

## Epoxidation and Hydroxylation of Liquid Natural Rubber (Pengepoksidaan dan Penghidroksilan Getah Asli Cecair)

NUR HANIS ADILA AZHAR, HAMIZAH MD RASID & SITI FAIRUS M. YUSOFF\*

### ABSTRACT

Liquid natural rubber (LNR) was functionalized into liquid epoxidized natural rubber (LENR) and hydroxylated LNR (LNR-OH) via oxidation using a  $\text{Na}_2\text{WO}_4/\text{CH}_3\text{COOH}/\text{H}_2\text{O}_2$  catalytic system. Microstructures of LNR and functionalized LNRs were characterized using Fourier Transform Infrared (FTIR) and Nuclear Magnetic Resonance (NMR) spectroscopies. The effect of  $\text{CH}_3\text{COOH}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{Na}_2\text{WO}_4$ , reaction time and temperature on epoxy content were investigated. LNR-OH was obtained when oxidation reaction was conducted at a longer reaction time, higher temperature or excess amount of catalyst. Thermogravimetric analysis (TGA) reported the thermal behavior of functionalized LNRs. Molecular weight and polydispersity index (PDI) were determined using gel permeation chromatography (GPC).

**Keywords:** Diols; epoxidation; hydroxylated; liquid natural rubber; oxidation

### ABSTRAK

Getah asli cecair (LNR) telah diperfungsikan kepada getah asli cecair terepoksida (LENR) dan getah asli cecair terhidroksil (LNR-OH) melalui tindak balas pengoksidaan menggunakan sistem pemangkinan  $\text{Na}_2\text{WO}_4/\text{CH}_3\text{COOH}/\text{H}_2\text{O}_2$ . Mikrostruktur LNR dan LNR diperfungsikan dicirikan menggunakan spektroskopi Fourier transformasi inframerah (FTIR) dan resonans magnet nukleus (NMR). Kesan  $\text{CH}_3\text{COOH}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{Na}_2\text{WO}_4$ , masa dan suhu tindak balas ke atas kandungan epoksi dikaji. LNR-OH diperolehi apabila tindak balas pengoksidaan dijalankan pada masa yang lebih panjang, suhu yang lebih tinggi atau lebih amaan pemangkin. Analisis termogravimetri (TGA) melaporkan sifat terma LNR yang terfungsikan. Berat molekul dan indeks kepoliserakan (PDI) ditentukan melalui kromatografi penelapan gel (GPC).

**Kata kunci:** Diol; getah asli cecair; pengepoksidaan; pengoksidaan; terhidroksil

### INTRODUCTION

Natural rubber (NR) is originated from the sap of rubber tree or also known as *Hevea brasiliensis*. The major uses of NR are for tires, molded goods, medical devices, personal protective equipment and mechanical parts due to its excellent elasticity and good mechanical behaviors (Puskas et al. 2014). Nevertheless, NR is a natural polymer having high molecular weight and can be chemically depolymerized into liquid natural rubber (LNR).

LNR is a derivative of NR with similar microstructure as NR but has a shorter polymeric chain (Nur Hanis Adila et al. 2015). LNR can be produced via thermal, oxidative degradation, mechanochemical peptisation, redox reaction, photolysis and photochemical oxidation (Claranma et al. 1991; Mohd Suzeren et al. 2006; Nair et al. 1997; Suhawati et al. 2014). Recently, LNR has becoming prominent due to efficiency of the reaction in liquid form and the reactants can be mixed easily with lower energy usage (Hussin & Ebdon 1998). LNR can be applied as compatibilizers in polymer blends, reactive plasticizers, viscosity modifier, sealing agent, adhesive, varnishes, coatings and binders (Ibrahim 1994; Suhawati et al. 2014).

NR/LNR is known to have poor ageing properties, wet grip properties, oil and weather resistance due to the

unsaturation of the carbon-carbon double bond (C=C) within polyisoprene backbones (Gelling & Porter 1988; Wongthong et al. 2013). The drawbacks of NR/LNR led to various kinds of chemical modifications. Chemical modifications of NR/LNR have been studied to improve the performances of basic polymer and produce new polymeric materials (Brosse et al. 2000). Examples of NR/LNR modifications include epoxidation, hydrogenation, halogenation, grafting and cyclisation (Cai et al. 2007; Hanafi et al. 2005; Nur Hanis Adila et al. 2015; Riyajan 2007; Rosniza et al. 2012).

Epoxidized natural rubber (ENR) is a modified NR having epoxy groups (Baker & Gelling 1987). Epoxidation can improve some properties of NR such as oil and organic solvent resistance, air permeability, damping properties, good compatibility with polar polymers and abrasion resistance (Dobre et al. 2011; Li et al. 2013; Soheil-moghaddam et al. 2013; Yu et al. 2008). Liquid epoxidized natural rubber (LENR) can act as good precursors for the synthesis of new polymeric materials with specific properties in relation with the expected application (Brosse et al. 2000). Previously, ENR was synthesized using performic acid at 50°C for 4-5 h but they managed to get only 25 mol% of epoxy content (Yoksan

2008). Zhang et al. (2010) has studied the oxidation of NR via  $\text{Na}_2\text{WO}_4/\text{CH}_3\text{COOH}/\text{H}_2\text{O}_2$  catalytic system resulted in 92% of epoxy content at a higher reaction temperature (90°C) and longer reaction time (24 h).

There are only a few paper reported on the hydroxylated NR/LNR compared to the research of hydroxylated oil. Hydroxylated oils can be produced through prolonged heating of oxidation reaction (Okieimen et al. 2005). Gan and Ziana (1997) has reported the partially cleavage of epoxide rings in ENR-50 into diols using lead tetraacetate and periodic acid. Hydroxylated NR is very reactive due to the hydroxyl groups in its polymer chain. Therefore, hydroxylated NR can acts as intermediates for other reaction such as esterification.

This paper reports oxidation of LNR using  $\text{Na}_2\text{WO}_4/\text{CH}_3\text{COOH}/\text{H}_2\text{O}_2$  catalytic system to give functionalized LNRs. LNR and functionalized LNRs were analyzed using FTIR,  $^1\text{H}$  NMR, TGA and GPC. The effect of  $\text{CH}_3\text{COOH}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{Na}_2\text{WO}_4$ , reaction time and temperature on epoxy content were investigated.

## MATERIALS AND METHODS

### MATERIALS

NR was purchased from Malaysian Rubber Board. Toluene, *o*-xylene, hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), ethanol and methanol were provided by R&M Chemicals. Methylene blue, rose Bengal and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) were supplied from Sigma Aldrich. Sodium tungstate ( $\text{Na}_2\text{WO}_4$ ) was provided by Acros Organics and acetic acid ( $\text{CH}_3\text{COOH}$ ) was purchased from System.

### SYNTHESIS OF LNR

LNR was prepared using photosensitized degradation method (Kargarzadeh et al. 2015). NR (1 kg) was cut into small cubes (1 cm<sup>3</sup> approximately). NR was immersed in toluene for 2 days. The mixture of methylene blue (0.10 g) and rose Bengal (0.15 g) in methanol were added into the swollen rubber. The rubber mixture was stirred continuously using a mechanical stirrer in the presence of visible light at 70°C for 10 to 14 days. Finally, LNR was centrifuged to separate the gel formed during photosensitized degradation.

### OXIDATION OF LNR

Oxidation of LNR was conducted using a method previously described by Zhang et al. (2010) with slight modifications. Oxidation of LNR was carried out using LNR in toluene followed by addition of  $\text{CH}_3\text{COOH}$ .  $\text{Na}_2\text{WO}_4$  was added dropwise in  $\text{H}_2\text{O}_2$  solution (30%) while stirring the solution at 80°C. After the reaction has completed, the products were precipitated in ethanol, followed by soaking in 1%  $\text{Na}_2\text{CO}_3$  solution for 24 h. Then, the products were washed with deionized water and dried in vacuum oven at 60°C for 24 h.

### HYDROXYLATION OF LNR

Hydroxylation of LNR was conducted as described for oxidation of LNR, with slight modifications by manipulating the parameter of  $\text{CH}_3\text{COOH}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{Na}_2\text{WO}_4$ , reaction time and temperature (Okieimen et al. 2005).

### CHARACTERIZATION

Fourier transform infrared (FTIR) and  $^1\text{H}$  nuclear magnetic resonance (NMR) spectroscopies were used to determine the chemical structure of the products formed. Attenuated total reflectance-FTIR (ATR-FTIR) spectroscopy (Perkin Elmer) was used to determine any changes in the functional groups that might have been induced by the oxidation reaction. The samples were analyzed in transmittance mode within range of 4000-600 cm<sup>-1</sup>. NMR spectroscopy was used to examine the microstructure of the products. The samples were dissolved in  $\text{CDCl}_3$  for measurements using Fourier Transform NMR 400 MHz Cryoprobe (FT-NMR 400 MHz Cryo). Integration of signals from proton NMR ( $^1\text{H}$  NMR) was used to estimate the epoxy content,  $X_{\text{epoxy}}$ , and hydroxyl content,  $Y_{\text{hydroxyl}}$ .  $X_{\text{epoxy}}$  (1) and  $Y_{\text{hydroxyl}}$  (2) were calculated by comparing the integration area of signals at chemical shifts 2.7, 3.4, 3.9 and 5.1 ppm that correspond to epoxy methine protons, hydroxyl methine protons, diols and olefinic protons, respectively, as shown:

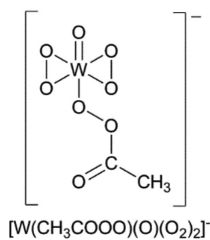
$$X_{\text{epoxy}} = \frac{I_{2.7}}{I_{2.7} + I_{5.1}} \times 100. \quad (1)$$

$$Y_{\text{hydroxyl}} = \frac{I_{3.9}/2}{I_{2.7} + I_{3.4} + I_{3.9}/2 + I_{5.1}} \times 100. \quad (2)$$

The degradation temperatures of samples were determined using thermogravimetric analysis (TGA) and differential thermal gravimetry (DTG) (TGA/SDTA 851<sup>e</sup>, Mettler Toledo, Switzerland). Gel permeation chromatography (GPC) was used to investigate the molecular weight ( $M_w$ ) and polydispersity index (PDI) of LNR, LENR and LNR-OH (Waters 1515 Isocratic HPLC Pump equipped with a Waters 2414 Refractive Index detector, Waters Corporation, USA).

## RESULTS AND DISCUSSION

In this paper, the  $\text{Na}_2\text{WO}_4/\text{CH}_3\text{COOH}/\text{H}_2\text{O}_2$  catalytic system was expected to catalyze efficiently the oxidation of LNR. This is due to the nature of tungstic anion [ $\text{W}(\text{CH}_3\text{COOO})(\text{O})(\text{O}_2)_2$ ] (Scheme 1) which having two active epoxidation sites will act interactively to enhance the epoxidation of LNR (Zhang et al. 2010). Nevertheless, the epoxy group produced will undergo ring-opening reaction when the amount of catalyst, reaction time and temperature were increased.



SCHEME 1. Chemical structure of tungstic anion

### STRUCTURAL ANALYSIS OF LNR AND FUNCTIONALIZED LNRs

Infrared spectra of LNR, LENR and LNR-OH are shown in Figure 1. Each of the spectra showed different main absorption peaks. The crucial peaks that appeared on LNR spectrum are 1665 and 834  $\text{cm}^{-1}$  corresponding to C=C stretching and olefinic C-H bending, respectively. For LENR spectrum, the main peaks located at 1251 and 877  $\text{cm}^{-1}$  are assigned for symmetric and asymmetric stretching of epoxide ring, respectively. Important peak of LNR-OH spectrum around 3600-3100  $\text{cm}^{-1}$  is a broad peak due to OH functional group. LENR spectrum also showed a slightly broad O-H stretching due to partial cleavage of oxirane into diols during epoxidation (Fieser & Fieser 1967; Norman & Coxon 1993). In addition, the presence of peaks around 3000-2850 and 1730  $\text{cm}^{-1}$  due to  $\text{sp}^3$  C-H stretching and signal of carbonyl group in LNR and functionalized LNRs spectra. Carbonyl groups in the polymer chain generated during chain scission reactions is a result of hydroxylation (Scheme 2).

<sup>1</sup>H NMR spectra of LNR, LENR and LNR-OH are shown in Figure 2. LNR spectrum shows signals at 1.70, 2.10 and 5.10 ppm, which attributed to the protons of unsaturated methyl (*b*), unsaturated methylene (*c*) and olefinic (*a*), respectively. Oxidation of LNR caused the signals in LENR

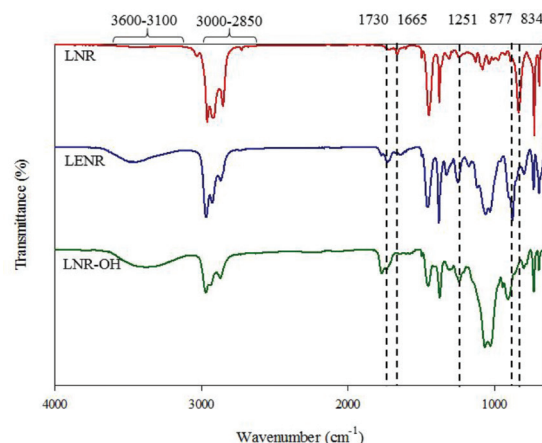
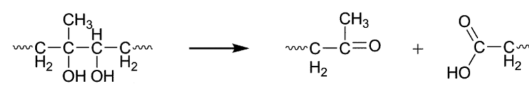


FIGURE 1. FTIR spectra of LNR, LENR and LNR-OH



SCHEME 2. Chain scission reaction

spectrum to appear at 2.70 ppm that correspond to the epoxy methine proton (*d*). As the epoxide was ring-opened to diol structure, the hydroxyl methine proton (*g*) on LNR-OH spectrum was detected at 3.40 ppm. Diols gave a broad O-H peak (*j*) at 3.90 ppm.

### PARAMETER STUDIES ON EPOXIDATION OF LNR EFFECT OF $\text{CH}_3\text{COOH}/\text{H}_2\text{O}_2$

The influence of  $\text{CH}_3\text{COOH}$  and  $\text{H}_2\text{O}_2$  in the oxidation of LNR was investigated by fixing the amount of LNR,  $\text{Na}_2\text{WO}_4$ , temperature and reaction time. Table 1 shows that

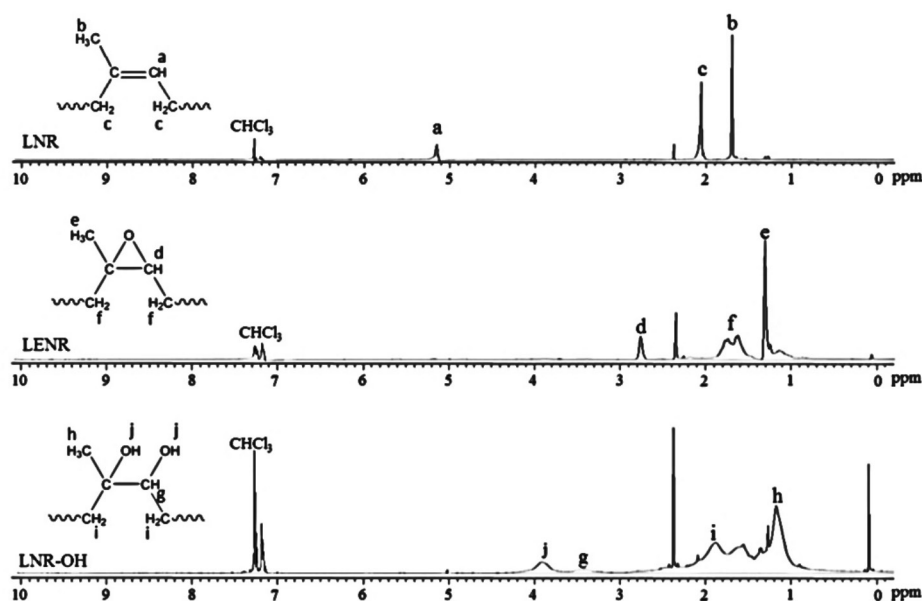
FIGURE 2. <sup>1</sup>H NMR spectra of LNR, LENR and LNR-OH

TABLE 1. Effect of CH<sub>3</sub>COOH/H<sub>2</sub>O<sub>2</sub> on oxidation of LNR

Experiment	CH <sub>3</sub> COOH (mmol)	H <sub>2</sub> O <sub>2</sub> (mmol)	Epoxy Content (%)
1	27	90	46.1
2	27	180	49.3
3	54	90	42.6
4	54	180	98.3

Condition: LNR = 60 mmol, Na<sub>2</sub>WO<sub>4</sub> = 0.5 mmol, T = 80°C, reaction time = 8 h

increasing volume of CH<sub>3</sub>COOH and H<sub>2</sub>O<sub>2</sub> will increase the epoxy content because CH<sub>3</sub>COOH and H<sub>2</sub>O<sub>2</sub> are significant in oxidation of LNR as both involved in the formation of peracetic acid. H<sub>2</sub>O<sub>2</sub> is prone to oxidize vinylic carbon of LNR to form epoxy ring and water as the byproducts (Suhawati et al. 2014).

#### EFFECT OF Na<sub>2</sub>WO<sub>4</sub>

Table 2 shows the effect of Na<sub>2</sub>WO<sub>4</sub> on oxidation of LNR. The results showed increasing amount of Na<sub>2</sub>WO<sub>4</sub> will increase the epoxy content of LENR. We had done experiment for the amount of Na<sub>2</sub>WO<sub>4</sub> higher than 1 mmol with the same reaction conditions, which resulted into the disappearance of proton on epoxide ring and appearance of O-H peak on NMR spectrum (Gan & Ziana 1997). Both 0.5 and 1 mmol of Na<sub>2</sub>WO<sub>4</sub> contained almost the same epoxy content. Hence, the optimum amount of catalyst was 0.5 mmol.

TABLE 2. Effect of Na<sub>2</sub>WO<sub>4</sub> on oxidation of LNR

Experiment	Na <sub>2</sub> WO <sub>4</sub> (mmol)	Epoxy Content (%)
5	-	25.1
6	0.25	29.9
7	0.5	39.2
8	1.0	43.5

Condition: LNR = 60 mmol, CH<sub>3</sub>COOH = 27 mmol, H<sub>2</sub>O<sub>2</sub> = 90 mmol, T = 80°C, reaction time = 4 h

TABLE 3. Effect of reaction time on oxidation of LNR

Experiment	Reaction Time (h)	Epoxy Content (%)
11	4	39.2
12	6	68.6
13	8	98.3
14	24	78.0

Condition: LNR = 60 mmol, Na<sub>2</sub>WO<sub>4</sub> = 0.5 mmol, CH<sub>3</sub>COOH = 54 mmol, H<sub>2</sub>O<sub>2</sub> = 180 mmol, T = 80°C

TABLE 4. Effect of temperature on oxidation of LNR

Experiment	Temperature (°C)	Epoxy Content (%)
15	60	33.3
16	70	35.8
17	80	68.6

Condition: LNR = 60 mmol, Na<sub>2</sub>WO<sub>4</sub> = 0.5 mmol, CH<sub>3</sub>COOH = 54 mmol, H<sub>2</sub>O<sub>2</sub> = 180 mmol, reaction time = 6 h

#### EFFECT OF REACTION TIME

The influences of reaction time were studied in various reaction times which are 4, 6, 8 and 24 h (Table 3). From 4 to 8 h of reaction time, the epoxy content increase significantly but for the reaction of 24 h, epoxy content of LENR gradually decreased because epoxide tend to ring-open after all the double bond had fully oxidized. This proved that after 8 h of reaction time, olefinic C=C of LNR had almost fully oxidized (98.3%).

#### EFFECT OF TEMPERATURE

The temperature was varied from 60°C until 80°C in order to investigate the effect of temperature on the epoxidation of LNR (Table 4). As for 60°C and 70°C, the epoxy contents were 33.3% and 35.8%, respectively. But when the temperature was elevated to 80°C, epoxy content of LENR was doubled. An increase in temperature also increases the rate of epoxidation and degradation of LNR. Reaction

with temperature above 90°C should be avoided because H<sub>2</sub>O<sub>2</sub> is unstable at high temperature (Zhang et al. 2010).

#### HYDROXYLATION OF LNR

Hydroxylated LNR (LNR-OH) was resulted from cleavage and hydrolysis of epoxide ring resulting in diols polymer. Scheme 3 shows the proposed reaction for the formation of LNR-OH (Okieimen et al. 2005). The production of LNR-OH through oxidation reaction is simpler compared to other methods that required separate reaction after epoxidation. Table 5 shows the reaction conditions that has been used to obtain LNR-OH.

#### THERMAL ANALYSIS OF LNR AND FUNCTIONALIZED LNRS

Figures 3 and 4 show the two steps changes on LNR, LENR and LNR-OH thermograms. The first stage degradation of LNR and functionalized LNRS were within temperature range of 120-337°C due to the loss of moisture, residual solvent and low-molecular-weight oligomers (Lodha et al. 2001; Wan Ahmad Kamil & Mohammad Hossein 2015). According to DTG thermograms (Figure 4), the maximum

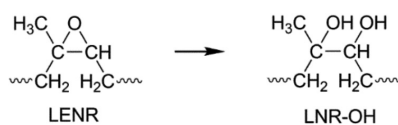
decomposition temperature of LNR, LENR and LNR-OH were 382°C, 420°C and 404°C, respectively. Beyond 454°C, weight loss of LNR and functionalized LNRS corresponded to the cyclized rubber (Asaletha et al. 1998). After being heated up to 600°C, LNR-OH still has 4% weight of remaining sample. This shows that LNR-OH is more stable compared to LNR and LENR.

#### MOLECULAR WEIGHT OF LNR AND FUNCTIONALIZED LNRS

The number average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ) and polydispersity index (PDI) of samples were shown in Table 6. According to GPC value of LNR,  $M_w$  and PDI were 170 000 g/mol and 2.72, respectively. Molecular weight of LENR and LNR-OH were lower than LNR because of the chain scission during oxidation reaction. The polymer chain degraded due to the presence of heat and acid in the reaction (Hahn 1992).

#### CONCLUSION

LNR had been functionalized into LENR and LNR-OH using Na<sub>2</sub>WO<sub>4</sub>/CH<sub>3</sub>COOH/H<sub>2</sub>O<sub>2</sub> catalytic system. The



SCHEME 3. Formation of LNR-OH via hydroxylation

TABLE 5. Reaction conditions of LNR-OH

Experiment	Temperature (°C)	Reaction Time (h)	LNR (mmol)	Na <sub>2</sub> WO <sub>4</sub> (mmol)	CH <sub>3</sub> COOH (mmol)	H <sub>2</sub> O <sub>2</sub> (mmol)	Hydroxyl Content (%)
18	60	24	14	0.5	27	90	49.1
19	90	6	60	0.5	54	180	55.4

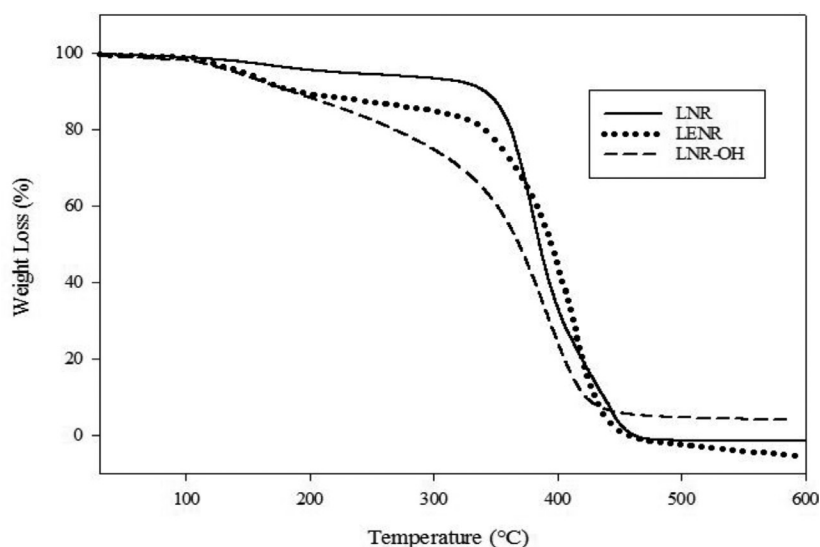


FIGURE 3. TGA thermograms of LNR, LENR and LNR-OH



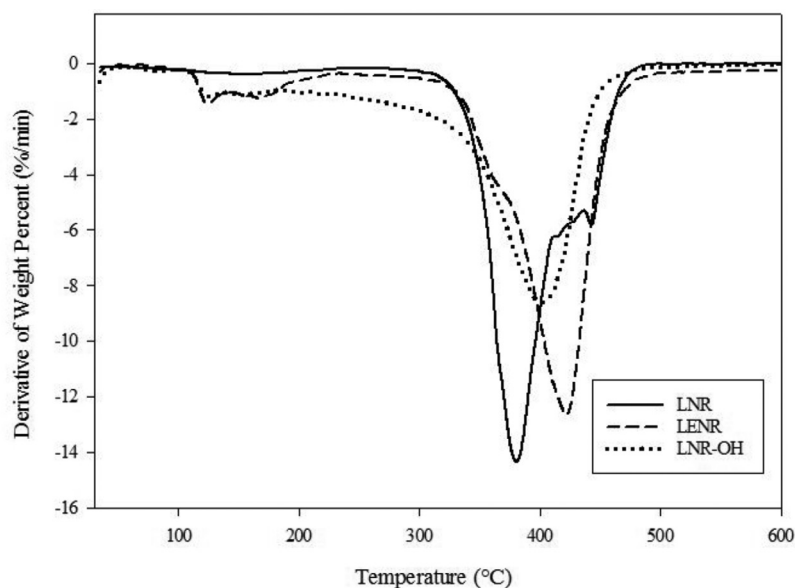


FIGURE 4. DTG thermograms of LNR, LENR and LNR-OH

TABLE 6. Molecular weight and PDI of LNR and functionalized LNRs

Sample	$M_n$ (g/mol)	$M_w$ (g/mol)	PDI
LNR	62 500	170 000	2.72
LENR	19 200	44 000	2.29
LNR-OH	1 800	3 200	1.78

microstructure of LNR and functionalized LNRs had been analyzed using ATR-FTIR and  $^1\text{H}$  NMR spectroscopies. The effect of  $\text{CH}_3\text{COOH}/\text{H}_2\text{O}_2$ ,  $\text{Na}_2\text{WO}_4$ , reaction time and temperature on epoxy content were studied. The highest epoxy content of LENR (98.3%) was achieved with 60 mmol of LNR in toluene, 54 mmol  $\text{CH}_3\text{COOH}$ , 0.5 mmol  $\text{Na}_2\text{WO}_4$  and 180 mmol solution of  $\text{H}_2\text{O}_2$  (30%) at  $80^\circ\text{C}$  for 8 h. LNR-OH was successfully generated via *in situ* multi step reactions.

#### ACKNOWLEDGEMENTS

The authors would like to acknowledge Universiti Kebangsaan Malaysia (UKM) for the research grants (GUP-2015-020 and DIP-2014-16), Ministry of Science, Technology and Innovation (MOSTI), Malaysia for the research grant (03-01-02-SF1207) and Centre for Research and Instrumentation (CRIM) at UKM for their facilities.

#### REFERENCES

- Asaletha, R., Kumaran, M.G. & Thomas, S. 1998. Thermal behavior of natural rubber/polystyrene blends: Thermogravimetric and differential scanning calorimetric analysis. *Polymer Degradation and Stability* 61(3): 431-439.
- Baker, C.S.L. & Gelling, I.R. 1987. Epoxidized natural rubber. In *Development of Rubber Technology - 4*, edited by Whelan, A. & Lee, K.S. London: Elsevier Applied Science. pp. 87-117.
- Brosse, J.C., Campistron, I., Derouet, D., Hamdaoui, A.E., Houdayer, S., Reyx, D. & Ritoit-Gillier, S. 2000. Chemical modifications of polydiene elastomers: A survey and some recent results. *Journal of Applied Polymer Science* 78(8): 1461-1477.
- Cai, Y., Li, S.D., Li, C.P., Li, P.W., Wang, C., Lv, M.Z. & Xu, K. 2007. Thermal degradations of chlorinated natural rubber from latex and chlorinated natural rubber from solution. *Journal of Applied Polymer Science* 106(2): 743-748.
- Claramma, N.M., Nair, N.R. & Mathew, N.M. 1991. Production of liquid natural rubber by thermal depolymerization. *Indian Journal of Natural Rubber Research* 4: 1-7.
- Dobre, T., Parvulescu, O.C., Sanchez-Marcano, J., Stoica, A., Stroescu, M. & Iavorschi, G. 2011. Characterization of gas permeation through stretched polyisoprene membranes. *Separation and Purification Technology* 82(1): 202-209.
- Fieser, L.F. & Fieser, M. 1967. In *Reagents for Organic Synthesis*. New York: Wiley. p. 773.
- Gan, S.N. & Ziana Abdul Hamid. 1997. Partial conversion of epoxide groups to diols in epoxidized natural rubber. *Polymer* 38(8): 1953-1956.
- Gelling, I.R. & Porter, M. 1988. Chemical modification of natural rubber. In *Natural Rubber Science and Technology*, edited by Roberts, A.D. Oxford: Oxford University Press. p. 359.
- Hahn, S.F. 1992. An improved method for the diimide hydrogenation of butadiene and isoprene containing polymers. *Journal of Polymer Science A: Polymer Chemistry* 30(3): 397-408.
- Hanafi Ismail, Arjulizan Rusli & Azura A. Rashid. 2005. Maleated natural rubber as a coupling agent for paper sludge filled natural rubber composites. *Polymer Testing* 24(7): 856-862.
- Hussin Mohd Nor & Ebdon, J.R. 1998. Telechelic liquid natural rubber: A review. *Progress in Polymer Science* 23(2): 143-177.

- Ibrahim Abdullah. 1994. Liquid natural rubber: Preparation and application. In *Progress in Pacific Polymer Science 3. Proceedings of the Third Pacific Polymer Conference*, edited by Ghiggino, K.P. Verlag Berlin Heidelberg: Springer. pp. 351-365.
- Kargarzadeh, H., Ishak Ahmad, Ibrahim Abdullah, Thomas, R., Dufresne, A., Thomas, S. & Aziz Hassan. 2015. Functionalized liquid natural rubber and liquid epoxidized natural rubber: A promising green toughening agent for polyester. *Journal of Applied Polymer Science* 132(3): 41292.
- Li, C., Liu, Y., Zeng, Q.Y. & Ao, N.J. 2013. Preparation and antimicrobial activity of quaternary phosphonium modified epoxidized natural rubber. *Materials Letters* 93: 145-148.
- Lodha, A., Kilbey, S.M., Ramamurthy, P.C. & Gregory, R.V. 2001. Effect of annealing on electrical conductivity and morphology of polyaniline films. *Journal of Applied Polymer Science* 82(14): 3602-3610.
- Mohd Suzeren Jamil, Ishak Ahmad & Ibrahim Abdullah. 2006. Effects of rice husk filler on the mechanical and thermal properties of liquid natural rubber compatibilized high-density polyethylene/natural rubber blends. *Journal of Polymer Research* 13(4): 315-321.
- Nair, N.R., Thomas, S. & Mathew, N.M. 1997. Liquid natural rubber as a viscosity modifier in nitrile rubber processing. *Polymer International* 42(3): 289-300.
- Norman, R.O.C. & Coxon, J.M. 1993. *Principle of Organic Synthesis*. New York: Blackie Academic & Professional. pp. 587-620.
- Nur Hanis Adila Azhar, Naharullah Jamaluddin, Hamizah Md Rasid, Muhammad Jefri Mohd Yusof & Siti Fairus M. Yusoff. 2015. Studies on hydrogenation of liquid natural rubber using diimide. *International Journal of Polymer Science* 243038: 1-6.
- Puskas, J.E., Chiang, K. & Barkakty, B. 2014. Natural rubber (NR) biosynthesis: Perspectives from polymer chemistry. In *Chemistry, Manufacture and Applications of Natural Rubber*, edited by Kohjiya, S. & Ikeda, Y. Cambridge: Elsevier. pp. 30-67.
- Okieimen, F.E., Pavithran, C. & Bakare, I.O. 2005. Epoxidation and hydroxylation of rubber seed oil: One-pot multi-step reactions. *European Journal of Lipid Science and Technology* 107(5): 330-336.
- Riyajan, S.A., Liaw, D.J., Tanaka, Y. & Sakdapipanich, J.T. 2007. Cationic cyclization of purified natural rubber in latex form with a trimethylsilyl triflate as a novel catalyst. *Journal of Applied Polymer Science* 105(2): 664-672.
- Rosniza Hamzah, Mohamad Abu Bakar, Melati Khairuddean, Mohammed, I.A. & Rohana Adnan. 2002. A structural study of epoxidized natural rubber (ENR-50) and its cyclic dithiocarbonate derivative using NMR spectroscopy techniques. *Molecules* 17(9): 10974-10993.
- Suhawati Ibrahim, Rusli Daik & Ibrahim Abdullah. 2014. Functionalization of liquid natural rubber via oxidative degradation of natural rubber. *Polymers* 6(12): 2928-2941.
- Soheilmoghaddam, M., Wahit, M.U. & Akos, N.I. 2013. Regenerated cellulose/epoxidized natural rubber blend film. *Materials Letters* 111: 221-224.
- Wan Ahmad Kamil Mahmood & Mohammad Hossein Azarian. 2015. Thermal, surface, nanomechanical and electrical properties of epoxidized natural rubber (ENR-50)/ polyaniline composite films. *Current Applied Physics* 15(5): 599-607.
- Wongthong, P., Nakason, C., Pan, Q., Rempel, G.L. & Kiatkamjornwong, S. 2013. Modification of deproteinized natural rubber via grafting polymerization with maleic anhydride. *European Polymer Journal* 49(12): 4035-4046.
- Yoksan, R. 2008. Epoxidized natural rubber for adhesive applications. *Kasetsart Journal (Natural Science)* 42: 325-332.
- Yu, H., Zeng, Z., Lu G. & Wang, Q. 2008. Processing characteristics and thermal stabilities of gel and sol of epoxidized natural rubber. *European Polymer Journal* 44(2): 453-464.
- Zhang, J., Zhou, Q., Jiang, X.H., Du, A.K., Zhao, T., Kasteren J.V. & Wang, Y.Z. 2010. Oxidation of natural rubber using a sodium tungstate/acetic acid/hydrogen peroxide catalytic system. *Polymer Degradation and Stability* 95(6): 1077-1082.
- Nur Hanis Adila Azhar, Hamizah Md Rasid & Siti Fairus M. Yusoff\*  
School of Chemical Sciences and Food Technology  
Faculty of Science and Technology  
Universiti Kebangsaan Malaysia  
43600 Bangi, Selangor Darul Ehsan  
Malaysia
- Siti Fairus M. Yusoff\*  
Polymer Research Center (PORCE)  
Faculty of Science and Technology  
Universiti Kebangsaan Malaysia  
43600 Bangi, Selangor Darul Ehsan  
Malaysia

\*Corresponding author; email: sitifairus@ukm.edu.my

Received: 24 June 2016

Accepted: 15 August 2016