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Hydroxytelechelic Natural Rubber from Natural Rubber and Epoxidised Natural Rubber

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Hydroxytelechelic natural rubber (HTNR), a chemically modified form of natural rubber which can be used as a polyol precursor in the elaboration of natural rubber based polyurethane was synthesised. In this study, the effects of different types of starting materials including natural rubber (NR) and epoxidised natural rubber (ENR) on properties of HTNR were explored. Two steps of controlled methodology were applied. The first oxidative degradation step using periodic acid yielded carbonyltelechelic natural rubbers (CTNRs) having similar chemical structures as proven by ^{1}H-NMR and FTIR analysis. However, they were different in carbonyl content, percent yield and molecular weight, as well as in appearance. The results suggest different degradation mechanisms occurring in NR and ENR. The HTNRs were later prepared in a second step by reduction of the CTNRs with sodium borohydride followed by hydrolysis with cool water. Using the ENR-based CTNR as intermediate in the second step provided the HTNR with hydroxyl content, percent yield, OH-value higher than that using the NR-based CTNR, whereas molecular weight and acid number were lower. These meant that the ENR was more suitable than NR to be selected for production of HTNR.

Keywords: epoxidised natural rubber; hydroxytelechelic natural rubber; carbonyltelechelic natural rubber

Natural rubber, a renewable resource polymer, has been investigated as an alternative raw material for preparation of telechelic liquid natural rubber (TLNR) in order to replace the petrochemical product and it plays an important role in many applications. Owing to its reactive chain end, it can be applied as compatibiliser, reactive polymeric material in polymer blends and also used as precursor for the synthesis of new polymers[1,2]. Important products from the TLNR are polyurethane, graft-copolymer, reactive plasticiser, sealant, adhesive and coating[3–5]. Nor and Ebdon[6] reviewed three different methods, *i.e*., redox, photochemical and oxidation methods, for cleavage degradation of natural and synthetic polyisoprenes and showed that they yielded TLNR products with different terminal functional groups and molecular weights. Oxidative degradation, however, turned out to be an interesting method for this work. Phenyl hydrazine, potassium persulphate and propanal reagents had been used to reduce NR molecular weight forming carbonyl functional oligoisoprenes[7–9]. Nowadays, there is extensive use of periodic acid instead,

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because the former reagents are toxic, impart colouration and are difficult to remove after finishing[10]. Furthermore, using periodic acid with THF solvent in the system provided telechelic *cis*-1,4 oligoisoprene (CTPIs) with a markedly reduced molecular weight and without epoxides being detected[11,12]. Reductive amination or reduction of the carbonyl group chain end to hydroxyl group was studied and reported by many groups[13–17]. However, until now there are no reports that compare results in terms of performance achieved from different rubber substrates. In this work, the authors contribute information on the effects of different types of starting material, including natural rubber (NR) and epoxidised natural rubber (ENR), on chemical structure, percent (%) yield, molecular weight, OH-value, acid number and appearance of the HTNR.

EXPERIMENTAL

Materials

High ammonia natural rubber latex having dry rubber content (DRC) of approximately 60% which was used as raw material for the preparation of epoxidised natural rubber was manufactured by Yala Latex Co., Yala, Thailand. The air dried sheet (ADS) natural rubber was purchased from Khuan Pun Tae Farmer Co-operation, Phattalung, Thailand. The periodic acid (H_5IO_6) exploited in this experiment as an oxidative reagent was supplied by Fluka. The sodium borohydride ($NaBH_4$) used for the reduction reaction was manufactured by LabScan. Other chemicals and solvent used were of analytical grade.

Preparation of Epoxidised Natural Rubber (ENR)

High ammonia natural rubber latex (60% DRC) was diluted with water to 20% DRC and stabilised by 3 p.h.r. Terric N10 at room temperature for 12 h before epoxidation. The epoxidation was carried out at 60ºC with *in-situ* generated performic acid from a reaction between formic acid ([HCOOH]/[Isoprene unit] = 0.3/1 mol/mol) and hydrogen peroxide ($[H_2O_2]$/[HCOOH] = 1/1 mol/mol) for 8 h. After that, the ENR was coagulated with methanol and dried in vacuum at 40ºC for two days. The chemical structure of the ENR was determined from a proton nuclear magnetic resonance (^{1}H-NMR) spectrometer and a Fourier Transform Infra Red (FTIR) spectrophotometer analysis. The level of epoxide content was calculated by using *Equation 1*.

$$\text{Epoxide content (\%)} = \frac{I_{2.70}}{I_{2.70} + I_{5.14}} \times 100 \quad \ldots 1$$

where $I_{2.70}$ and $I_{5.14}$ represent the integrated area of epoxy methine proton of the ENR and olefinic methine proton of the NR, respectively.

Preparation of Carbonyltelechelic Natural Rubbers (CTNRs)

Two types of rubber, NR (Air Dried Sheet) and ENR (prepared from previous section), were used as starting materials for synthesis of the CTNRs. The preparation process is shown in *Figure 1(A)*. A solution of approximately 8% periodic acid (H_5IO_6) (H_5IO_6/Epoxide molar ratio = 0.8/1 or H_5IO_6/Isoprene molar ratio = 0.08/1) dissolved in THF (50mL), was added dropwise. The reaction was left for 6 h after which traces of iodic acid and THF were removed. The product was then dissolved into methylene chloride, neutralised with saturated sodium bicarbonate, sodium thiosulphate and sodium chloride solution followed by evaporation of methylene chloride.

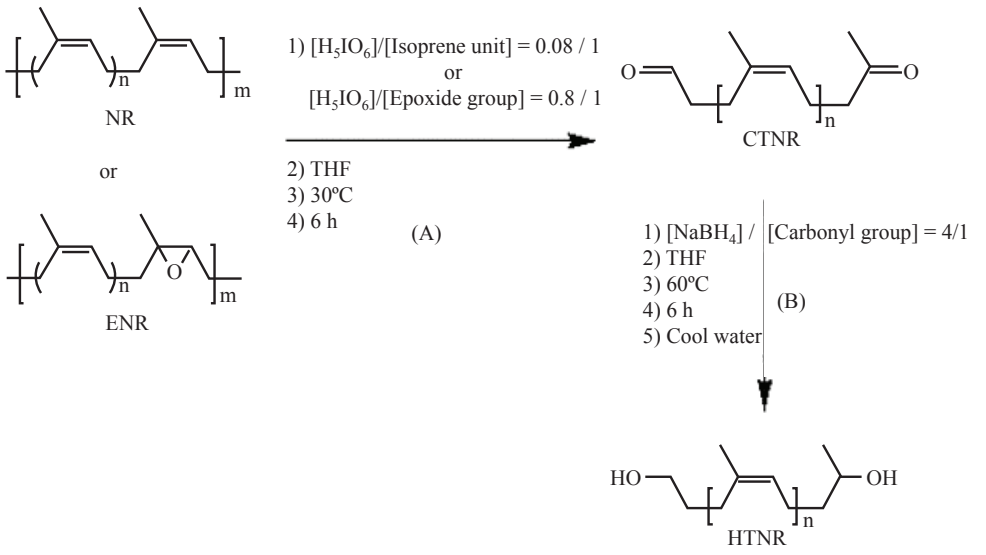


Figure 1. Controlled methodology of preparation process of hydroxytelechelic natural rubber.

Preparation of Hydroxytelechelic Natural Rubbers (HTNRs)

The reduction of the CTNR to HTNR was done in this step using a solution of sodium borohydride ($NaBH_4$) as seen in *Figure 1(B)*. The excess amount of $NaBH_4$ solution in THF reacted for 6 h against the slowly dropped CTNR solution at a temperature of 60ºC. The solution was cooled to room temperature and hydrolysed with 100 mL of cool water. The product was purified by saturated sodium chloride (NaCl) solution and dehydrated with magnesium sulphate ($MgSO_4$) followed by removing the solvent.

Molecular Structure Characterisation

Two techniques were applied to analyse the chemical structures of the prepared rubbers. They were a ^{1}H-NMR spectrometer (model Varian EM390, Varian, Inc., USA.) with 500 MHz proton signal permanent magnet and a FTIR spectrophotometer (model Omnic ESPMagna-IR 560, Nicolet Instrument Corp., Madison, WI) with the wavelengths of the mid-IR region (*i.e.*, the ranges of wavenumber from 4000 to 400 cm^{-1}).

Determination of OH-Value in HTNR

The HTNR (3 g) was dissolved in 20 mL of solvent mixture of phthalic anhydride and benzene at 1:6 parts. The solution was refluxed at 50˚C for 1 h and then cooled to room temperature. 50 mL of distilled water was added into the solution before titration with 1 N sodium hydroxide (NaOH) solution using phenophthalene as indicator. Titration was done until the end point of colour changed from colourless to pink. The OH-value of the HTNR was then calculated using *Equation 2*[17].

$$\text{OH-Value} = 56.1 \times \frac{[\text{B-A}]}{W} \times N + C \quad \ldots 2$$

where A and B are volumes of NaOH for sample and blank titration (mL), respectively, W is the sample weight (g), N is the concentration of NaOH standard solution (N) and C is the acid number.

Acid Number Test

The HTNR (5 g) was dissolved in 50 mL of titration solution of ethanol/benzene (50/50 wt %). The HTNR solution was then titrated with 0.1 N potassium hydroxide (KOH) solution using phenophthalene as indicator. The point at which the colour of the solution changed from colourless to pink was the end of the titration. Acid number was calculated using *Equation 3*.

$$\text{Acid number} = 56.1 \times \frac{[\text{A-B}]}{W} \times N \quad \ldots 3$$

where A and B are volumes of KOH for sample and blank titration (mL), respectively. W is the sample weight (g) and N is the concentration of KOH standard solution (N).

RESULTS AND DISCUSSION

Preparation of CTNRs from NR and ENR-12

The chemical structure of ENR is shown in *Figure 4*. Epoxide content calculated with *Equation 1* was 12%. Comparative results of the prepared CTNRs through oxidative degradation of NR and ENR-12 solution with periodic acid are given in *Table 1* and in *Figures 3–6*. The percentage of yield can be calculated from *Equation 4*,

$$\text{Yield (\%)} = \left[\frac{W_r}{W_i}\right] \times 100 \quad \ldots 4$$

where W_r and W_i are residual and initial weight of polymer, respectively.

The number-average molecular weight (Mn) of the CTNRs was then calculated using *Equation 5*.

$$\overline{Mn} = \left[\frac{I_{5.12}}{I_{9.8}}\right] \times 68 + 100 \quad \ldots 5$$

where $I_{5.12}$ and $I_{9.8}$ are integral areas of the signal of vinyl proton of the NR and aldehyde proton of the CTNR, respectively.

Results of % yield and molecular weight of the prepared CTNRs in *Table 1* are attributed to the oxidative degradation process which occurred in the rubber molecules. The steps of degradation of the ENR are easily performed through ring opening of oxirane rings. However, in the case of NR two-step mechanisms[12], the H_5IO_6 reacted first with the double bonds to give epoxides or α-glycol groups. These groups will then undergo cleavage to low molecular weight molecules having a carbonyl chain end as described in *Figure 2*. As a result, the CTNR which was prepared from ENR-12 showed higher % yield of product with a lower molecular weight than the NR-based CTNR.

Preparation of HTNRs

The reduction of carbonyl groups in the CTNRs to hydroxyl groups in the HTNRs using $NaBH_4$ solution is illustrated in *Figure 1(B)*. ^{1}H-NMR spectra of the HTNRs prepared from NR and ENR-12 are shown in *Figures 3* and *4*, respectively. Important specific signals

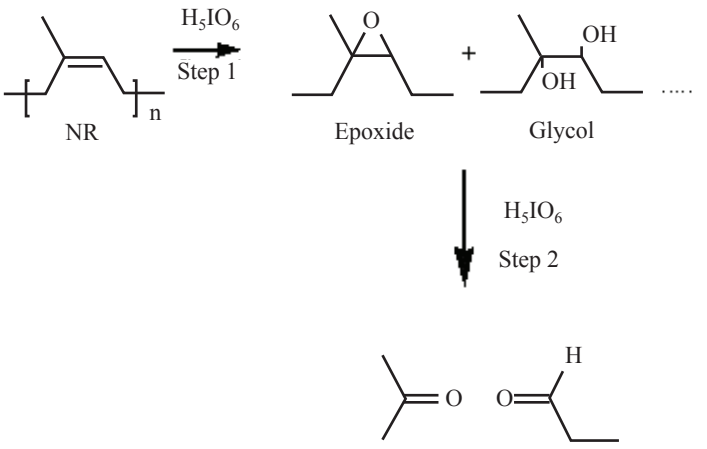


Figure 2. Oxidative degradation of NR by periodic acid[12].

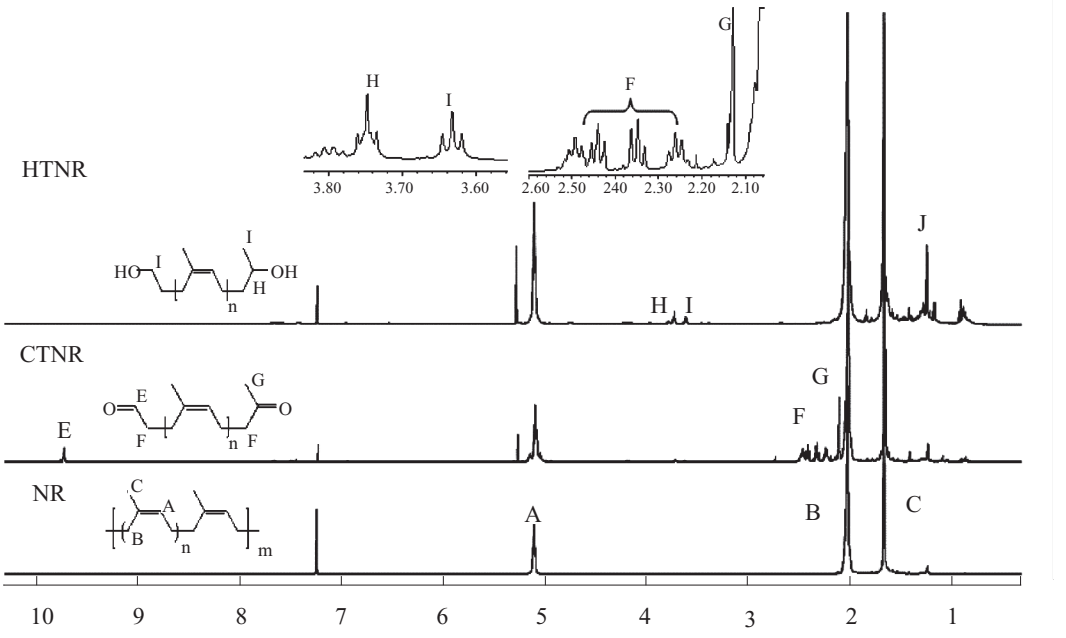


Figure 3. [1]H-NMR spectra of HTNR and CTNR prepared from NR.

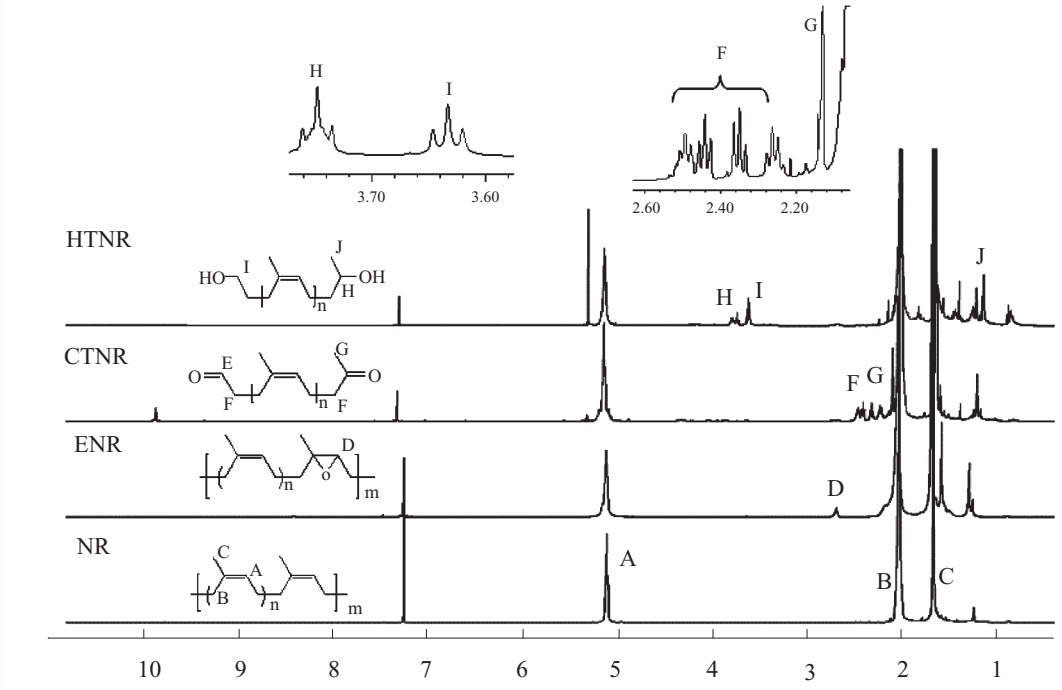


Figure 4. [1]H-NMR spectra of HTNR, CTNR and ENR prepared from ENR-12.

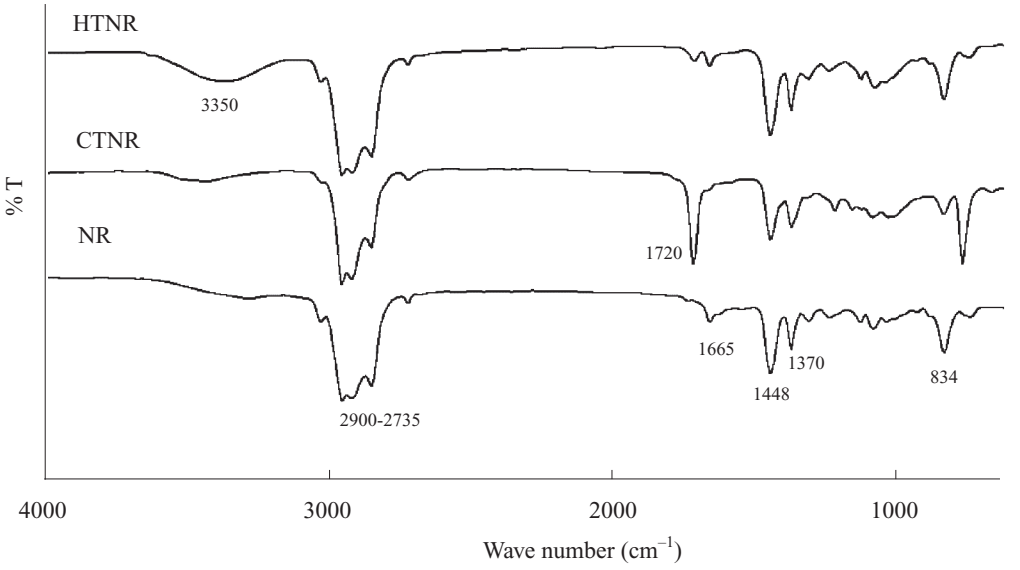
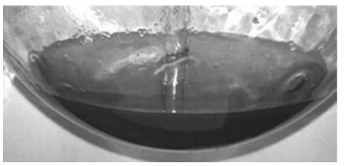
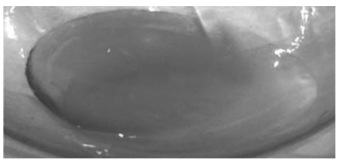


Figure 5. FTIR spectra of HTNR and CTNR prepared from NR.

TABLE 1. CHARACTERISTICS OF THE PREPARED CTNRs

Starting material	Yield (%)	$\overline{Mn}$	Appearance
NR	44	4900	Yellow-brown viscous liquid 
ENR-12	81	850	Light yellow viscous liquid 

correlated to functional groups for each rubber appeared clearly. The signal of vinyl proton (as shown by letter A in the spectra) (=$CH_{isoprene}$, 5.14 p.p.m.) of NR remained in all structures. Epoxidation showed the specific signal of a proton adjacent to the epoxide ring (D) at 2.70 p.p.m. and a proton in $–CH_3$ at 1.30 p.p.m. in ENR-12. Further chemical modification of ENR-12 *via* oxidative degradation, aldehyde proton (E) at 9.80 p.p.m., methylic proton in ketone end group (G) at 2.13 p.p.m. and α and β positions of $-CH_2$ in the carbonyl terminal functional group (F) in a range of 2.26 to 2.48 p.p.m. were observed in the CTNRs. The last proton signal (2.26-2.48) in the CTNRs disappeared after reduction. However, new signals as seen on the HTNRs spectra corresponded to CH (H) (3.80 p.p.m.), CH_2 (I) (3.60 p.p.m.) adjacent to alcohol group at the terminal chain and aliphatic protons adjacent to secondary alcohol (J) at 1.25 p.p.m.

The chemical structure of modified NR was also proven by FTIR technique. Results as illustrated in *Figures 5* and *6* are in accordance with the results obtained from the ^{1}H-NMR. Apart from important signals correlated with the NR structure (C-H out of plane bending at 834 cm^{-1}, C=C stretching at 1665 cm^{-1}, C-H stretching at 2735-2900 cm^{-1}, C-H bending at 1448, 1370 cm^{-1} in $-CH_2$ and $-CH_3$), the strong peak of C=O stretching at 1720 cm^{-1} was clearly observed in the CTNRs structure. However, this peak was absent in the spectra of the HTNRs together with the presence of a new peak at 3350 cm^{-1} of OH-stretching. This means that the reduction of carbonyl group was successfully done. Most of the carbonyl end groups in the CTNR structure became the hydroxyl end group in the HTNR. Furthermore, no difference of signals was observed on the spectra of the CTNR and the HTNR obtained from different starting rubbers.

Table 2 shows characteristics of the prepared HTNRs while % Yield of HTNRs was determined by using *Equation 4*, whereas $\overline{Mn}$ of the HTNRs was calculated using *Equation 6*.

$$\overline{Mn} = \left[2 \times \frac{I_{5.12}}{I_{3.6}}\right] \times 68 + 104 \qquad \ldots 6$$

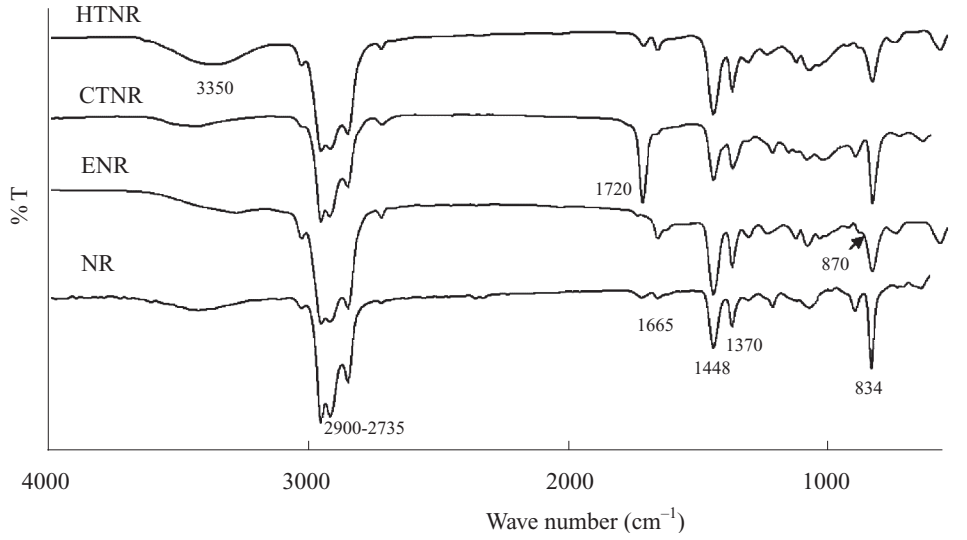


Figure 6. FTIR spectra of HTNR, CTNR and ENR prepared from ENR-12.

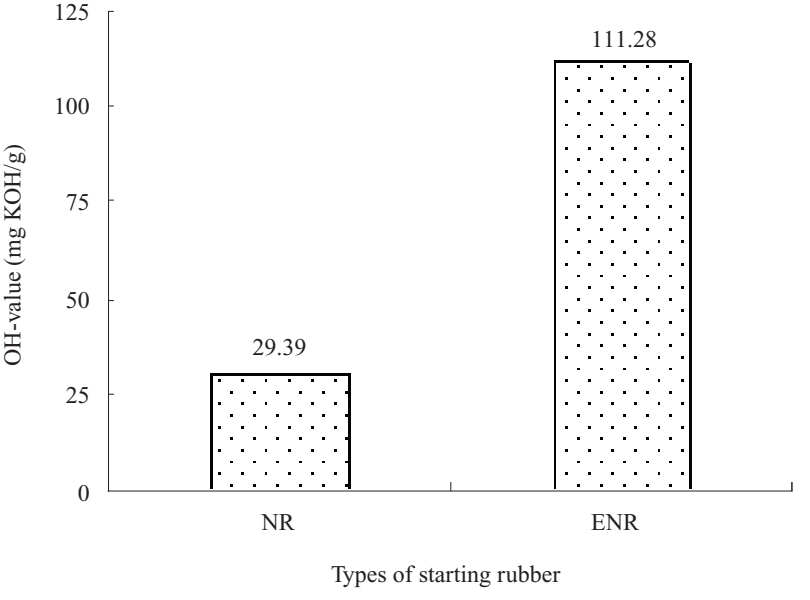


Figure 7. OH-value of the prepared HTNRs.

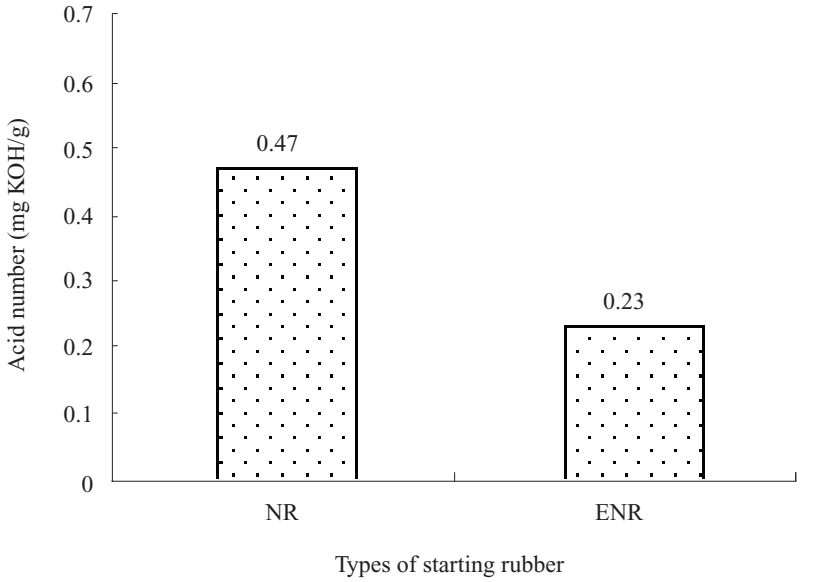


Figure 8. Comparing acid number content of HTNRs.

where $I_{5.12}$ and $I_{3.6}$ are integral areas of the signal of vinyl proton of the NR and CH_2 proton adjacent to alcohol group at the terminal chain end of the HTNR, respectively.

Data in *Table 2* reveal that the HTNR which was prepared from the ENR-based CTNR provided higher % yield and lower molecular weight and was of lighter colour of viscous liquid than the HTNR from the NR based CTNR.

Results of OH-value and acid number are shown in *Figures 7* and *8*. The high content of OH-value and low content of acid number indicate that the final product of HTNR from the ENR-based CTNR consisted of very high concentration of hydroxyl chain end. This shows that using ENR as a starting rubber for the HTNR preparation was a successful way to produce polyol precursor and was better than using NR.

Eventhough the epoxidation took several hours, the HTNR prepared from the ENR-based CTNR gained some more advantages over the HTNR prepared from the NR-based CTNR. The HTNR was of a light colour making it suitable for further applications, and a lower quantity of H_5IO_6 was used in the step of CTNR production. These findings suggest that ENR is more suitable to be selected for production of HTNR than NR.

CONCLUSION

Different starting rubbers *i.e*., NR and ENR, yielded CTNR and HTNR with different functional performance and production. Modification of NR through epoxidation before oxidative degradation and reduction made its products, CTNR and HTNR, perform better in terms of % yield, molecular weight, OH-value and acid number than those

TABLE 2. CHARACTERISTICS OF THE PREPARED HTNRs

Starting material	Yield (%)	$\overline{Mn}$	Appearance
NR	70	3,400	Yellow-brown viscous liquid 
ENR	78	700	Light yellow viscous liquid 

products obtained from NR. Furthermore, the light colour of the product and low consumption of periodic acid used were other advantages of the HTNR prepared from the ENR-based CTNR.

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