hydrogenation reagent such as diimide without using of any reactor. In this work, LNR was synthesized by photooxidative degradation of NR and was hydrogenated by thermolysis of *p*-toluenesulfonyl hydrazide (TSH). The thermal properties of LNR and hydrogenated liquid natural rubber (HLNR) also were studied.

EXPERIMENTAL

Materials and Instrumentation

Methylene blue, rose bengal, and TSH were purchased from Sigma Aldrich. NR was supplied by Rubber Research Institute of Malaysia (RRIM). Solvents such as toluene, methanol, and ethanol were purchased from RM Chemical. FTIR and NMR spectroscopy were studied by using FTIR spectrometer (Spectrum BX, PerkinElmer, USA) and NMR spectrometer (JNM-ECP 400, JEOL, Japan), respectively. Thermal properties of LNR and HLNR were examined by using thermogravimetric analysis (TGA) and its derivatives (TGA/SDTA 851°, Mettler Toledo, Switzerland).

Preparation of LNR

First, 600 g of NR was soaked in 1 L of toluene in a glass jar until it was completely swollen. Then, catalytic amount of rose bengal and methylene blue were dissolved in 10 mL of methanol before added to the swollen NR. The mixture was then stirred with a mechanical stirrer for 10 days. Toluene was adding to the mixture every an hour or two while stirring until the NR was settle down. Finally, the LNR formed was centrifuged to separate the gel and other impurity after stirring process. The product was then characterized and analysed by FTIR, NMR spectroscopy, and TGA.

Synthesis of HLNR

LNR (3 g) was diluted with 15 mL of toluene before TSH (9 g, 0.048 mol) was added. Next, the mixture was refluxed for 6 hours at 130 °C. After reflux process, the product formed was filtered and added into separation funnel for separation process. Then, coagulation process was done with ethanol to separate the by-product of TSH degradation. Lastly, the precipitate from coagulation process was dried in vacuum oven for overnight and the dried product was characterized and analysed by FTIR, NMR spectroscopy, and TGA.

RESULTS AND DISCUSSION

Hydrogenation of LNR

The microstructures of LNR and HLNR were analyzed by FTIR and NMR spectroscopies. FIGURE 1 shows the spectrum of FTIR of LNR and HLNR. There are two important peaks in this work to focus on which located about 1664 and 834 cm^{-1} . Both peaks are corresponding to stretching of C=C (1664 cm^{-1}) and bending of olefinic C-H (834 cm^{-1}) [5]. After hydrogenation, the intensity of these two peaks was reduced due to the decreasing number of C=C and olefinic C-H groups. On the other hand, stretching of sp^3 C-H at 3000–2800 cm^{-1} was increased after hydrogenation due to the increasing of alkane group. Peak around 1590 cm^{-1} was identified due to the residual toluene.

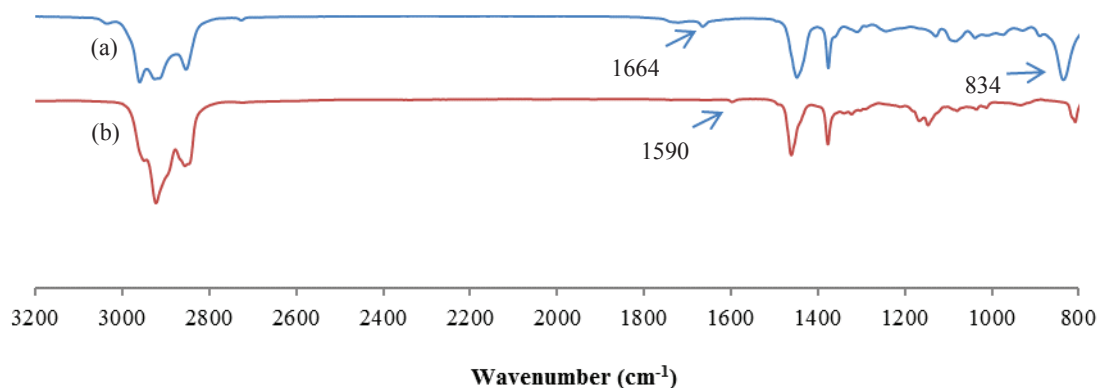


FIGURE 1. FTIR spectra of (a) LNR and (b) HLNR.

The NMR spectra of LNR and HLNR were shown in FIGURE 2. The NMR spectrum of LNR shows signals at 1.71, 2.09 and 5.16 ppm which are attributed to unsaturated methyl, unsaturated methylene and olefinic proton respectively [5]. After hydrogenation, signal of unsaturated methyl, unsaturated methylene and olefinic proton were reduced and new signals appear in the range of 0.8 - 1.4 ppm corresponding to methine, methylene and methyl group. The HLNR signals are broader compared to LNR signals because of phenomenon of nuclear relaxation. Increasing number of alkane group after hydrogenation leads the rate of spin-lattice relaxation to go higher which broaden the signals. Percentage of hydrogenation was calculated based on the ratio between integration of olefinic proton signal and integration of the signals in the range of 0.8 - 2.2 ppm. Signals around 2.2 - 2.3 ppm and 3.7 ppm are due to residual toluene and ethanol signals, respectively. TABLE (1) shows the NMR data of LNR and HLNR.

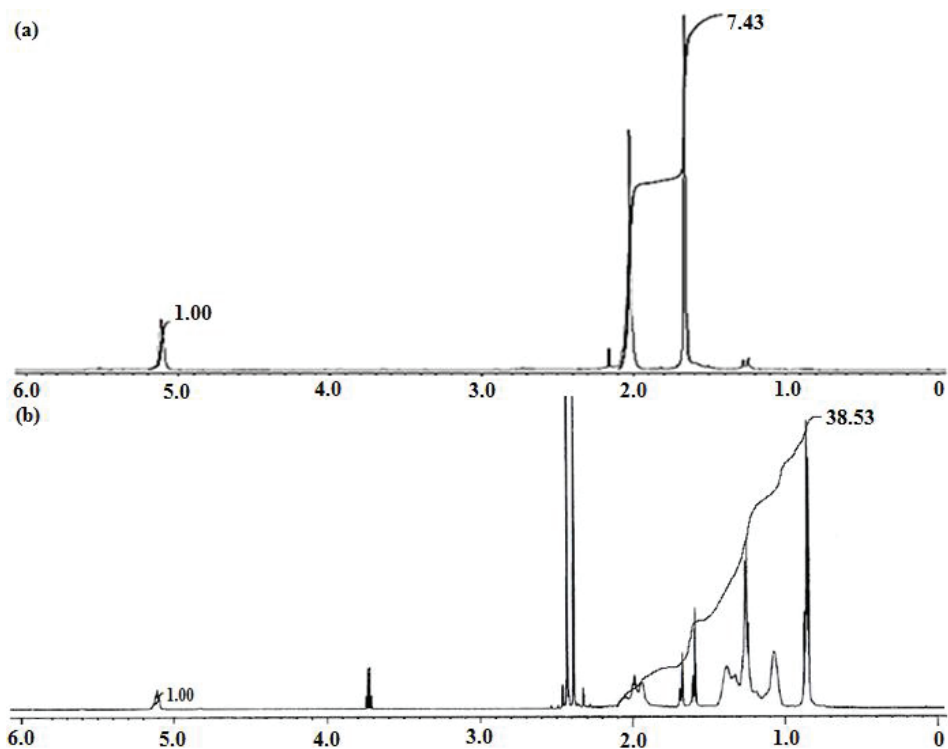


FIGURE 2. NMR spectra of (a) LNR and (b) HLNR.

TABLE (1). NMR data of LNR and HLNR

Rubbers	Chemical shift (ppm)	Group Inference and observations
LNR	1.71	unsaturated methyl group (R-CH ₃)
	2.09	unsaturated methylene group (R-CH ₂ -R)
	5.16	olefinic proton (R-CH=C-R ₂)
HLNR	0.80-1.40	methane, methylene, methyl (new peak)
	1.40-2.20	unsaturated methyl, methylene (decreased and broaden)
	5.16	olefinic proton (decreased)

Thermal Properties of LNR and HLNR

The thermal properties of LNR and HLNR were studied by using TGA. Thermograms of TGA of LNR and HLNR are shown in FIGURE 3 and its derivatives are shown in FIGURE 4. The decomposition temperature of LNR was compared with HLNR at 75.9 and 94.3% hydrogenation (TABLE (2)). Based on FIGURE 3 and FIGURE 4, the maximum decomposition temperature was increased after hydrogenation occurred. Thermogram of LNR shows a maximum decomposition temperature at 377 °C. Meanwhile, thermograms of HLNR at 75.9 and 94.3% hydrogenation show maximum decomposition temperature at 447 and 458 °C, respectively. Decomposition temperature in HLNR thermograms at around 245 °C were due to the site products of thermolysis of TSH. Based from comparison between both HLNR thermograms, a higher percentage of conversion of HLNR also increased the decomposition temperature.

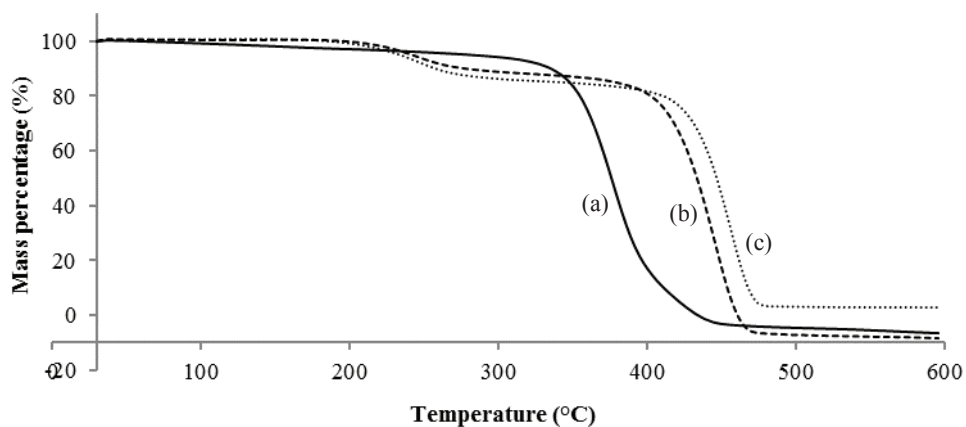


FIGURE 3. TGA thermograms of (a) LNR, (b) HLNR at 75.9% hydrogenation, and (c) HLNR at 94.3% hydrogenation.

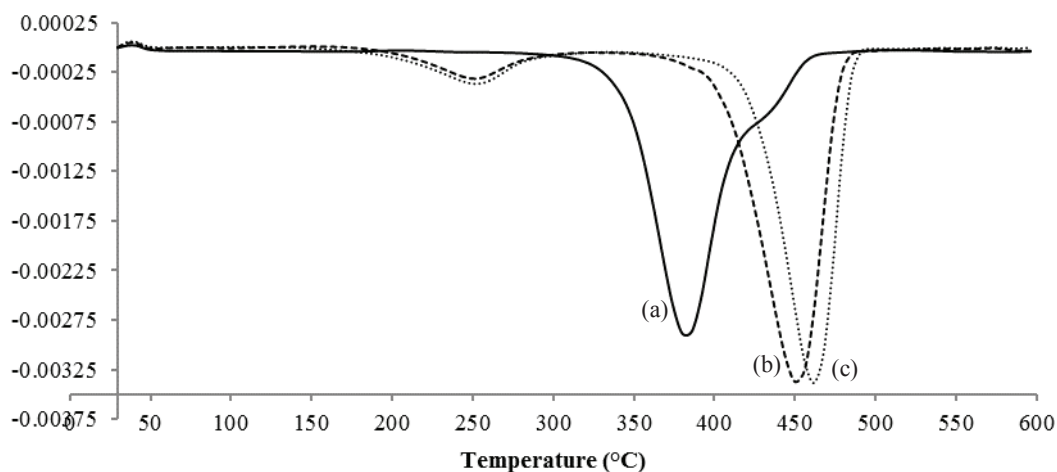


FIGURE 4. Derivatives of thermogravimetry curves of (a) LNR, (b) HLNR at 75.9% hydrogenation, and (c) HLNR at 94.3% hydrogenation.

TABLE (2). Decomposition temperatures of rubber samples

Rubber	Hydrogenation (%)	$T_{\text{decomposed}}$ (°C)
LNR	–	259–377
HLNR	75.9	343–447
HLNR	94.3	360–458

CONCLUSION

Thermolysis process of TSH producing diimide is found to be suitable for hydrogenation of LNR. FTIR and NMR spectra proved the basis changes of the main peak after hydrogenation which is carbon-carbon unsaturated bonds. The thermal properties of LNR were enhanced by the increments of decomposition temperatures after hydrogenation process. Increasing of decomposition temperature was found to be directly proportional to the percentage of conversion.

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REFERENCES

1. Y. Tanaka, *Rubber Chem. and Technol.* **74**, 355-375 (2001)
2. Institut de Recherches sur le Caouthchouc (IRCA). *Development of liquid rubber*. Final report. United Nations Industrial Development Organization (UNICO), 1985. Project no. UF/GLO/81/059.
3. N. Hinchiranan, K. Chrmondusit, P. Prasassarakich, G. L. Rempel, *J. Appl. Polym. Sci.* **100**, 4219 (2006)
4. X. Lin, Q. Pan, G. L. Rempel, *Appl. Cat. A* **276**, 123 (2004)
5. D. L. Pavia, G. M. Lampman, G. S. Kriz, J. R. Vyvyan, In *Introduction to Spectroscopy*, 4th edition; Lockwood, L., Ed.; Brooks/Cole: Belmont, CA, 2010. pp 29, 125, 178.