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Chemical Modifications of Liquid Natural Rubber

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Abstract. Liquid natural rubber (LNR) was synthesized via photosensitized degradation of natural rubber (NR). LNR was modified into epoxidized liquid natural rubber (LENR) and hydroxylated liquid natural rubber (LNR-OH) using $\text{Na}_2\text{WO}_4/\text{CH}_3\text{COOH}/\text{H}_2\text{O}_2$ catalytic system. Chemical structures of LNR and modified LNRs were characterized using Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) and ^1H Nuclear Magnetic Resonance (NMR) spectroscopies. Integration of ^1H NMR was used to calculate the epoxy content (%) of LENR. ^1H NMR detected the formation of LNR-OH after prolonged heating and increased of catalyst in oxidation reaction.

Keywords: liquid natural rubber, oxidation, epoxidation, hydroxylated

INTRODUCTION

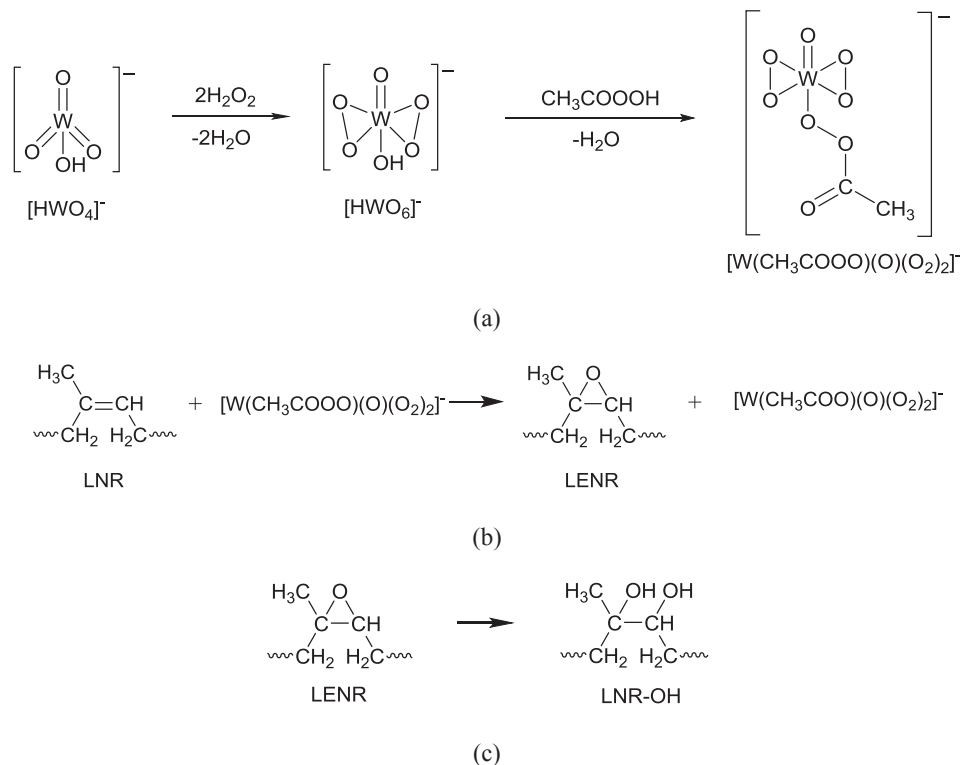
Natural rubber (NR) is a biopolymer being tapped from Para rubber tree, *Hevea brasiliensis* [1]. Studies reveals that the major component in NR is *cis*-1,4-polyisoprene [2]. NR has a very good tensile strength, excellent flexibility, fatigue resistance, high resilience, and resistance to impact and tear. NR is attractive for several applications such as heavy-duty tyres, balloons, gloves, condoms, and suspension element in buildings [3]. However, due to the presence of C=C in the polyisoprene chain, NR become less resistant toward oxidation, ozone or weathering.

Chemical modifications of NR has developed widely to produce new functional polymeric materials. Therefore, chemical modifications of NR attribute many possibilities to enhance the properties of NR such as gas permeability, resistance to oils or fire resistance. Several modifications had been done to modify NR are epoxidation, hydrogenation, halogenation, hydroboration, cyclisation, and maleinization [4,5].

Liquid natural rubber (LNR) is another type of NR having similar microstructure as NR, with shorter polymeric chains and lower molecular weight [6]. There are several methods for production of LNR such as mechanochemical peptisation, thermal, mechanical, photolysis and redox methods [7,8]. LNR can improve processability of NR, since LNR can acts as viscosity modifier, compatibilizer, adhesive, tackifier, sealing agent, plasticizer and caulking compound [6,9]. Nowadays, LNR is used in the reaction instead of NR because of relatively low molecular weight, easily dissolved in non-polar solvents, processability, and contain reactive terminal groups [10-13].

Epoxidized NR (ENR) and hydroxylated NR (NR-OH) are derivatives of NR having epoxy and hydroxyl groups within polyisoprene backbones, respectively. Oxidation is one of the methods to transform the unsaturated parts in polyisoprene into epoxy groups. The main purposes of epoxidation of NR are to improve the properties of NR such as oil resistance, air permeability, and also abrasion resistance [14]. The commercially available ENRs are ENR-25 and ENR-50 which contain 25 mol % and 50 mol % of epoxy content, respectively [6]. ENR and NR-OH can act as intermediate for the other reaction because of the reactive epoxy and hydroxyl groups in polyisoprene chains.

We present our recent study on oxidation of LNR into epoxidized liquid natural rubber (LENR) and hydroxylated liquid natural rubber (LNR-OH) using $\text{Na}_2\text{WO}_4/\text{CH}_3\text{COOH}/\text{H}_2\text{O}_2$ catalytic system (Scheme 1 a, b and c) [15, 16]. The $\text{Na}_2\text{WO}_4/\text{CH}_3\text{COOH}/\text{H}_2\text{O}_2$ catalytic system can efficiently oxidizes LNR into LENR due to active epoxidation site in the structure of tungstic anion $[\text{W}(\text{CH}_3\text{COOO})(\text{O})(\text{O}_2)_2]^-$ [15]. Microstructures of LNR and modified LNRs were characterized using Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) and ^1H Nuclear Magnetic Resonance (NMR) spectroscopies.



SCHEME 1. (a) Oxidation mechanism for $\text{Na}_2\text{WO}_4/\text{CH}_3\text{COOH}/\text{H}_2\text{O}_2$ catalytic system (b) Epoxidation of LNR (c) Hydroxylation of LENR into LNR-OH

EXPERIMENTAL

Materials and Instrumentation

NR in this study was supplied by Rubber Research Institute of Malaysia (RRIM). Toluene, hydrogen peroxide, methanol and ethanol were purchased from R&M Chemicals (Himachal Pradesh, India). Methylene blue, rose Bengal and sodium carbonate were supplied by Sigma Aldrich (Missouri, USA). Sodium tungstate was purchased from Acros Organics. Acetic acid was purchased from System. FTIR and NMR spectroscopies were analysed by using ATR-FTIR spectrometer (Spectrum BX, PerkinElmer, USA) and NMR spectrometer (JNM-ECP 400, JEOL, Japan), respectively.

Preparation of LNR

NR (1 kg) was cut into small cubic of 1 cm^3 approximately. NR was soaked in toluene for 2 days until it become swollen. The mixture of methylene blue (0.1 g) and rose Bengal (0.15 g) were dissolved in methanol before added into the swollen rubber. The rubber mixture was stirred continuously using a mechanical stirrer in the presence of visible light at $70\text{ }^\circ\text{C}$ for 10 to 14 days. Finally, LNR was centrifuged to separate the gel formed during photosensitized degradation [17].

Oxidation of LNR

Oxidation of LNR was carried out using $\text{Na}_2\text{WO}_4/\text{CH}_3\text{COOH}/\text{H}_2\text{O}_2$ catalytic system [15]. LNR was diluted in toluene followed by addition CH_3COOH . $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ in H_2O_2 solution (30%) was added dropwise while stirring solution at 80 °C. The products were precipitated in ethanol, followed by soaking in 1% Na_2CO_3 solution for 24 hours. Then, deionized water was used to wash the sample before dried in vacuum oven at 60 °C for 24 hours.

Hydroxylation of LNR

LNR-OH was synthesized as same procedure as oxidation of LNR, with a slight modifications by increasing the reaction time, temperature and amount of catalyst used in the reaction.

RESULT AND DISCUSSIONS

Oxidation of LNR

In $\text{Na}_2\text{WO}_4/\text{CH}_3\text{COOH}/\text{H}_2\text{O}_2$ catalytic system, active epoxidation site of tungstic anion $[\text{W}(\text{CH}_3\text{COOO})(\text{O})(\text{O}_2)_2]^-$ will efficiently oxidizes LNR into LENR. The addition of CH_3COOH is used to increase the electrophilicity of the diperoxo complex, $[\text{HWO}_6]^-$, thus, enhance the catalytic activity of the reaction. LNR was effectively oxidizes into LENR because of the active epoxidation site in tungstic anion $[\text{W}(\text{CH}_3\text{COOO})(\text{O})(\text{O}_2)_2]^-$. At reaction higher than 90 °C, reaction should be avoided because H_2O_2 is unstable at higher temperature [15]. Scheme 1 shows the oxidation of LNR into LENR.

FTIR spectra of LNR and LENR were shown in Fig. 1. In LNR spectrum the important peaks are located at 1665 and 834 cm^{-1} corresponding to stretch of $\text{C}=\text{C}$ and bend of olefinic $\text{C}-\text{H}$, respectively. The crucial peaks of LENR spectrum located at 1251 and 877 cm^{-1} . Both peaks correspond to symmetric stretch of epoxide ring and asymmetric stretch of epoxide ring, respectively. LENR spectrum showed a broad OH stretching due to cleavage of epoxide ring during oxidation [18].

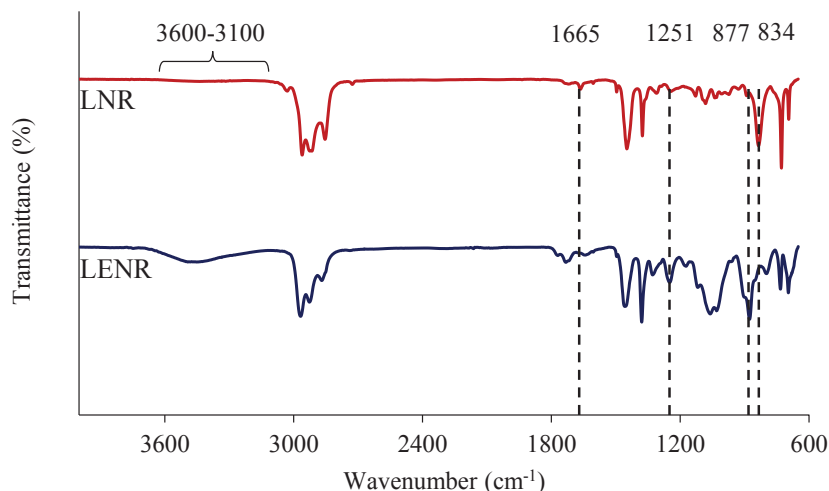


FIGURE 1. FTIR spectra of LNR and LENR

Figure 2 showed ^1H NMR spectra of LNR, LENR-50 and LENR-98. LENR-50 and LENR-98 correspond to 50 % and 98 % of epoxy content, respectively. For LNR spectrum, signal appeared at 1.7, 2.1, and

5.1 ppm, which corresponded to unsaturated methyl (*b*), unsaturated methylene (*c*), and olefinic proton (*a*), respectively. LENR-50 and LENR-98 spectra showed the signal at 2.7 ppm that attribute to the epoxy methine proton (*d*). The epoxy content, X_{epoxy} , of LENR was calculated by comparing the integration areas at chemical shifts 2.7 ppm and 5.1 ppm of ^1H NMR (Eq. 1).

$$X_{\text{epoxy}} = \frac{I_{2.7}}{I_{2.7} + I_{5.1}} \times 100\% \quad (1)$$

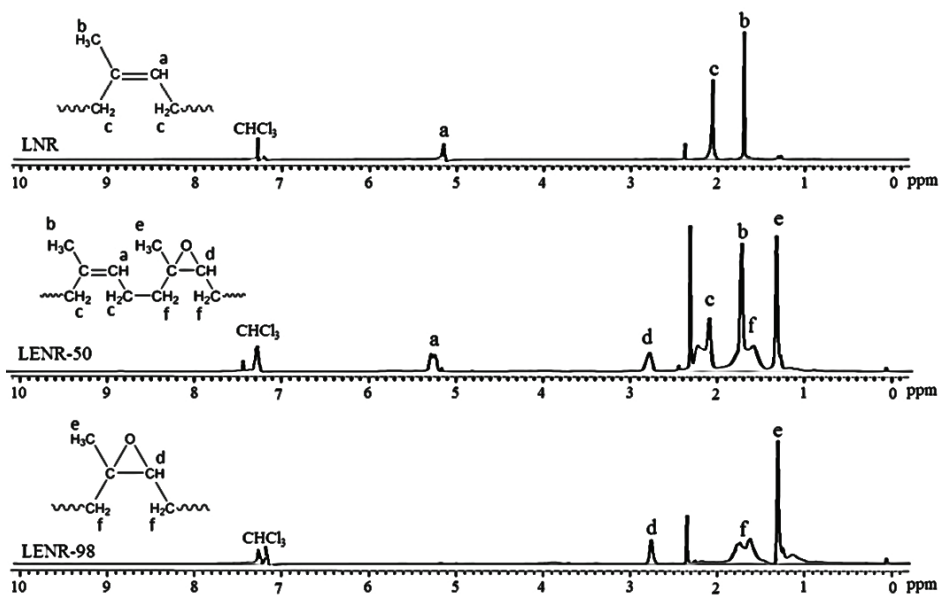


FIGURE 2. ^1H NMR spectra of LNR, LENR-50 and LENR-98

Hydroxylation of LNR

LNR-OH was produced via the same method as oxidation of LNR, but a slight modification by increasing the amount of catalyst, reaction time and temperature of reaction. The epoxy groups produced in oxidation reaction will hydrolyse and ring opened to produce diols and carbonyls. Scheme 1 (c) shows hydroxylation of LENR into LNR-OH.

In Fig. 3, FTIR spectrum of LNR-OH showed a broad peak around $3600\text{--}3100\text{ cm}^{-1}$ that assigned for OH stretching. The presence of carbonyl groups in LNR-OH were detected at 1730 cm^{-1} due to chain scission reactions [19]. The absorption signal in LNR-OH spectrum around $1260\text{ to }1000\text{ cm}^{-1}$ indicated the presence of C-O stretch.

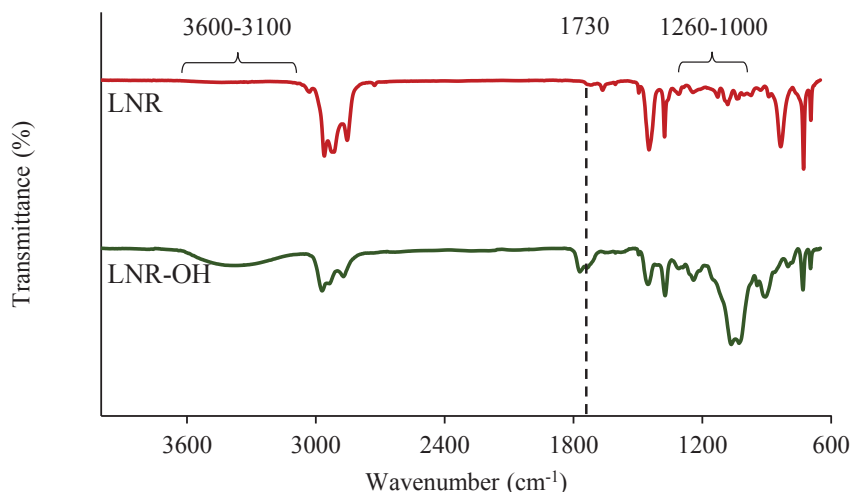


FIGURE 3. FTIR spectra of LNR and LNR-OH

According to Fig. 4, LNR-OH spectrum observed the presence of hydroxylated proton (*g*) and diols (*j*) at 3.4 ppm and 3.9 ppm, respectively.

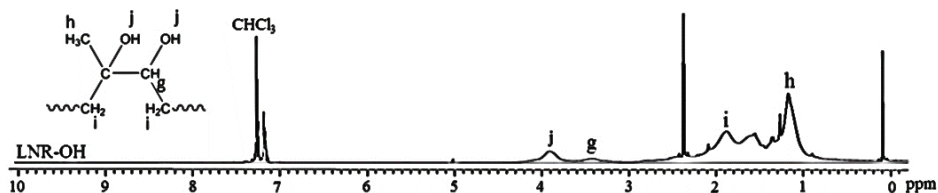


FIGURE 4. ^1H NMR spectrum of LNR-OH

CONCLUSION

LNR was successfully modified into LENR and LNR-OH via oxidation reaction using $\text{Na}_2\text{WO}_4/\text{CH}_3\text{COOH}/\text{H}_2\text{O}_2$ catalytic system. The chemical structures of LNR and modified LNRs were characterized using FTIR and ^1H NMR spectroscopies. In future, LENR and LNR-OH will be used as compatibilizers in polystyrene/natural rubber blend.

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