

The Characterization of Hydroxyl Terminated Epoxidized Natural Rubber (HTENR) via Oxidation Degradation Method

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The degradation of epoxidized natural rubber (ENR-50) and liquid epoxidized natural rubber (LENR) was done via oxidative degradation method for the production of hydroxyl terminated epoxidized natural rubber (HTENR) and hydroxyl terminated liquid epoxidized natural rubber (HTLENR) has been analysed. Cobalt (II) acetylacetonate (CAA) were used as an oxidizing agent for chain scission reaction at temperature 60 °C in the presence of ethanol. The reaction temperature was fixed at 60 °C meanwhile reaction time and the amount of CAA were varied according to the reaction formulation. The HTENR and HTLENR obtained have been characterized using Gel Permeation Chromatography (GPC), Fourier Transform Infrared (FTIR) and Nuclear Magnetic Resonance (NMR). GPC were used to determine the molecular weight before and after the oxidative degradation of respected HTENR and HTLENR were compared with ENR-50 and LENR. The lowest M_n and M_w of HTLENR that were obtained from the oxidative degradation method were found to be 5,163 g/mol and 58,087 g/mol. The appearances of OH end groups were verified by FTIR and NMR analyses to validate the position of each OH functional groups. FTIR analysis confirmed that HTENR and HTLENR contained OH group with the appearance of a broad peak around 3,400 cm^{-1} to 3,550 cm^{-1} after the reaction. The presence of OH end groups was verified by NMR analysis with the appearance at 3.39 ppm and 3.66 ppm, corresponding to methylene proton adjacent to hydroxyl group in $\text{HOCH}_2\text{CH}_2\text{CH}_2$ and methane proton adjacent to OH group in $\text{CH}_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$.

1. Introduction

Degradation of polymeric materials are of wide interest to research scientists as they often produce new materials that cannot be prepared or are costly to prepare by means of conventional polymerization reactions. These methods are also used to improve the properties of some commercial polymers or to introduce specific reactive intermediates on the polymer chains for further modification. The degradation of the polymers in solution is advantageous as it provides better heat transfer rates and degradation in a single phase. The oxidative degradation of the polymer in solution usually occurs by random chain scission of the polymer chains. *Amongst the degradation methods*, photo and oxidative degradations are *widely reported*. Phinyocheep et al. (2005) studied on chemical degradation of epoxidized natural rubber (ENR) was prepared from the epoxidation of natural rubber in latex phase using performic acid generated in situ by the reaction of hydrogen peroxide and formic acid. As well as, Chaikumpollert et al. (2009) investigated the low temperature degradation and characterization of natural rubber which was performed with potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$). According to the degradation mechanism, the introduction of the carbonyl and formyl groups at both terminated were appeared due to the oxidative degradation of rubber. Recently, Baharulrazi (2015) reported on the synthesis and characterization of hydroxyl terminated epoxidized natural rubber as a binder for solid rocket propellant. Oxidative degradation of deproteinized natural rubber (DPNR) by CAA in the presence of ethanol yielded the lowest molecular weight compared to other alcohols employed. Epoxidized natural rubber

(ENR) is an established commercial rubber polymer which is chemically modified natural rubber is a very significant polymer due to its outstanding mechanical performance besides low cost and great mechanical properties. This material is a very good tensile strength due to inherent strain-induced crystallization property of NR, beside the reactivity of epoxy group can open its ring structure to form covalent linkage with carboxylic acid group of modified rubbers. According to Nouparvar et al. (2014), they reported that ENR exhibits good mechanical properties offering high strength, due to their ability to undergo strain crystallization and has a high glass transition temperature. However, ENR has high molecular weight which limits its solubility and its processability. Liquid epoxidised natural rubber (LENR) can be a good candidate due to the lower molecular weight compared to ENR and the presence of the epoxy group in the structure. Liquid epoxidized natural rubber (LENR) could be obtained from the degradation of ENR. LENR molecule exhibits three different functionalities that are available for possible cross-linking. These include double bonds, epoxy, and acid groups in the main chain, while retaining most of the properties of natural rubber (Ravindran et al., 1988). The epoxide groups are randomly distributed along the natural rubber chain. Epoxy group is expected to react to produce hydroxyl terminated liquid epoxidised natural rubber (HTLENR) via the reduction process. By conducting this research, an in-depth study on the properties of LENR compared with ENR which can be done extensively to further develop and improve its usage for a wider range of applications in the future. This paper presents some results concerning the preparation of HTENR and HTLENR using cobalt (II) acetylacetonate (CAA) as a reagent and the characterization of the HTENR and HTLENR obtained by GPC, FTIR, ¹H-NMR and ¹³C-NMR spectroscopic analysis is presented in this paper.

2. Experimental

2.1 Materials

The raw material used throughout this work was Epoxidized Natural Rubber (ENR-50) and Liquid Epoxidized Natural Rubber (LENR) that was obtained from Malaysian Rubber Board (MRB), Sungai Buloh, Selangor. For synthesizing HTLENR and HTENR, the chemical used were toluene (Merck), sodium borohydride (Merck), cobalt (II) acetylacetonate (CAA) (QReC), anhydrous magnesium sulphate (QReC), sulphuric acid (J.T.Baker) and ethanol (J.T.Baker). For characterization, Deuterated chloroform (Merck) was used for NMR, chloroform (Merck) was used for FTIR and tetrahydrofuran (J.T.Baker) was used for gel permeation chromatography.

2.2 Synthesis of HTENR and HTLENR

10 g of ENR-50 and LENR was dissolved in 900 mL of toluene by stirring at 500 rpm overnight using a magnetic stirrer. The degradation of ENR-50 and LENR was done via the oxidative degradation method. The oxidising agent, namely cobalt (II) acetylacetonate (CAA), was used in the presence of ethanol, where 100 mL of ethanol was added to the rubber solution and followed by the addition of a specific amount of CAA. The effects of reaction parameters on the reduction of molecular weight were studied by varying the reaction times from 2 and 5 hours while the amounts of the oxidising agent were being varied from 3, 5 and 7 wt%. Sample solution was poured into jacketed reactor vessel that was heated up at 80 °C and subsequently mixed at 280 rpm. Cooling procedure was then taken all samples they were kept at 25 °C.

2.3 Introduction of Sodium Borohydride (H₂SO₄) to produce HTENR and HTLENR

500 mL of ethanol were dissolved in 500 mL of distilled water to produce 50 % aqueous ethanol. 26 g of sodium borohydride was dissolved in 1,000 mL of 50 vol% aqueous ethanol. When the temperature reaches 25 °C, sodium borohydride solution was being added drop wise into sample solution in 1 h whilst blending the sample solution. The solution was being heated and maintained at 60 °C for 2 h. The solution was then left overnight at room temperature before the washing process.

2.4 Washing process

The process began by acidifying the solution with 10 vol% of sulfuric acid (H₂SO₄) solution was used to remove unreacted sodium borohydride. Afterwards, acid solution was used to wash the sample followed by washing with distilled water for three times to remove remaining H₂SO₄. Then, the sample solution was nightly dried over anhydrous magnesium sulphate (MgSO₄) to eliminate the remaining water. The sample solution was then filtered and concentrated using a rotary evaporator at 60 °C and 140 rpm to obtain a viscous solution known as HTENR and HTLENR.

2.5 Sample characterisation

GPC is a technique used to determine the average molecular weight distribution of a polymer sample. The GPC used in this experiment consists of the water pump of model Waters 1500 Series HPLC Pump and a manual injector with refractive index detector model Waters 2410. Tetrahydrofuran (THF) was used as a

solvent at a flow rate of 1 mL/min. About 20 mg of sample was dissolved in 2 mL of tetrahydrofuran using 4 mL of vials. The solutions were filtered using 0.5 μm pore size filter unit (Millipore, Millex-PRC). 20 μL of the solutions were injected into the chromatograph using 25 μL syringes.

FTIR is a technique used to *identify* whether a specific functional group is present. FTIR spectrum was recorded using Perkin Elmer spectrum 2000 explorer at room temperature. Infrared spectra were recorded in the transmission mode as a result of 20 scans. One drop of 5 mg/mL concentration was placed on the potassium bromide (KBr) disk was dissolved in 1.0 mL chloroform. The solvent was evaporated from the sample prior to test using 100-watt lamp and was placed on FTIR holder to record the spectrum.

NMR is a technique used to determine the structure of its molecules. The instrument used was a Bruker 400 Ultrashield FT-NMR. The spectrometer was working at 100 MHz for carbon-13 and 400 MHz for proton. About 1 - 5 mg of sample was used for proton-1 and 10 - 20 mg of the sample for carbon 13.5 mm Pabbo-BB probe was used for all measurements.

3. Result and discussion

3.1 Gel Permeation Chromatography (GPC)

Gel Permeation Chromatography (GPC) analysis was used to determine the number average molecular weight (M_n) and weight average molecular weight (M_w) of ENR-50 and LENR before and after the oxidative degradation which is has been monitored at 60 $^{\circ}\text{C}$ at amount of CAA (2 wt%, 5 wt% and 7 wt%) after 2 h and 5 h. Figure 1a shows the effect of reaction time and amount of CAA for ENR samples and Figure 1b shows the effect of reaction time and amount of CAA for LENR samples. The M_n and M_w of ENR-50 and LENR before oxidative degradation are shown in Table 1. The value of M_n and M_w obtained are quite different from previous study which is around 245,000 g/mol (Baharulrazi et al., 2017) and 133,000 g/mol (Abdul Razak et al., 2016). 2 h reaction time gave the lowest M_n , whereas prolonged reaction times in 5 h showed slight increases in the molecular weight.

Table 1: The molecular weight of ENR-50 and LENR

Sample	M_n (g/mol)	M_w (g/mol)	PDI
ENR-50	121,227	2,643,668	21.8
LENR	9,668	38,669	4.0

From the result obtained as shown in Figure 1a and b, the lowest M_n and M_w of HTLENR recorded was 5CAA 2E (LENR) which is 5,163 g/mol and 58,087 g/mol. Addition in the percentage of CAA from 3 wt% to 5 wt% had resulted in decreasing of molecular weight (M_n). The similar trend was observed for 2 h reaction where, M_n was continuously decreased till 5 wt% of CAA used in the reaction. Higher amount of oxidizing agent may result in better degradation process as more sites for the formation of the unstable terminal group could be produced. Too much oxidizing agents would form high amount of unstable terminal groups, which might lead to the increasing of the possibility of chain recombination reaction.

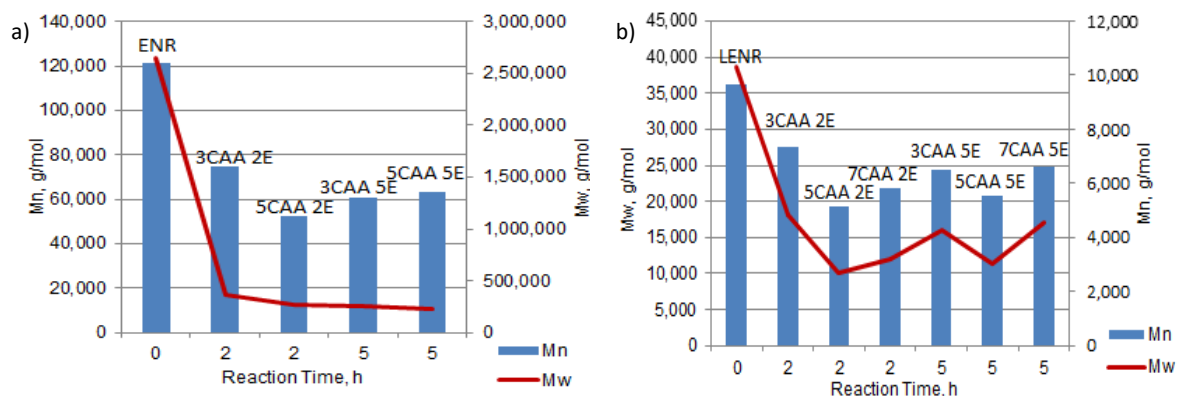


Figure 1: (a) The effect of reaction time and amount of CAA (3 wt% and 5 wt%) for ENR samples (b) The effect of reaction time and amount of CAA (3 wt%, 5 wt% and 7 wt%) for LENR sample.

From the result, the optimum percentage of CAA used in the reaction was 5 wt% where the lower M_n could be achieved. The higher amount of oxidizing agent would be generated the higher amount of macro radical and it possibly increases the chain recombination at prolonged reaction times (Baharulrazi, 2015).

3.2 FTIR Analysis

The FTIR analysis of the prepared HTENR and HTLENR was conducted to confirm the presence of OH group in the molecule. Figure 2 shows the combination of IR spectra of HTENR after degradation for 3 wt% and 5 wt% at various reaction times 2 h and 5 h at –OH group region. Based on FTIR spectra, it can be seen that there is not much different in terms of the peak obtained compared to ENR-50 prior to modification. It can be seen that the intensity of OH functional group are similar for 3CAA 2E, 3CAA 5E and 5CAA 2E samples but slightly different whereby the intensity increasing for 5CAA 5E samples. As mentioned earlier, the presence of OH in ENR-50 spectra was the non-bonded OH while presence of OH in HTENR was the bonded molecule with the rubber chain show broad absorption band at range $3,400 - 3,550 \text{ cm}^{-1}$. This FTIR analysis confirmed the presence of OH in the rubber chain. Other peak that may concern is epoxide, C-O stretch group at the $1,215 \text{ cm}^{-1}$. From the spectra, it can be seen that this peak was decreased its intensities gradually for each of the samples. This is proved that ENR-50 undergoes profound structural changes during degradation process (Abdul Razak et al., 2016). This peak remains along the oxidative degradation process that keeps the ENR-50 characteristic.

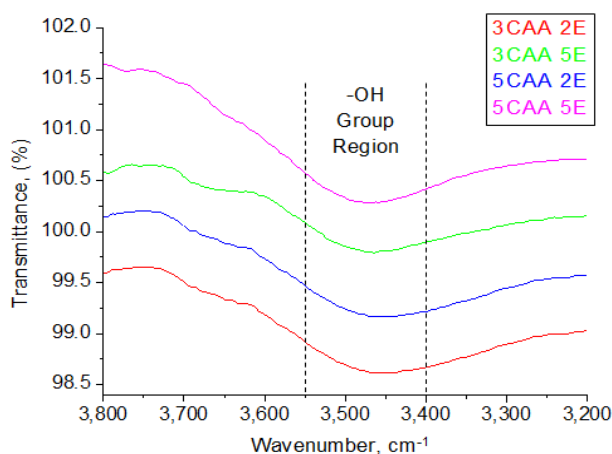


Figure 2: Combination of IR spectra of HTENR after degradation for 3 wt% and 5wt % at various reaction times 2 h and 5 h at –OH group region.

Figure 3 shows the combination of IR spectra of HTLENR after degradation for 3 wt%, 5 wt% and 7 wt% at various reaction times 2 h and 5 h at –OH region.

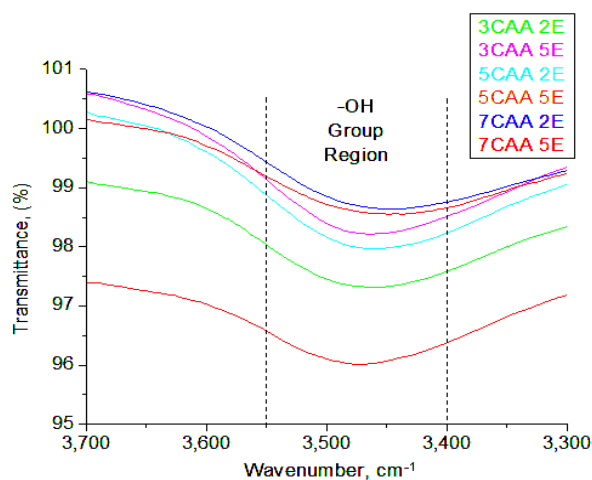


Figure 3: Combination of IR spectra of HTLENR after degradation for 3 wt%, 5 wt% and 7 wt% at various reaction times 2 h and 5 h at –OH group region.

HTLENR spectra show broad absorption bands at range $3,400 - 3,525 \text{ cm}^{-1}$ due to O-H stretching, and the intensities of the absorption bands for HTLENR are intense than LENR. The increment of HTLENR intensity at $3,400 - 3,525 \text{ cm}^{-1}$ arises due to the ring opening of epoxy groups into hydroxyl groups.

3.3 NMR Analysis

The HTLENR was characterized by ^{13}C NMR spectra, the results are presented in Figure 4a. Based on the ^{13}C NMR spectra of HTLENR, the main peaks on behalf of isoprene unit still maintain on the respective region, although it shifted slightly up-field comparable to the main LENR spectra (Salehuddin et al., 2018). This might be due to the variation of molecular weight between HTLENR that possess lower molecular weight, in contrast to the virgin LENR with high molecular weight (Nor and Ebdon, 2000). The main peaks which represent isoprene unit were being observed at δ 134.76 ppm ($-\text{C}(\text{CH}_3) = \text{CH}-$), δ 125.15 ppm ($-\text{C}(\text{CH}_3) = \text{CH}$), δ 32.00 ppm ($-\text{CH}_2\text{C}(\text{CH}_3)=$), δ 26.29 ppm ($=\text{CHCH}_2$) and δ 23.32 ppm ($-\text{C}(\text{CH}_3)=\text{CH}$). The peaks at δ 64.44 ppm and δ 60.78 ppm corresponded to $-\text{C}(\text{CH}_3)\text{OCHCH}_2$ and $\text{C}(\text{CH}_3)\text{OCHCH}_2$ of the epoxy unit. Figure 4b shows a ^1H NMR spectrum of HTLENR. Meanwhile, based on the ^1H NMR of HTLENR, the assignments of the chemical shifts in LENR spectra, seven major signals appeared at δ 1.28, 1.68, 2.05, 2.15, 2.71, 3.62 and 5.15 ppm while the assignments of the chemical shifts for HTLENR spectra showed the appeared at δ 1.30, 1.70, 2.10, 2.20, 2.74, 3.39, 3.66 and 5.20 ppm. ^1H NMR indicated that the chemical reaction had changed the chemical structure of the main LENR spectra. The end groups structures of HTLENR with the appearance of a peak at δ 3.39 ppm and 3.66 ppm that corresponded to CH and CH_2 nearby OH end groups in $\text{HOCH}_2\text{CH}_2\text{CH}_2-$ at one chain end and $-\text{CH}_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ at the other chain end. Thus it was concluded that the HTLENR contained OH groups as a terminal chain ends.

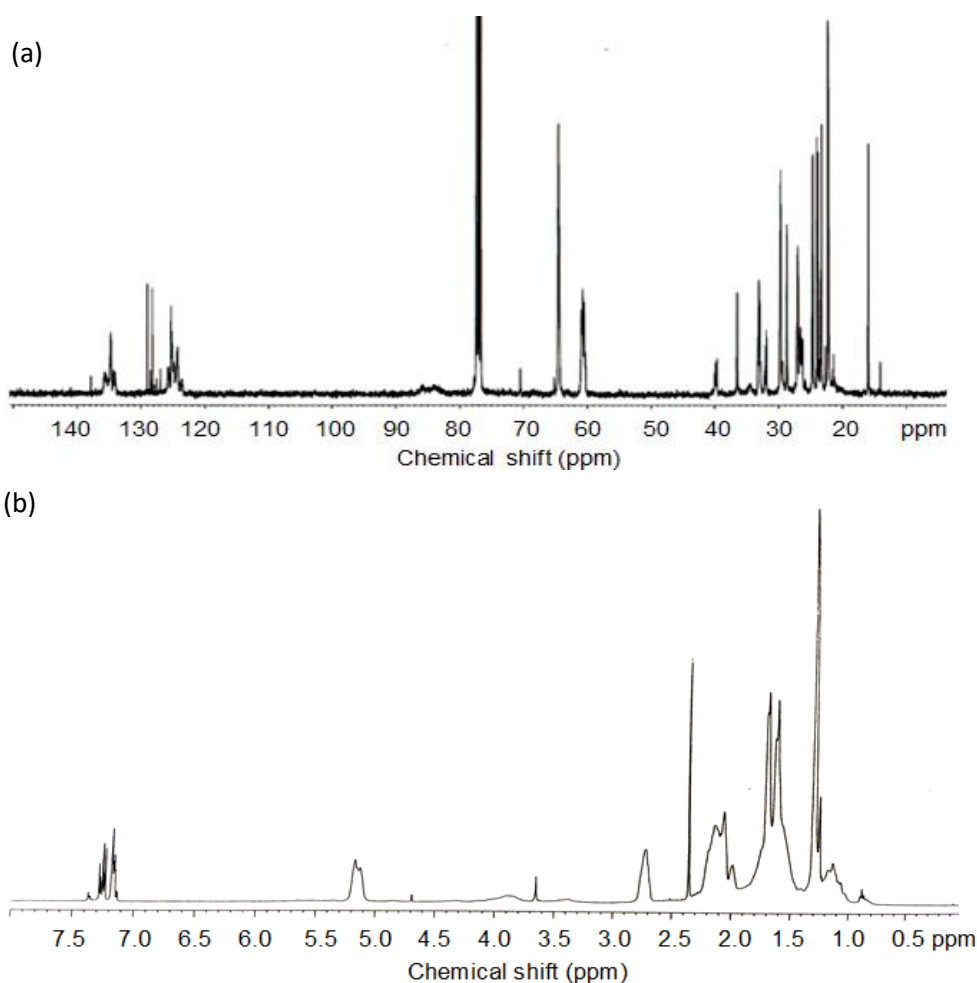


Figure 4: (a) ^{13}C -NMR spectrum of HTLENR (b) ^1H -NMR spectrum of HTLENR

4. Conclusions

Hydroxyl terminated epoxidised natural rubber (HTENR) and hydroxyl terminated liquid epoxidised natural rubber (HTLENR) had been successfully synthesised via the oxidative degradation method using cobalt acetylacetonate (CAA) as an oxidising agent for chain scission reaction. The reaction was carried at the temperature of 60 °C, in the presence of ethanol and followed by a treatment with sodium borohydride as a reducing agent to introduce the hydroxyl functional groups. The lowest M_n and M_w of HTLENR that were obtained from the oxidative degradation method were found to be 5,163 g/mol and 58,087 g/mol. The chemical structures of the obtained were confirmed by FTIR and NMR analyses. The appearances of OH end groups were verified by FTIR and NMR analyses to validate the position of each OH functional groups. The presence of hydroxyl (OH) functional group was verified using FTIR analysis with the appearance of the broad absorption at the range of 3,400 – 3,550 cm^{-1} for HTENR while HTLENR spectra show broad absorption bands at 3,400 - 3,525 cm^{-1} that corresponds to OH groups. ^1H NMR indicated that the end groups structures of HTENR were $\text{HOCH}_2\text{CH}_2\text{CH}_2-$ at one chain end and $\text{CH}_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ at the other chain end. It can be concluded that the HTENR contained OH groups as terminal chain ends.

Acknowledgments

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