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Preparation and Characterization of Hydroxyl Terminated Liquid Epoxidized Natural Rubber

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Hydroxyl terminated liquid epoxidized natural rubber (HTLENR) was successfully synthesized via oxidative degradation of liquid epoxidized natural rubber (LENR) in the presence of cobalt (II) acetyl acetonate (CAA) as the oxidizing agent. The effect of reaction time on molecular weight, chemical structures and hydroxyl content of HTLENR were investigated. The weight average molecular weight (Mw) and polydispersity index (PDI) of the prepared HTLENR were determined using gel permeation chromatography (GPC). The result shows that as the reaction time increased, the Mw decreased indicating the occurrence of higher chain scission. It was found that the lowest Mw was achieved at 10 h reaction time where the Mw and Mn were 37,545 g/mol and 3,233 g/mol. The structural analysis and hydroxyl content of HTLENR on the other hand, were studied by using fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR). The presence of OH group was confirmed by FTIR analysis with the appearance of broad peak at 3,200 – 3,600 cm^{-1}. Subsequently, NMR analysis also confirmed that the highest amount of hydroxyl content which is 7.56 % was achieved at the longest reaction time which is 10 h.

1. Introduction

Natural rubber (NR) is originated from the rubber tree known as Hevea brasiliensis. NR has been used in various field of applications due to its desirable properties and become one of important natural resources due to its good impact resistance, high elasticity and high resilience (Azhar et al., 2016). Due to the existence of unsaturated C=C double bond, NR has low oil resistance, poor ageing properties as well as sensitive towards oxidation and ozone. Thus, in order to enhance the properties of NR, some modifications such as epoxidation, hydrogenation and vulcanization have been conducted (Rooshenass et al., 2017).

Epoxidized natural rubber (ENR) is one of modification that has been done by epoxidation reaction which converted the unsaturated chain of C=C of natural rubber into epoxy group (Dreyer et al., 2010). ENR has better resistance towards oil and organic solvent, good abrasion and good wet grip compared to NR. Besides, the presence of reactive epoxy group in ENR backbone enables for further chain extension reaction or functionalization for property improvement. However, the high molecular weight and the presence of unsaturated double bonds in the polymeric chain of ENR has resulted in high energy processing and restricted its application. Liquid rubber can be an option to solve the problem (Azhar et al., 2017). Liquid epoxidized natural rubber (LENR) which is the product from depolymerization of ENR is a good candidate to replace ENR due to its low molecular weight (Mw) and shorter polymeric chain which has better processability compared to ENR. In 2012, the effect of ENR on the properties of epoxy have been studied (Bakar et al., 2012). From the research, it was reported that the mechanical properties such as flexural strength, fracture toughness and flexural modulus of the epoxy composite were improved with the addition of LENR. While, Kargarzadeh et al. (2015) studied the effect of liquid natural rubber (LNR) and LENR as a toughening agent in polyester. The LENR modified polyester exhibited superior improvement compared to LNR modified polyester in terms of mechanical properties. The existence of reactive groups such as epoxy in the backbone and good solubility in non-polar solvents enable LENR to undergo various modification such as grafting method (Azhar et al., 2016).

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Recently, much attention on the existence of functional group at the chain end of liquid rubber which also known as telechelic liquid rubber.

Telechelic liquid rubber is very useful for further modification such as grafting and chain extension due to the presence of active chain end in the rubber structure (Nor and Ebdon, 1998). Hydroxyl and carboxyl terminated liquid rubbers are example of telechelic liquid rubber which can be synthesized via oxidative degradation (Phinyocheep et al., 2005), ozonolysis (Nor and Ebdon, 2000), and photochemical degradation (Ravindran et al., 1988). To date, various researches were focused on liquid natural rubber (LNR) as starting material for the telechelic production. In 2017, Azhar et al. (2017) reported on the hydroxylation of LNR via oxidation method with addition of $Na_2WO_4CH_3COOH/H_2O_2$ as catalytic system. Nevertheless, the preparation of telechelic liquid rubber from LENR is not widely explored.

Thus, this paper was focusing on the synthesis and characterization of hydroxyl terminated liquid epoxidized natural rubber (HTLENR) by oxidative degradation method for the preparation of reactive liquid rubber which can serve as intermediate substance for various applications. In this research, LENR was used as a starting material. Synthesis of HTLENR from LENR has been done by oxidation method in the presence of ethanol, sodium borohydride ($NaBH_4$), and cobalt acetyl-acetonate (CAA) at 80 °C. Ethanol was used in this research due the study reported by Baharulrazi et al. (2017) shows that the lowest Mw of HTNR produced when using ethanol instead of other alcohols such as methanol, propanol and hexanol. Next, molecular weight of HTLENR has been characterized by using gel permeation chromatography (GPC). Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) was done for structural confirmation of the prepared HTLENR.

2. Research Methodology

2.1 Materials

Liquid epoxidized natural rubber (LENR) was used as a raw material and was obtained from Malaysian Rubber Board (MRB). While ethanol, toluene, sodium borohydride, sulphuric acid, cobalt acetyl acetonate and anhydrous magnesium sulphate were supplied by Permula Sdn. Bhd. All solvents used were analytical grade.

2.2 Synthesis of Hydroxyl Terminated Liquid Epoxidized Natural Rubber (HTLENR)

The production of HTLENR has been carried out by using oxidative degradation method. LENR was dissolved in toluene by 1 g of LENR in 1 L of toluene. The sample solution was left for 16 h.

Next, 100 mL of ethanol was added into 900 mL of rubber solution with the addition of 0.5 g cobalt (II) acetyl acetonate (CAA). The solution was transferred into the reactor and stirred for 10 h at 280 rpm and the reactor temperature was set at 80 °C. The reaction time were varied at 1 h, 4 h, 7 h, and 10 h. After 10 h, the solution was cooled down to 25 °C. Sodium borohydride ($NaBH_4$) solution was prepared by dissolving 26 g of $NaBH_4$ in 500 mL of ethanol and 500 mL of distilled water. At 25 °C, $NaBH_4$ solution was added slowly within 1 h under stirring. The solution was maintained at 52 °C for 2 h. Next the solution was left overnight at room temperature. Then the rubber solution undergone washing to remove the unreacted $NaBH_4$ by using sulphuric acid (H_2SO_4) solution with distilled water.

The sample was left for a few days with addition of anhydrous magnesium sulphate ($MgSO_4$) in order to remove the water residual in the sample solution. Subsequently, the viscous liquid form of HTLENR was recovered by using rotary evaporator.

2.3 Characterization

Gel permeation chromatography (GPC), fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) were used to determine the molecular weight and the structure of the HTLENR prepared.

3. Results and discussion

3.1 Structural analysis of LENR and HTLENR by FTIR and HNMR

FTIR analysis has been done in order to recognize the functional groups presence in LENR and HTLENR. The infrared spectrum of LENR and HTLENR at 10 h reaction time are shown in Figure 1.

Figure 1 shows the spectrum of HTLENR consists of similar characteristic band with spectrum of LENR but having a different intensity. The peaks at 3,023 cm^{-1}, 2,961 cm^{-1}, and 2,923 cm^{-1} which correspond to CH asymmetric stretching in $-CH_3$, CH asymmetric stretching in $–CH_2$ and CH asymmetric stretching in $-CH_3$ and $–CH_2$, shows a slight increase in intensities of HTLENR sample. This is because the chain scission occur at C=C of isoprene chain of LENR which increase the amount of methyl and methylene group in HTLENR. While peak at 3,200 – 3,600 cm^{-1} shows the presence of hydroxyl group in both of LENR and HTLENR structure. It can be seen that the OH intensity is more significant in HTLENR in comparison to LENR. The increase in OH intensity is suggested due to the chain scission of C=C into methyl and hydroxyl group during oxidation reaction (Azhar et al., 2017).

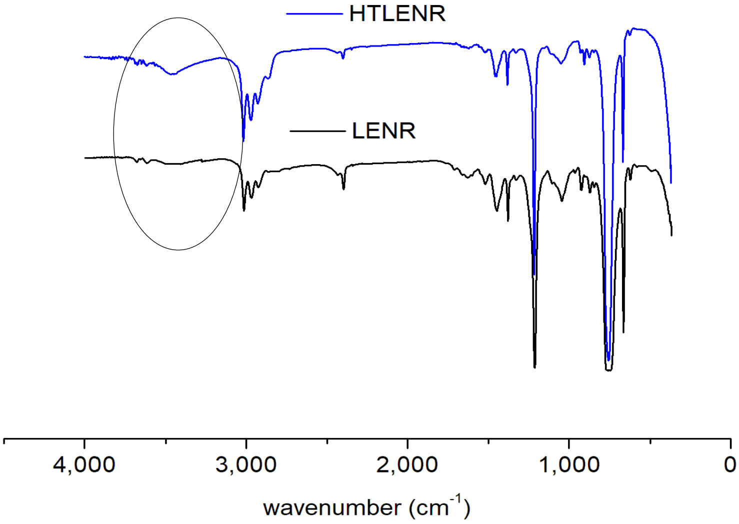

Figure 1: FTIR spectra of LENR and HTLENR.

While Figure 2 shows the HTLENR spectra at 1 h, 4 h, 7 h, and 10 h reaction time. In Figure 2, the changes can be seen at peak 3,450 cm^{-1}, 3,023 cm^{-1}, 2,961 cm^{-1}, 2,923 cm^{-1} and 1,372 cm^{-1} which correspond to OH stretching in HTLENR, C-H asymmetric stretching in CH_3, C-H asymmetric stretching in $-CH_2$, C-H asymmetric stretching in CH_3 and $-CH_2-$, C-H asymmetric stretching in $–CH_2$ and C-H asymmetric stretching in $-CH_3$. From the figure, it can be seen significant changes occurs at peak 3,450 cm^{-1} which corresponding to the OH groups. As the reaction time increased, the OH intensity increase accordingly.

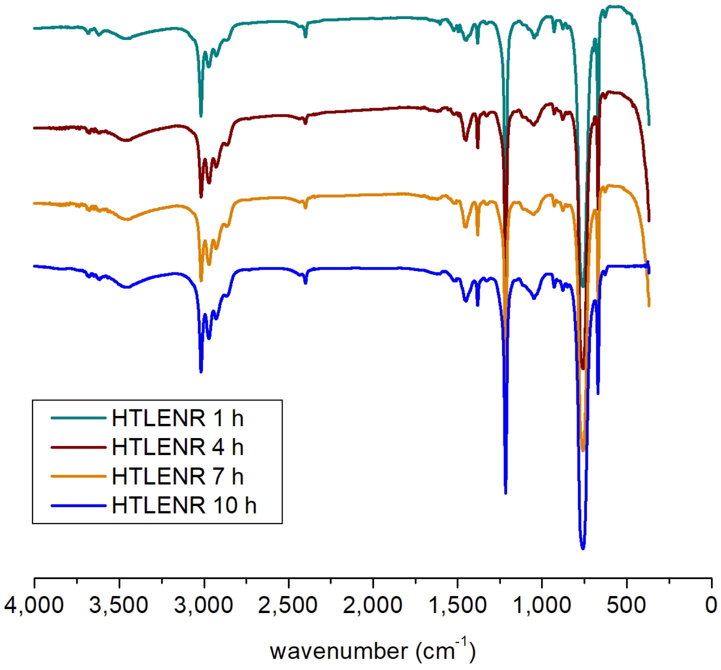

Figure 2: Combination of IR Spectra of HTLENR at various reaction time

While, HNMR spectra for both LENR and HTLENR at 10 h reaction time are shown in Figure 3. For comparison with LENR, HTLENR at 10 h reaction was chosen due to optimum increment both in FTIR and

HNMR analysis. The LENR spectrum shown in Figure 3 is in agreement with spectrum reported by Saito et al. (2007). Referring to the spectrum of LENR, the main characteristics peak of LENR still appeared in the HTLENR structure but with different intensity which confirm that LENR undergo structural changes during degradation process. From Figure 3, it can be seen that the chemical shift for HTLENR at 3.60 to 4.00 ppm which correspond to methylene and methine proton adjacent to hydroxyl group is broader than LENR indicated the amount of hydroxyl group increase with increasing reaction time. These observations are in agreement with Saetung (2009) that reported the methylene and methine proton adjacent to hydroxyl group in $HOCH_2CH_2CH_2$- and $–CH_2CH_2CH(OH)CH_3$ were observed at the peak of 3.38 ppm and 3.88 ppm. Most HNMR spectra are recorded by using a deuterated solvent in order to avoid spectra dominated by the solvent signal. Even so, deuteration is not 100% thus signals for the residual protons can be observed at 7.20-7.30 ppm. The different peak intensity between LENR and HTLENR at 7.20 - 7.30 ppm is due to the difference concentration of the deuterated chloroform used. Similar observation was also reported by Azhar et al. (2017).

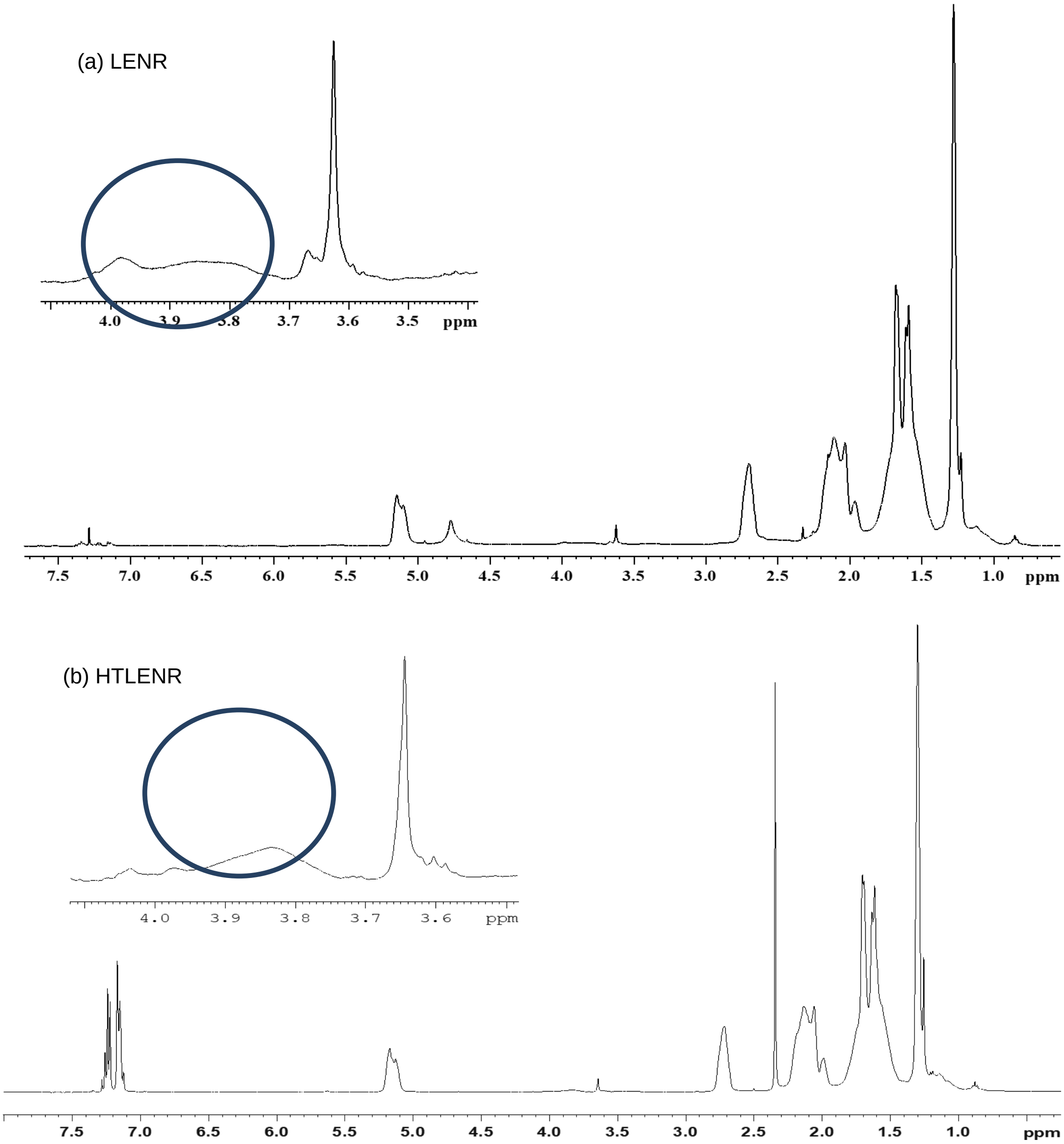

Figure 3: HNMR of (a) LENR and (b) HTLENR

In order to estimate the percentage of the hydroxyl group in HTLENR prepared, integration of signals from proton HNMR was used. Table 1 shows the hydroxyl content of HTLENR at different reaction time. From Table 1, it shows that higher reaction time help to produce more hydroxyl group in HTLENR structure.

Table 1: Hydroxyl content of HTLENR at different reaction time

Sample	Hydroxyl Content %
LENR	3.28
HTLENR 1 h	3.75
HTLENR 4 h	4.06
HTLENR 7 h	5.93
HTLENR 10 h	7.56

3.2 Molecular weight of LENR and HTLENR

Table 2 shows the weight average molecular weight (Mw), number average molecular weight (Mn) and polydispersity index (PDI) of LENR before and after undergoing oxidative degradation process. The result shows that HTLENR produced lowest Mn and Mw after 10 h reaction time. The first 1 h reaction shows that Mw and Mn were decreased almost half from the starting LENR. Depolymerization reaction was successfully occurred due to the chain scission of LENR into shorter chain of HTLENR which also help to decrease the Mw. While, the decrease of Mn is due to the reduction of high Mw polymer which increased in number of HTLENR chains. This reaction also showed a high PDI suggesting a broader molecular weight distribution of molecular mass in the sample.

Table 2: Mw and Mn of LENR and HTLENR sample

Sample	Mw (g/mol)	Mn (g/mol)	PDI
LENR	94,112	25,259	3.73
HTLENR 1 h	47,414	7,762	6.10
HTLENR 4 h	50,196	7,188	6.98
HTLENR 7 h	40,400	4,050	10.00
HTLENR 10 h	37,545	3,233	9.68

From the Mn obtained, the average number of chain scission (S) were calculated from Eq(1), while Figure 4 shows the number of chain scission of HTLENR at different reaction time.

$$S = \frac{(\mathrm{Mn})\mathrm{o}}{\mathrm{Mn}} - 1 \qquad \text{Eq(1)}$$

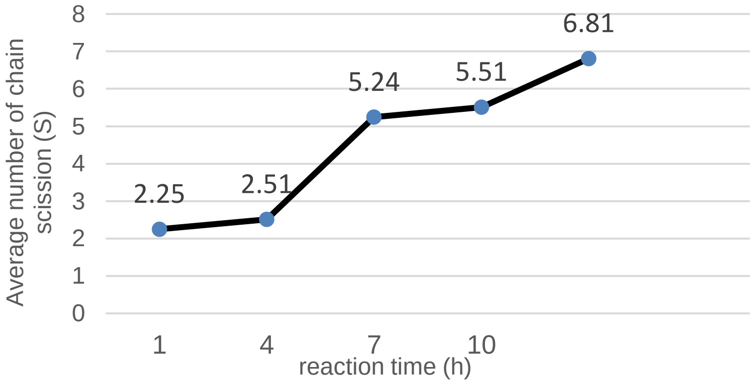

Figure 4: The average number of chain scission at different reaction time

From the figure, it shows that the amount of chain scission is highest at the longest reaction time. Thus, low molecular weight molecule was successfully produced due to more chain scission occur as the reaction time increased and this result was consistent with the research reported by Salehuddin et al. (2018). However, lower Mn was achieved in this research which is 3,233 g/mol at 10 h compared to 34,000 g/mol at 20 h as reported by Salehuddin et al. (2018). The differences might due to the different method and parameters applied in both researches.

4. Conclusion

As a conclusion, HTLENR was successfully synthesized from LENR via oxidative degradation method. GPC analysis confirmed that HTLENR achieved lowest Mw and Mn of 37,545 g/mol and 3,233 g/mol, at 10 h reaction time. The formation of hydroxyl group in the HTLENR prepared was confirmed by FTIR analysis by the presence of broader hydroxyl peak at 3,200-3,600 cm^{-1} in comparison to LENR spectrum. As the reaction time increased, the amount of hydroxyl group in the HTLENR structure increased accordingly. NMR analysis confirmed the highest amount of hydroxyl content which is 7.56 % was achieved at the longest reaction time of 10 h which consistent with the result from FTIR. The prepared HTLENR in this study can be further functionalized at the reactive hydroxyl chain ends for the production of various rubber-based materials or composites for diverse fields including medical and structural applications.

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References

Azhar N.H.A., Rasid H.M., Yusoff, S.F.M., 2016, Chemical modifications of liquid natural rubber, The 2016 UKM FST Postgraduate Colloquium, AIP Conference Proceedings,13th-14th April, Selangor, Malaysia, 1784.

Azhar N. H. A., Rasid H. M., Yusoff S.F.M., 2017, Epoxidation and hydroxylation of liquid natural rubber, Sains Malaysiana, 46, 485-491.

Baharulrazi N., Man S., Mohamad Z., Mohd Nor H., Wan Ali W., 2017, Effect of Various Alcohols and Reaction Time on the Properties of Hydroxyl Terminated Natural Rubber Synthesized via Oxidative Degradation, Chemical Engineering Transactions, 56, 583-588.

Bakar, A., Ahmad, S., Kuntjoro, W., 2012, Effect of epoxidized natural rubber on mechanical properties of epoxy reinforced kenaf fibre composites, Pertanika Journal of Science and Technology, 20,129-137.

Kargarzadeh, H., Ahmad, I., Abdullah, I., Thomas, R., Dufresne, A., Thomas, S., 2015, Functionalized liquid natural rubber and liquid epoxidized natural rubber: A promising green toughening agent for polyester, Journal of Applied Polymer Science, 132.

Nor H.M., Ebdon J.R., 1998, Telechelic liquid natural rubber: A Review. Progress in Polymer Science, 23, 143-177.

Nor H.M., Ebdon J.R., 2000, Ozonolysis of natural rubber in chloroform solution Part 1: A study by GPC and FTIR spectroscopy, Polymer, 41, 2359-2365.

Phinyocheep, P., Phetphaisit, C., Derouet, D., Campistron, I., Brosse, J., 2005, Chemical degradation of epoxidized natural rubber using periodic acid: Preparation of epoxidized liquid natural rubber, Journal of Applied Polymer Science, 95, 6-15.

Ravindran T., Nayar M.G., Francis D.J., 1988, Production of hydroxyl-terminated liquid natural rubber-mechanism of photochemical depolymerization and hydroxylation, Journal of applied polymer science, 35, 1227-1239.

Rooshenass P., Yahya R., Gan S.N., 2017, Preparation of Liquid Epoxidized Natural Rubber by Oxidative Degradations Using Periodic Acid, Potassium Permanganate and UV-Irradiation, Journal of Polymers and the Environment, 26, 1378-1392.

Saetung A., 2009, Preparation of polyurethane foams from Hydroxytelechelic oligoisoprenes obtained by controlled degradation of natural rubber: A study of their physico-mechanical, thermal, and acoustic properties, PhD Thesis, Prince of Songkla University, Pattani, Thailand.

Saito T., Klinklai W., Kawahara S., 2007 Characterization of epoxidized natural rubber by 2D NMR spectroscopy, Polymer, 48, 750-757.

Salehuddin S.M.F., Baharulrazi N., Shuhadah Abd Razak N.E., Che Man S.H., Nor H.M., Wan Ali W.K., 2018, The Effect of Amount of Oxidising Agent and Reaction Time on the Properties of Hydroxyl Terminated Epoxidised Natural Rubber (HTENR) via Oxidative Degradation, Chemical Engineering Transactions, 63, 409-414.