# A structural study of epoxidized natural rubber (ENR-50) ring opening under mild acidic condition

Rosniza Hamzah,[1] Mohamad Abu Bakar,[2] Omar Sabbar Dahham,[1] Nik Noriman Zulkepli,[1] Saad Sabbar Dahham[3]

[1]Center of Excellence Geopolymer and Green Technology, Faculty of Engineering Technology, Universiti Malaysia Perlis, Perlis, Malaysia
[2]Nanoscience Research Laboratory, School of Chemical Sciences, Universiti Sains Malaysia, Minden Penang 11800, Malaysia
[3]EMAN Research and Testing Laboratory, School of Pharmaceutical Sciences, Universiti Sains Malaysia, Minden Pulau Pinang 11800, Malaysia
Correspondence to: R. Hamzah (E-mail: rosnizahamzah@unimap.edu.my)

**ABSTRACT:** A structural study of ring opening reaction of purified epoxidized natural rubber (ENR) with acetic acid was conducted using the NMR techniques and its thermal characteristic was evaluated with Thermal gravimetry/Differential Thermal Gravimetry (TG/DTG) and Differential Scanning Calorimetry (DSC) analyses. ^{1}H-NMR revealed that 19.56% of epoxide was ring-opened from the total amount of the epoxide unit in ENR-50 and this was supported by Fourier Transform Infrared (FTIR) spectroscopy. ^{13}C-NMR suggests the fixation of alkyl (R) i.e., acetate group to the epoxide carbon via ester linkage and formation of hydroxyl groups in the polymer chains. The attachment location of R occurred at both most (↑) and least (↓) hindered carbons of the epoxide. The TG/DTG results of acid treated ENR-50 showed three decomposition steps at 235–338, 338–523, 523–627 °C due to the presence of the polymer chains mixture, i.e., ring-opened and intact epoxide of ENR-50. This increases the $T_g$ value of acid treated ENR-50 at 24.6 °C as compared to purified ENR-50 at −17.7 °C. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 44123.

## INTRODUCTION

Epoxidized natural rubber (ENR) is a commercial polymer produced from the epoxidation process of natural rubber (NR) with formic peroxide or acetic peroxide in a reactor.[1,2] ENR contains both epoxidized isoprene (E) and isoprene (C) units in the polymer chains.[3,4] Epoxide ring is the reactive site of the E unit while the double bond is the reactive site for C unit, respectively. The epoxide at E unit is involved with the ring opening reaction while the double bond at C unit is involved with crosslinking.[5–8] Epoxide or oxirane is an ether in which the oxygen atom is incorporated into the C=C bond to form a three-membered ring. Ethylene oxide is the simplest form of epoxide. The carbons in an epoxide are very reactive electrophile thus able to react with a variety of nucleophile. The ring strain in the three-membered ring of epoxide is able to relieve through the ring opening reaction.[9] The majority of epoxide reactions are studied in solution and most of the reaction involves the epoxide ring opening and addition of a molecule of reagent.[10] In practice, the oxirane ROR is a common reaction during the preparation of ENR. The ring opening products vary

the properties and application of ENR.[11] Thus, this reaction offers opportunities to functionalize ENR with other reactive substances, fillers, or polymers. The oxirane ring is reactive toward nucleophilic reagents such as amine, carboxylic acid, alcohol, dibutylphosphate, and phosphoric acid derivatives.[12–14]

ENR is a pH sensitive polymer and favors neutral pH.[15,16] The exposure of ENR to pH below than 7 (acidic) is able to catalyst the ring opening reaction of an epoxide and provides crosslinking amongst the polymer chains through the ether groups.[15–17] The excessive reaction temperature and too low pH contribute to the secondary ring opening reaction of ENR-50 such as diol and furans.[18,19] Typically, acidity and temperature are the main factors for the formation of ring opening products, i.e., hydroxyl-acetates, diols, and intermolecular ethers.[11] The cleavage of epoxide ring under acidic condition involves the formation of oxonium ion. Then this oxonium ion is attacked by the nucleophile in a $S_N2$ displacement that produced β-alkoxy alcohols. However, the addition of nucleophile onto epoxide ring is difficult to obtain under acidic condition due to the undesirable side reactions obtained.[13] The ring opening reaction of epoxide
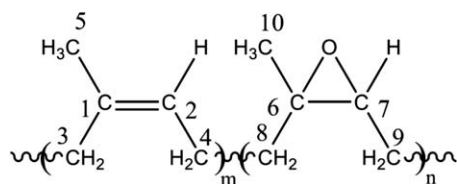
**Scheme 1.** The general structure and numbering of carbon atom C and E units in ENR-50 employed in this work.[3]

using acid treatments is preferred due to their simplicity and low cost.[4,10,20] The ring opening reaction of ENR-50 using periodic acid will produce heterotelechelic NR. It involves chain scission at the epoxide structure and degradation of ENR chains.[10,21] However, periodic acid works as an oxidizing agent due to the formation of carbonyl group after prolonged reaction time.[21] A ring opening reaction in acid solution produces formyl ester and an alcohol group.[22] Acid catalyzed the ring opening of the epoxide and formed the crosslinked ether.[1] The acid treatment is more preferred because, at a neutral pH, the epoxide structure of the ENR is stable toward the epoxide ring opening.[4] However, at a low pH (not less than 3), organic acids such as acetic acid, methacrylic acid, benzoic acid, and other carboxylic acids are capable of inducing the epoxide ring opening reactions.[23–25] Typically the products are an ester, alcohol, hydroxyl, and diol. NMR spectroscopy is a well-known and reliable method to determine the mole percentage of epoxidation as well as the extent of the ring opening reaction.[15,22,26,27] 1D NMR provides structural information such as the extent of ring opening reaction of the monomer unit in the polymer chains. Meanwhile, 2D NMR provides details on structural arrangement of the C and E unit including the ring-opened epoxide of the E unit within the triad sequence.[3,27] Previous researchers have elucidated all possible triad sequences of ENR-50 which contains randomly located E and C monomers units in the arrangement of three monomer units that are called as a triad sequence.

The main focus of this study is to give a complete assignment of the acid treated ENR-50 using the NMR spectroscopy techniques. This complete assignment covered the 1D and 2D NMR spectroscopy techniques supported by thermal characteristics using the TG/DTG and DSC analyses. The type of ENR-50 used in this study is a low molecular weight fraction of ENR-50 obtained by sol–gel technique. This work differs from other reported works in term of the degree of epoxidation and physical form of rubber.[27,28]

## NOMENCLATURE

The arrangement of C and E unit in the ENR-50 polymer chains is randomly distributed. Thus, the arrangement of three units as a group is called a triad sequence. There are eight possible triad sequences of ENR-50 as discussed by previous researchers.[3,27] In this work, the general structure and the numbering of the carbon atom of C and E units are given in Scheme 1 and the reaction of acetic acid with epoxidized isoprene and its carbon numbering are given in Scheme 2.

The ring opening reaction of epoxidized isoprene can occur in the presence of an arbitrary ring opening reagent (RX). RX can be acid, base, alkyl halide, or metal salt. It has two possible

carbon positions for the attachment of $R^+$ or $X^-$ i.e., either at the most hindered carbon or least hindered carbon of the epoxide as shown in Scheme 3. Different positions of R attachment, either at the most or least hindered carbon, give rise to different chemical shifts in NMR spectrum due to the changes in the respective carbon environment.[29] Therefore, further notations were used to indicate the positions of R attachment to the respective carbon of the ring-opened epoxidized isoprene. The ring opening reaction and R attachment at the most hindered carbon are indicated as (↑) and the attachment at the least hindered carbon is indicated as (↓) with respect to the $E^6$ carbon and $E^7$ carbon of the epoxide ring. In the case of multiple ring openings of epoxide that occur in a triad, the attachment or position of epoxide carbons can be similarly indicated. For example, the possible attachment positions of ring-opened epoxidized isoprene of ENR-50 and its carbon numbering (reaction with acetic acid) are given in Scheme 4.

## EXPERIMENTAL

### Materials

All chemicals were obtained commercially and used without further purification unless otherwise stated. The ENR with 50% epoxidation (ENR-50) was obtained from the Rubber Research Institute, Malaysia. The acetic acid glacial 99.8% ($CH_3COOH$) was purchased from Hamburg Chemicals, Germany. The deuterated chloroform ($CDCl_3$) was obtained from Fluka Chemicals, Switzerland. The *n*-hexane and toluene were from Systerm, Malaysia.

### Preparative Procedure

**Purification of ENR-50.** ENR-50 (about 20.00 g) was swelled in chloroform (400 mL) and stirred for 24 h at room temperature. The solution was then filtered through a pack of cotton gauze to separate the gel (high molecular ENR-50) from the extract (low molecular weight ENR-50, $M_w = 294{,}000$). The latter was precipitated in *n*-hexane while stirring using a glass rod. The white precipitate stuck to the glass rod was transferred to a Petri dish and dried in a vacuum oven at 50 °C for two days. The mass of purified ENR-50 sample was recorded daily until a constant weight was achieved.

**Acid-Treated ENR-50.** In a typical preparation, about 200 mg ($1.32 \times 10^{-3}$ mol) of purified ENR-50 was dissolved in 40 mL toluene with stirring. The pH of the solution was adjusted to pH 3 by the addition of 4 mL of glacial acetic acid ($69.80 \times 10^{-3}$ mol). The mixture was stirred until the homogenous solution was obtained and later refluxed at 110 °C for 3 h. The reaction mixture was then cooled to room temperature. The mixture was later washed with 150 mL of water to remove the excess acid. This procedure was repeated until the washing attained a neutral pH. Upon separation, the organic layer was then cast onto Teflon dishes before drying in vacuum oven at 80 °C for 24 h.

### Measurements and Characterization Techniques

FTIR spectra were recorded on a Perkin–Elmer 2000-FTIR using single beam transmittance onto a film of the sample on the zinc selenide (ZnSe) window in the range of 4000–600 cm$^{-1}$. The FTIR samples were prepared by swelling the sample (100.00 mg) in chloroform (5 mL). The sample solution was
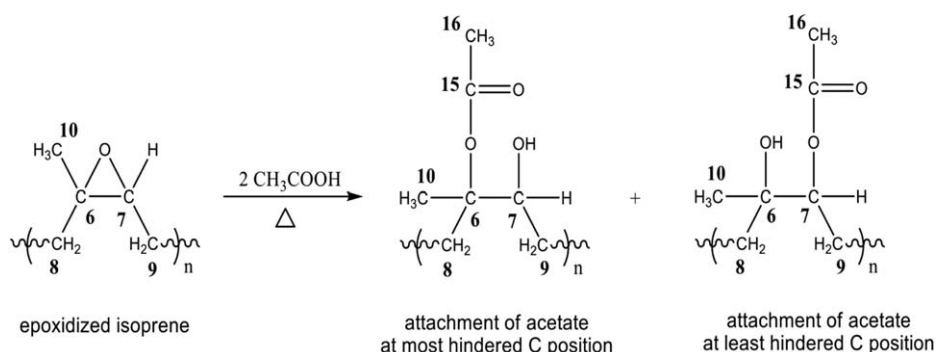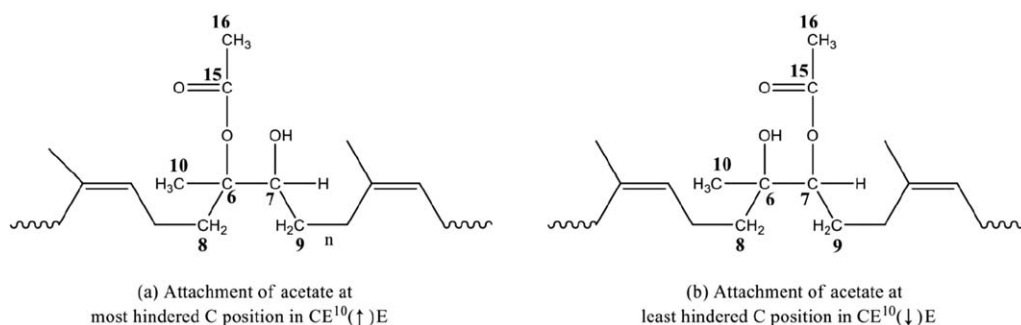
**Scheme 2.** Reaction of acetic acid with epoxidized isoprene and its carbon numbering.
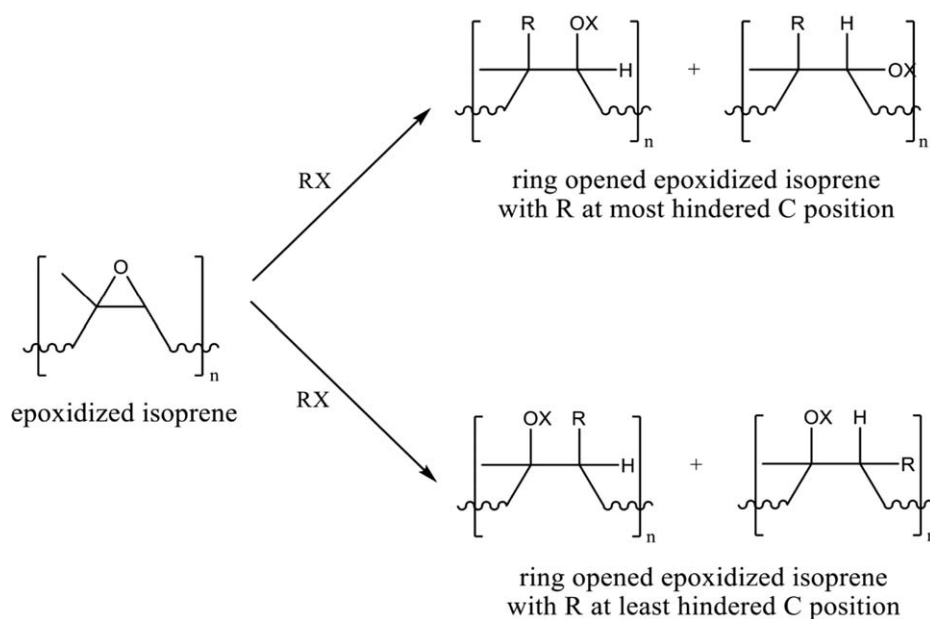


**Scheme 3.** The reactions of RX with epoxidized isoprene.

cast onto Teflon mold of dimension 3.0 cm × 1.0 cm × 0.5 cm and air dried. The thin film obtained was further dried in a vacuum oven at 50 °C for an hour and later transferred onto the ZnSe window. 1D and 2D NMR spectra were obtained using a Bruker Avance 500 MHz instrument in CDCl$_3$ at 25 °C. A sample was swelled for at least three days in the NMR tube before the analysis. A 10.00 mg sample was used for $^1$H- while

50.00 mg was used for the 13C-NMR, heteronuclear multiple quantum coherence (HMQC), heteronuclear multiple bond coherence (HMBC), and correlation spectroscopy (COSY) analyses. The respective range of the spectra and number of scan for $^1$H- and for 13C-NMR measurements were 15–0 ppm with 16 scans and 200–0 ppm with 15,000 scans, respectively. For quantitative 13C-NMR measurements, 1000 scans were applied with



(a) Attachment of acetate at most hindered C position in CE$^{10}$(↑)E

(b) Attachment of acetate at least hindered C position in CE$^{10}$(↓)E

**Scheme 4.** Possible attachment positions of the ring-opened epoxidized isoprene of ENR-50 and its carbon numbering (reaction with acetic acid).

60 s relaxation delay. The number of scans applied for HMQC, HMBC, and COSY were 8, 2000, 128, 256, and 40 scans, respectively. A Perkin Elmer TGA-7 thermal gravimetric (TG) analyser was used to investigate the thermal property of the sample. About 10.00 mg sample was heated under a nitrogen atmosphere from 30 °C to 900 °C at the heating rate of 20 °C min$^{-1}$ in all cases. The differential scanning calorimetry (DSC) measurements were carried out using a Perkin Elmer Pyris-6 (Shelton CT) using 10.00 mg sample sealed in an aluminium pan. The thermograms were recorded over a range of −50 to 140 °C at a heating rate of 20 °C min$^{-1}$ under a nitrogen atmosphere. The sample was initially heated from −50 to 140 °C and held at 140 °C for 1 min. Then it was quenched to −50 °C and held for another 5 min. Then it was reheated from −50 to 140 °C at the similar heating rate.

## Theoretical Treatments

The FTIR semi-quantitative treatments were based on the peak area of methyl and epoxide functional groups. The percentage of epoxide in purified ENR-50 of the epoxide was determined using eq. (1). In eq. (1), $N_{methyl}$ is the normalized peak area of the methyl signal, $A_{epoxide\ sample}$ is the peak area of epoxide functional group of the sample, and $A_{epoxide\ ENR-50}$ is the peak area of respective functional group stretching peak in purified ENR-50. The percentage of epoxide in acid treated ENR-50 was similarly determined using eq. (1).[20]

$$\%Epoxide = \frac{N_{methyl} \times A_{epoxidesample} \times 100\%}{A_{epoxideENR-50}} \quad (1)$$
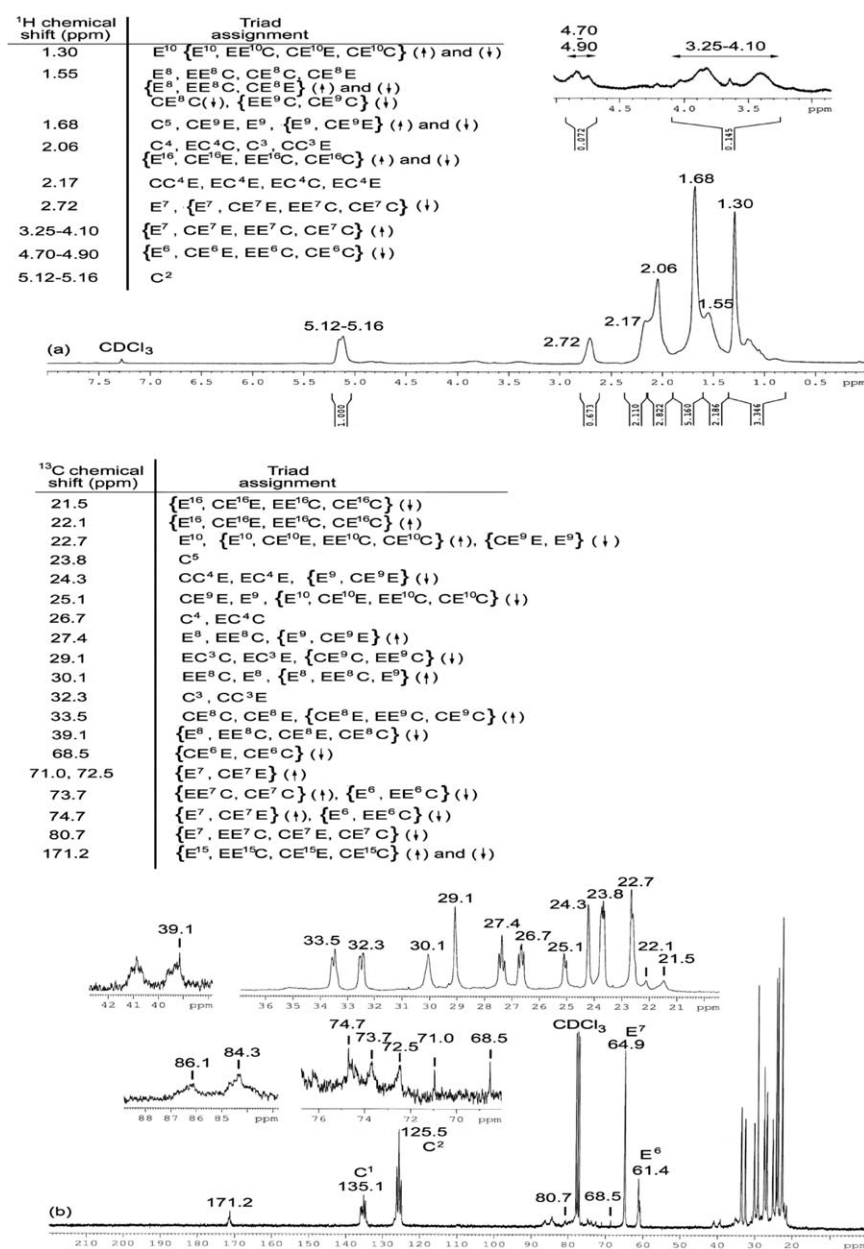


**Figure 1.** (a) 1H- and (b) 13C-NMR spectra of acid treated ENR-50 (in CDCl$_3$).

Table I. $^1$H-, $^{13}$C-NMR Chemical Shifts and HMQC, HMBC, and COSY Spin Coupling Correlations of Acid Treated ENR-50

| $^1$H chemical shift, δ (ppm) | $^{13}$C chemical shift, δ (ppm) | HMQC Triad assignments | HMBC coupling correlation Middle unit, δ (ppm) | COSY coupling correlation Middle unit, δ (ppm) | COSY coupling correlation Within same unit, δ (ppm) |
|---|---|---|---|---|---|
| 1.30 | 22.7 | $E^{10}$ (↑) | 27.4 ($E^8$), 71.0, 72.5, 74.7 ($E^7$), 84.3–86.1 ($E^6$) | None | None |
| | | $E^{10}$ | 30.1 ($E^8$), 61.4 ($E^6$), 64.9 ($E^7$) | | |
| | | $CE^{10}E$ (↑) | 33.5 ($E^8$), 71.0, 72.5, 74.7 ($E^7$), 84.3–86.1 ($E^6$) | | |
| | | $EE^{10}C$ (↑) | 27.4, 30.1 ($E^8$), 73.7 ($E^7$), 84.3–86.1 ($E^6$) | | |
| | | $CE^{10}C$ (↑) | 33.5 ($E^8$), 73.7 ($E^7$), 84.3–86.1 ($E^6$) | | |
| | 25.1 | $E^{10}$ (↓) | 39.1 ($E^8$), 73.7, 74.7 ($E^6$), 80.7 ($E^7$) | | |
| | | $CE^{10}E$ (↓) | 39.1 ($E^8$), 68.5 ($E^6$), 80.7 ($E^7$) | | |
| | | $EE^{10}C$ (↓) | 39.1 ($E^8$), 73.7, 74.7 ($E^6$), 80.7 ($E^7$) | | |
| | | $CE^{10}C$ (↓) | 39.1 ($E^8$), 68.5 ($E^6$), 80.7 ($E^7$) | | |
| 1.55 | 27.4 | $EE^8C$ (↑) | 22.7 ($E^{10}$), 73.7 ($E^7$), 84.3–86.1 ($E^6$) | | 1.68 ($E^9$) |
| | | $E^8$ | 22.7 ($E^{10}$), 74.7 ($E^7$), 84.3–86.1 ($E^6$) | | |
| | 29.1 | $CE^9C$ (↓) | 68.5 ($E^6$), 80.7 ($E^7$) | 2.72 ($E^7$) | 2.17 ($C^3$) |
| | | $EE^9C$ (↓) | 73.7, 74.7 ($E^7$) | | |
| | 30.1 | $EE^8C$ and $E^8$ | 22.7 ($E^{10}$), 61.4 ($E^6$), 64.9 ($E^7$) | None | 1.68 ($E^9$) |
| | | $E^8$ (↑) | 22.7 ($E^{10}$), 71.0, 72.5, 74.7 ($E^7$), 84.3–86.1 ($E^6$) | | |
| | | $EE^8C$ (↑) | 22.7 ($E^{10}$), 73.7 ($E^7$), 84.3–86.1 ($E^6$) | | |
| | 33.5 | $CE^8C$ and $CE^8E$ | 22.7 ($E^{10}$), 61.4 ($E^6$), 64.9 ($E^7$) | | 2.17 ($C^4$) |
| | | $CE^8E$ (↑) | 22.7 ($E^{10}$), 71.0, 72.5, 74.7 ($E^7$) 84.3–86.1 ($E^6$) | | |
| | | $EE^9C$ (↑) | 73.7 ($E^7$), 84.3–86.1 ($E^6$) | | 1.68 ($E^9$) |
| | | $CE^9C$ (↑) | 73.7 ($E^7$), 84.3–86.1 ($E^6$) | 2.72 ($E^7$) | |
| 1.68 | 39.1 | $E^8$ (↓) | 25.1 ($E^{10}$), 73.7, 74.7 ($E^6$), 80.7 ($E^7$) | None | 1.68 ($E^9$) |
| | | $EE^8C$ (↓) | 25.1 ($E^{10}$), 73.7, 74.7 ($E^6$), 80.7 ($E^7$) | | |
| | | {$CE^8E$, $CE^8C$} (↓) | 25.1 ($E^{10}$), 68.5 ($E^6$), 80.7 ($E^7$) | | |
| | 22.7 | $CE^9E$ (↓) | 68.5 ($E^6$), 80.7 ($E^7$) | 2.72 ($E^7$) | 1.55 ($E^8$) |
| | | $E^9$ (↓) | 73.7 ($E^6$), 80.7 ($E^7$) | | |
| | 23.8 | $C^5$ | 32.3 ($C^3$), 125.5 ($C^2$), 135.1 ($C^1$) | None | None |
| | 24.3 | $E^9$ (↓) | 73.7 ($E^6$), 80.7 ($E^7$) | 2.72 ($E^7$) | 1.55 ($E^8$) |
| | | $CE^9E$ (↓) | 68.5 ($E^6$), 80.7 ($E^7$) | | |
| | 25.1 | $CE^9E$ and $E^9$ | 61.4 ($E^6$), 64.9 ($E^7$) | | |
| | 27.4 | $E^9$ (↑) | 74.7 ($E^7$), 84.3–86.1 ($E^6$) | | |
| | 27.4 | $CE^9E$ (↑) | 71.0, 72.5, 74.7 ($E^7$), 84.3–86.1 ($E^6$) | | |

**Applied Polymer**
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**Table I.** *Continued*

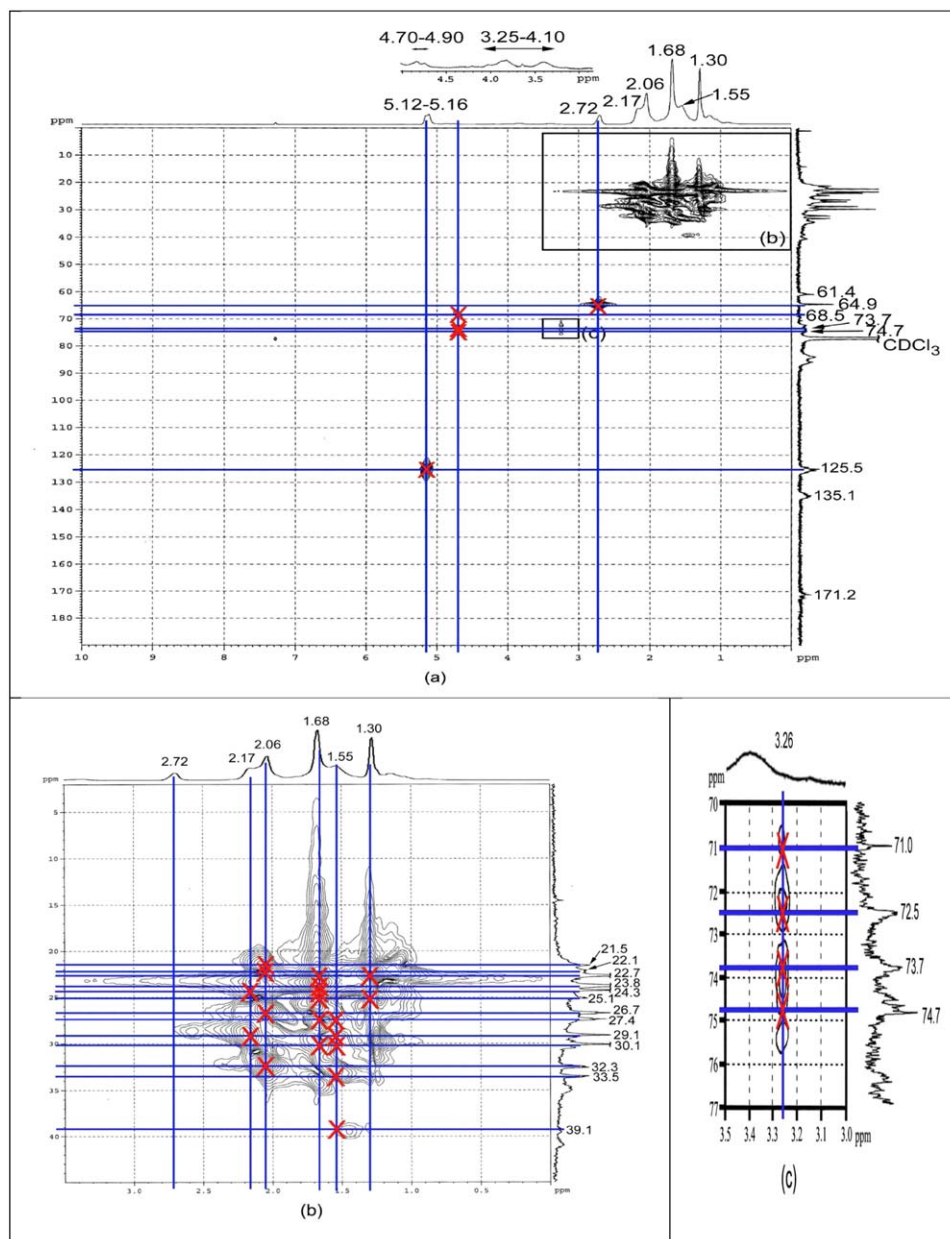| ¹H chemical shift, δ (ppm) | ¹³C chemical shift, δ (ppm) | HMQC — Triad assignments | HMBC coupling correlation — Middle unit, δ (ppm) | COSY coupling correlation — Middle unit, δ (ppm) | COSY coupling correlation — Within same unit, δ (ppm) |
|---|---|---|---|---|---|
| 2.06 | 30.1 | $E^9$ (↑) | 71.0, 72.5 ($E^7$), 84.3–86.1 ($E^6$) | | None |
|  | 21.5 | {$E^{16}$, $CE^{16}E$, $EE^{16}C$, $CE^{16}C$} (↓) | 171.2 ($E^{15}$) | None | |
|  | 22.1 | {$E^{16}$, $CE^{16}E$, $EE^{16}C$, $CE^{16}C$} (↑) | | | |
| 2.17 | 26.7 | $C^4$, $EC^4C$ | 125.5 ($C^2$), 135.1 ($C^1$) | 5.12–5.16 ($C^2$) | 2.06 ($C^3$) |
|  | 32.3 | $C^3$ and $CC^3E$ | 23.8 ($C^5$), 125.5 ($C^2$), 135.1 ($C^1$) | None | 2.06 ($C^4$) |
|  | 24.3 | $CC^4E$ and $EC^4E$ | 125.5 ($C^2$), 135.1 ($C^1$) | 5.12–5.16 ($C^2$) | 1.55 ($E^8$) |
|  | 29.1 | $EC^3C$ and $EC^3E$ | 23.8 ($C^5$), 125.5 ($C^2$), 135.1 ($C^1$) | None | 1.55 ($E^9$) |
| — | 61.4 | $E^6$ | — | — | — |
| 2.72 | 64.9 | $E^7$ | 22.7 ($E^{10}$), 25.1 ($E^9$), 30.1 ($E^8$), 61.4 ($E^6$) | 1.68 ($E^9$) | None |
|  | 80.7 | $E^7$ (↓) | 22.7, 24.3 ($E^9$), 25.1 ($E^{10}$), 73.7, 74.7 ($E^6$) | | |
|  | 80.7 | $CE^7E$ (↓) | 22.7 ($E^9$), 25.1 ($E^{10}$), 68.5 ($E^6$) | | |
|  | 80.7 | $EE^7C$ (↓) | 25.1 ($E^{10}$), 29.1 ($E^9$), 73.7, 74.7($E^6$) | 1.55 ($E^9$) | |
|  | 80.7 | $CE^7C$ (↓) | 25.1 ($E^{10}$), 29.1 ($E^9$), 68.5 ($E^6$) | | |
| 3.25–4.10 | 71.0, 72.5 | {$E^7$, $CE^7E$} (↑) | None | None | |
|  | 73.7 | {$EE^7C$, $CE^7C$} (↑) | | | |
|  | 74.7 | {$E^7$, $CE^7E$} (↑) | | | |
| 4.70–4.90 | 68.5 | {$CE^6E$, $CE^6C$} (↓) | | | |
|  | 73.7 | {$E^6$, $EE^6C$} (↓) | | | |
|  | 74.7 | {$E^6$, and $EE^6C$} (↓) | | | |
| — | 84.3–86.1 | {$E^6$, $CE^6E$, $EE^6C$, $CE^6C$} (↑) | — | — | — |
| 5.12–5.16 | 125.5 | $C^2$ | 23.8 ($C^5$), 26.7 ($C^4$), 32.3 ($C^3$) | 2.06 ($C^4$) | None |
|  | 135.1 | $C^1$ | — | — | — |
| — | 171.2 | {$E^{15}$, $EE^{15}C$, $CE^{15}E$, $CE^{15}C$} (↑) and (↓) | — | — | — |

**Figure 2.** (a) HMQC spectra of acid treated ENR-50 and (b, c) enlargement of the box region in (a). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

## RESULTS AND DISCUSSION

### NMR

**^{1}H- and 13C-NMR Spectroscopy.** The ^{1}H- and ^{13}C-NMR spectra of acetic acid treated ENR-50 are shown in Figure 1 and the respective chemical shifts are tabulated in Table I. From Figure 1(a), the chemical shifts of $C^2$ and $E^7$ appeared at $\delta$ 5.12–5.16 ppm and $\delta$ 2.72 ppm, respectively, and were similar to the ENR-50.[3] However, the proton integrals of $C^2$ and $E^7$ did not equate to that of the ENR-50. As previously noted, the degree of epoxidation can be determined by comparing the integration area of $C^2$ and $E^7$.[3,22,27] In this case, the integrals of $E^7$ (m,

0.673H) decreased as compared to $C^2$ (m, 1.000H). Using eq. (1), the result suggests that of the original epoxide ring, 19.56% of ring opening reaction has occurred. The ^{1}H-NMR spectrum also showed two regions of hydroxyl proton at $\delta$ 3.25–4.10 ppm (br s, 0.145H) and $\delta$ 4.70–4.90 ppm (br s, 0.072H).[30,31] Upon the ring opening reaction, $E^7$ hydroxyl was obtained at the ($\uparrow$) position while $E^6$ hydroxyl at the ($\downarrow$) position. Thus, the signal at $\delta$ 3.25–4.10 ppm corresponded to $E^7$ hydroxyl proton and at $\delta$ 4.70–4.90 ppm corresponded to $E^6$ hydroxyl proton. The broadness of these peaks was due to fast proton exchange between the hydroxyl group and the solvent in the system.[29,32,33] The integral at $\delta$ 2.06 ppm (m, 3.958 H) was, however, higher compared to that of the ENR-50 (m, 2.159 H).[3] This was due
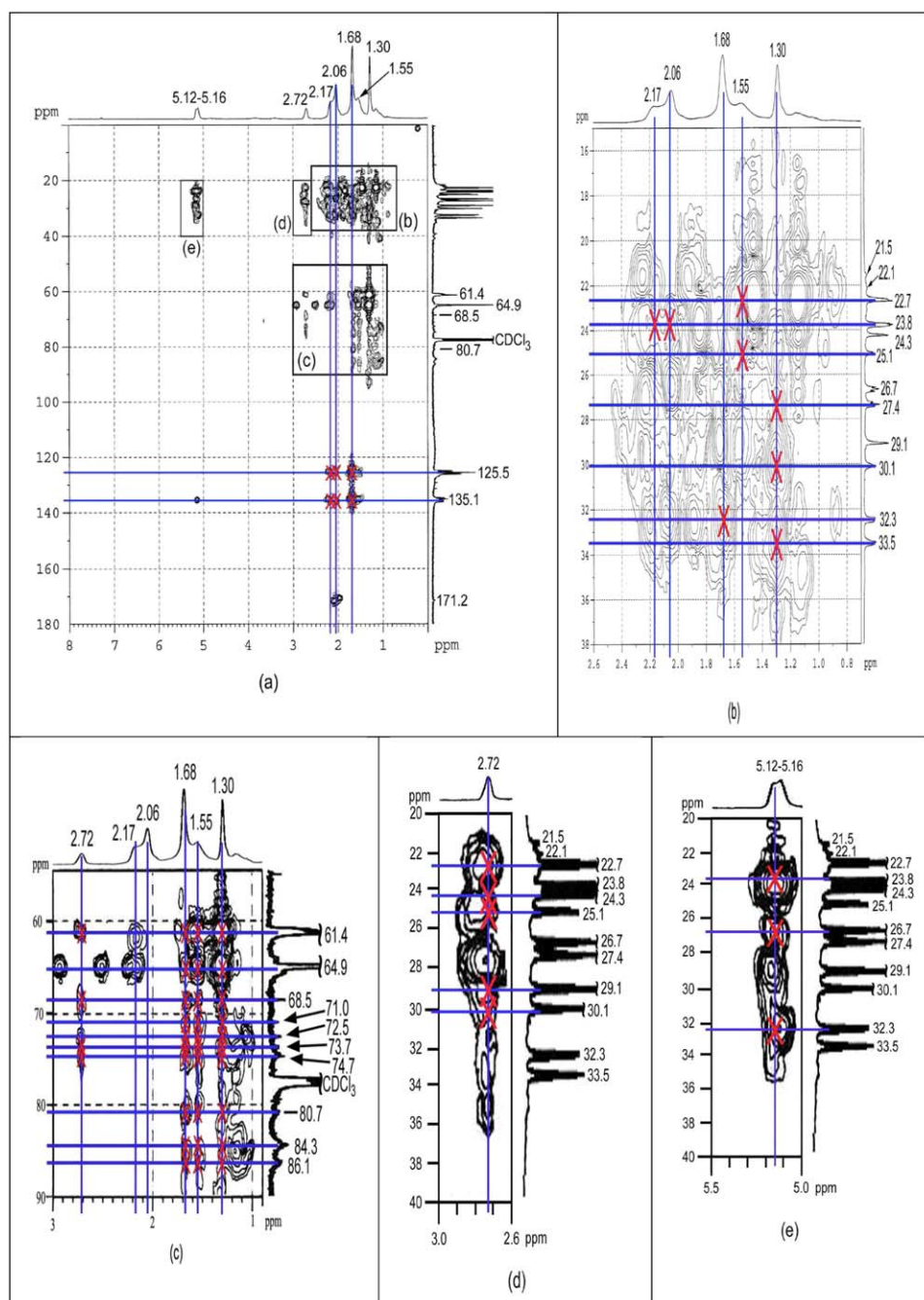
**Figure 3.** (a) HMBC spectra of acid treated ENR-50 and (b,c,d,e) enlargement of the box region in (a). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to the methyl protons of acetate of E1[6], EE[16]C, CE[16]E, and CE[16]C that overlapped with the methylene protons of C[3], CC[3]E, C[4], and EC[4]C of ENR-50. The signal at δ 0.8–1.3 ppm was also broader as compared to the ENR-50. This was due to the overlapping of methyl protons of ring-opened E10, EE[10]C, CE[10]E, CE[10]C, and methyl protons E[10] of ENR-50. The signal at δ 1.55 ppm represented the methylene protons of ring-opened epoxide at both the (↑) and (↓) for E8, EE[8]C, CE[8]E, EE[9]C, CE[9]C and at (↓) for CE[8]C and at (↓) for part of E9, CE[9]E that were shown together at δ 1.68 ppm. This signal also represented the

methylene protons of E8, EE[8]C, CE[8]E, CE[8]C of ENR-50. The signal at δ 1.68 ppm represented the methylene protons at (↑) for E9, CE[9]E and at (↓) for part of E9, CE[9]E that were shown together at δ 1.55 ppm. This signal appeared together with the methyl protons of C[5] of ENR-50. The signal at δ 2.17 ppm corresponded to the methylene protons of EC[3]C, EC3E, CC[4]E, EC[4]E similar to those of ENR-50. The signal at δ 2.72 ppm belonged to the methine proton at (↓) for E7, EE[7]C, CE[7]E, CE[7]C and the methine proton of E[7] of ENR-50. The methine proton of C[2] of ENR-50 remained at δ 5.12–5.16 ppm.
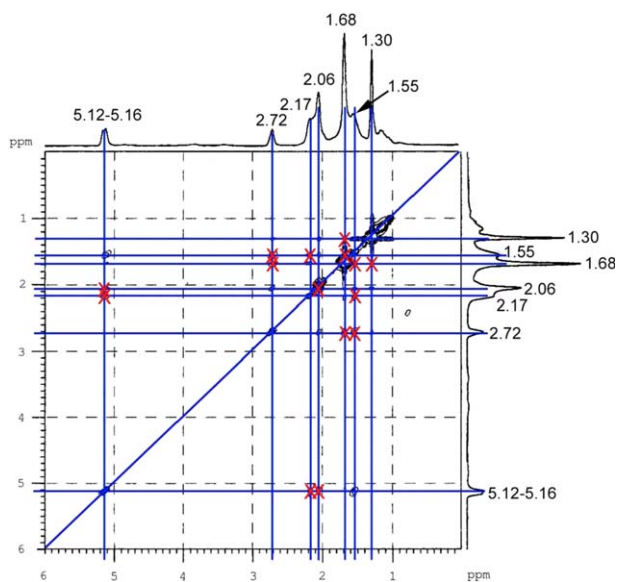
**Figure 4.** COSY spectra of acid treated ENR-50. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The $^{13}$C-NMR spectrum of acid-treated ENR-50 is shown in Figure 1(b) and the corresponding chemical shifts are tabulated in column 2 of Table I. The presence of acetate group within the ENR-50 was evident by two new peaks. Those peaks were carbonyl carbon of acetate $E^{15}$ at δ 171.2 ppm and methyl carbon of acetate $E^{16}$ at δ 21.5 and 22.1 ppm. At the (↓) position, the methyl carbon of acetate $E^{16}$ was located slightly upfield at δ 21.5 ppm while at (↑) position was located at δ 22.1 ppm. The hydroxyl attached to carbon $E^7$ gave rise to four different peaks at δ 71.0, 72.5, 73.7, and 74.7 ppm. This was due to the modification at the right (R) unit of the triad. The hydroxyl was able to form a hydrogen bond between proton and hydroxyl of R unit of the triads. Meanwhile, the hydroxyl attached to carbon $E^6$ was shown by peaks at δ 68.5, 73.7, and 74.7 ppm. It was influenced by the left (L) unit of the triad sequence. The ester carbons $E^6$ and $E^7$ were located at δ 84.3–86.1 and 80.7 ppm, respectively. The ester carbon of $E^7$ and methine carbon of $E^7$ were, in fact, a similar carbon. Meanwhile, the methyl carbon of $E^{10}$ showed two peaks at δ 22.7 and 25.1 ppm. The peak at δ 22.7 ppm was due to the attachment at (↑) while at δ 25.17 ppm was due to the attachment at (↓). The methylene carbon of $E^8$ at (↑) showed three peaks at δ 27.4, 30.1, and 33.5 ppm. The methylene carbon of $E^8$ at (↓) appeared at δ 39.1 ppm. The methylene carbon $E^9$ showed six peaks at δ 22.7, 24.3, 27.4, 29.1, 30.1, and 33.5 ppm. The peak at δ 22.7, 24.3, and 29.1 ppm were due to the attachment at (↓). If the R unit was C, it was located at δ 29.1 ppm compared to when R unit was E (δ 22.7, 24.3 ppm). Peaks at δ 27.4, 30.1, and 33.5 ppm were due to the attachment at (↑). Similarly above, if the R unit was C, it was located at δ 33.5 ppm. The carbon of C unit remained similar as the ENR-50. The methylene carbon of $C^3$ and CC3E were at δ 32.3; EC3C and EC3E were at 29.1 ppm. While the methylene carbon of $C^4$ and $EC^4C$ were at δ 26.7; $CC^4E$ and $EC^4E$ were at 24.3 ppm. The quartenary carbon $C^1$ and methine carbon $C^2$ remained at δ 125.1 and 135.1 ppm.

**HMQC.** Figure 2 sho1ws the HMQC spectra of acid-treated ENR-50 and the identified triad assignments are tabulated in

Table I (3rd column). The HMQC connected the directly bonded proton(s) to its carbon. It verified and confirmed the information on triad sequence of the ring-opened E since it appeared at the usual chemical shift of ENR-50. The ring-opening at the (↓) position was correlated to the methyl of acetate of $E^{16}$ at upfield region while at the (↑) position it was at the downfield region. As mentioned earlier, the attachment of MeCOO$^-$ at the (↑) position produced quartenary carbon $E^6$ while hydroxyl at carbon $E^7$. Attachment to the (↓) position produced hydroxyl at carbon $E^6$ and methine at carbon $E^7$. The quartenary carbon of $E^6$ was at the downfield region accordingly. The methine carbon of $E^7$ was to the downfield region accordingly where the middle unit was not ring-opened. The electron density of the quaternary carbon $E^6$ and methine carbon $E^7$ deshielded the carbon/proton which was geminally or vicinally bonded. At the (↑) position, the methyl of $E^{10}$ was vicinal to quartenary carbon $E^6$ (while at (↓), it was vicinal to hydroxyl carbon $E^6$). The methyl of $E^{10}$ at (↑) was shielded by electron density of quartenary carbon $E^6$ (while the methyl of $E^{10}$ at (↓) was deshielded by hydroxyl carbon $E^6$). Thus, the correlation of the methyl of $E^{10}$ at (↑) was located at the upfield region than it was at (↓). The correlation of the methylene of $E^8$ and $E^9$ depends on (↓) or (↑) positions or to the middle unit that is not ring-opened. In addition, it also depends on their vicinal neighbouring unit either ring-opened or otherwise. For example, the methylene of $E^8$ was influenced by the left neighboring unit, and methylene of $E^9$ was influenced by the right neighboring unit in all cases. The correlation of the methylene of $E^9$ at (↓) occurred at the upfield region where E was as the right unit of the triad. This was followed by the middle unit which was not ring-opened and finally at the (↑) position at the downfield region. Meanwhile, the correlation of the methylene of $E^8$ was at the downfield region with (↑), followed by the middle unit that was not ring-opened, and finally the (↓) position. The correlation of the methylene of $C^3$ and $C^4$ was similar to the ENR-50. The quartenary carbon of C1, methine of $C^2$
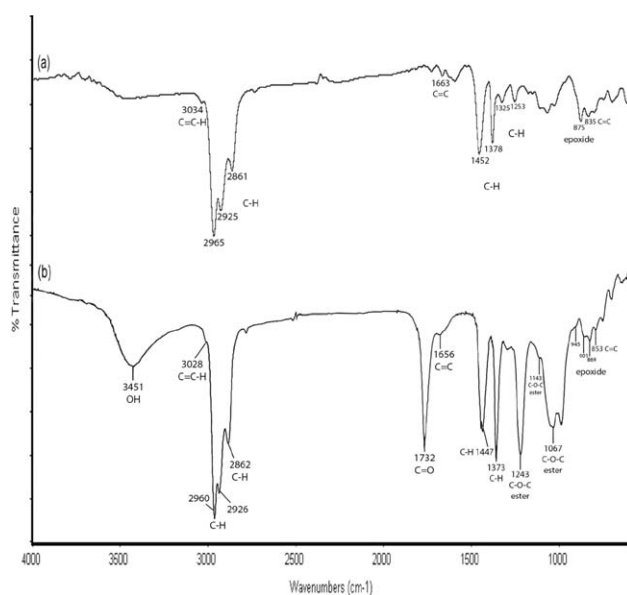


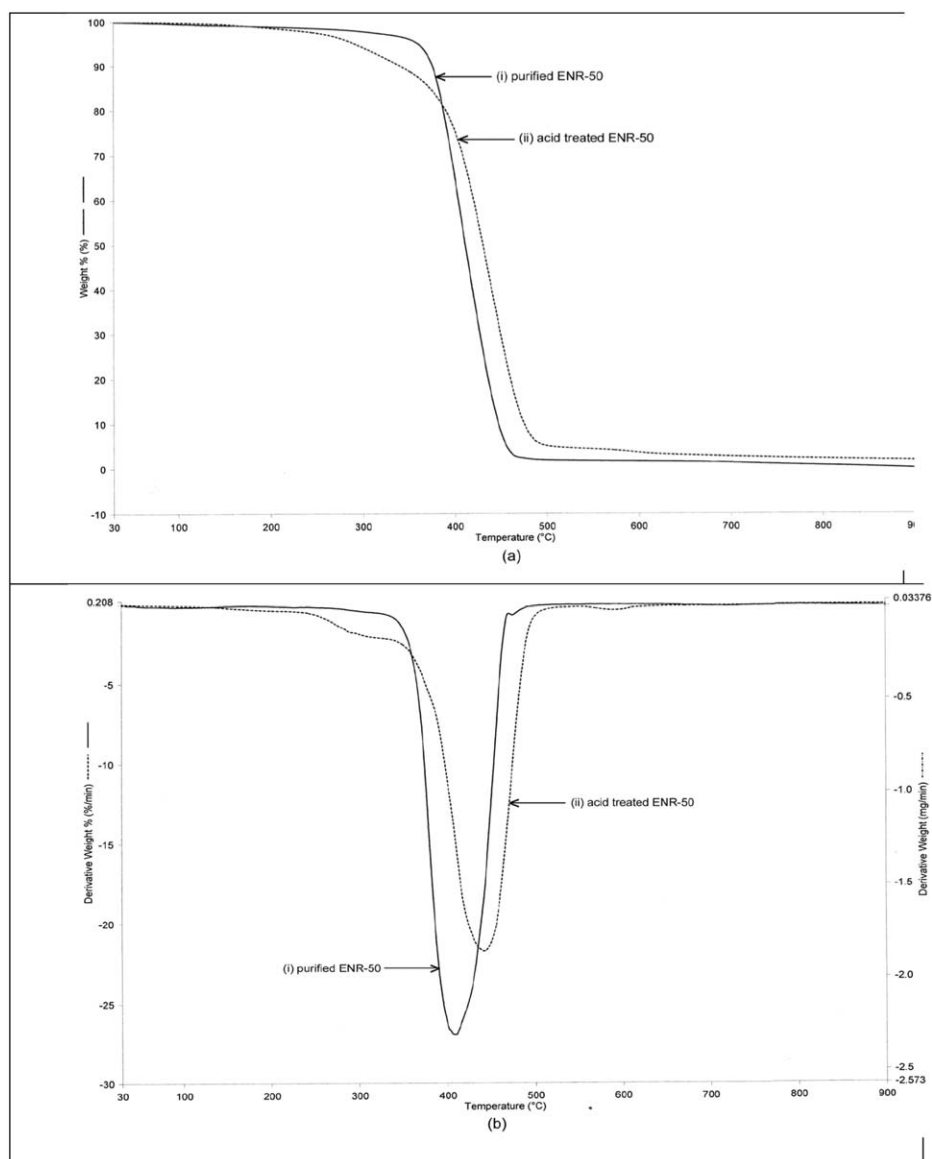**Figure 5.** FTIR spectra of (a) pure ENR-50 and (b) acid treated ENR-50.

**Figure 6.** (a) TG and (b) DTG thermograms of (i) purified ENR-50 and (ii) acid treated ENR-50.

and acetate of $E^{15}$ were shown at $\delta$ 125.1, 135.1, and 171.2 ppm, respectively. Their correlations were not influenced by the ring opening reaction.

**HMBC.** The HMBC spectra are shown in Figure 3. The results were used to scrutinize the assignment of HMQC results. The new peaks overlapped with the peaks of the ENR-50. The $^1\text{H}$–$^{13}\text{C}$ signal correlations of the middle unit are tabulated in Table I (4th column). The $^1\text{H}$–$^{13}\text{C}$ correlations mainly assign the overlapped of the epoxides ring-opened proton signals. The ring opening and acid anion attached at the ($\uparrow$) and ($\downarrow$) positions were confirmed via correlation of the methyl signal within the same unit of the triad sequences. The correlation of the methyl of acetate $E^{15}$ was to the acetate carbon of the same unit of the triad sequence. The methylene of E8, $E^9$ was shown via correlation of the same units of the triad sequence. This was similar to the methylene of $C^3$ and $C^4$. The correlation of the methine of $E^7$ and hydroxyl of $E^7$ at ($\uparrow$) position was not observed in the

spectra. This is due to the formation of strong intramolecular hydrogen bond between them, the oxygen atom of the carbonyl of acetate E15, and later intermolecular hydrogen bond with the polymer chains and the solvent.[33] A similar result was experienced by the hydroxyl of $E^6$ at the ($\downarrow$) position. The correlation of methyl of C5, quartenary carbon of C1, and methine carbon of $C^2$ was unchanged and consistent with the ENR-50.

**COSY.** The COSY of acid-treated ENR-50 is shown in Figure 4 and the related data are tabulated in Table I (5th and 6th column). COSY was conducted to evaluate the representation of the ring-opened product(s) at the ($\uparrow$) and ($\downarrow$) positions. Thus, COSY spectra showed correlations of $^1\text{H}$-NMR signals at $\delta$ 1.55, 1.68, 2.06, 2.17, 2.72, and 5.12–5.16 ppm. The signal at $\delta$ 1.55 ppm was correlated with the signals at $\delta$ 1.68, 2.17, and 2.72 ppm. The signal of $E^9$ methylene protons at $\delta$ 1.68 ppm was correlated with the methylene protons of ring-opened epoxide within the same unit of the triad sequences of E8, EE$^8$C, and
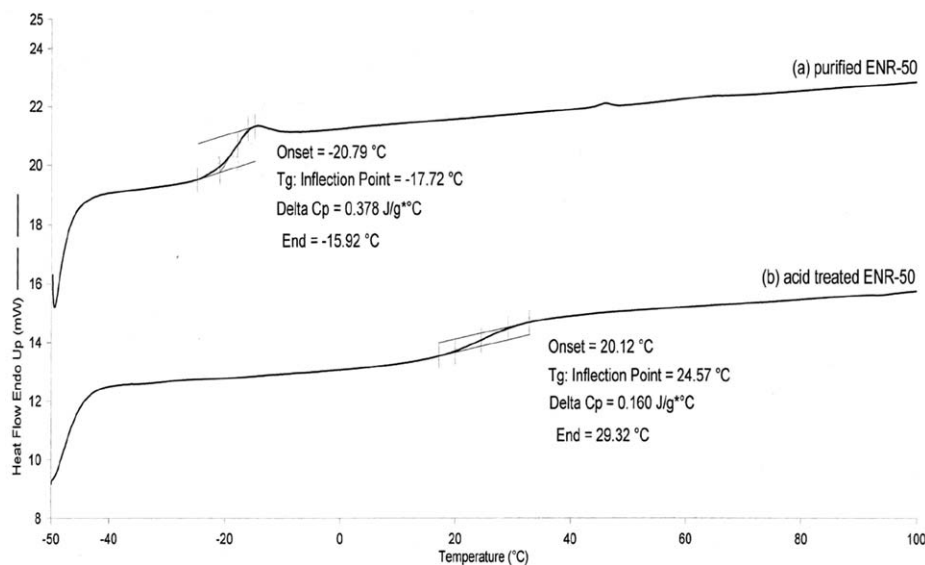
**Figure 7.** DSC thermograms of (a) purified ENR-50 and (b) acid treated ENR-50.

EE$^9$C. The methylene proton signal of C$^4$ at δ 2.17 ppm was correlated with methylene protons of the ring-opened epoxide within the same unit of the triad sequences of EE$^9$C, CE$^9$C, and CE$^8$E. The signal of methine proton at δ 2.72 ppm was correlated with the methylene protons of the ring-opened epoxide of the middle unit of the triad sequences of EE$^9$C and CE$^9$C. The signal representing the methylene protons of the ring-opened epoxide of E$^9$ and CE$^9$E at δ 1.68 ppm was correlated with the signal at δ 1.55 and 2.72 ppm. These methylene protons were correlated to the methine proton of E$^7$ of the middle unit and methylene protons of E$^8$ of the same triad. The signal at δ 2.06 ppm represented the methylene protons of CC$^3$E and all methyl protons of acetate of E$^{16}$ and was correlated with the signal at δ 2.06 and 5.12–5.16 ppm. These methylene protons were correlated to the methine proton of C$^2$ middle unit and methylene protons of C$^3$ and C$^4$ within the same triad. The signal at δ 2.17 ppm was correlated with the signal at δ 5.12–5.16 ppm within the middle unit and at δ 1.55 ppm within the same triad. The signal at δ 2.72 ppm was correlated to the methylene protons of E$^9$ ring-opened epoxide of middle unit of triad at δ 1.55 and 1.68 ppm. The signal at δ 5.12–5.16 ppm was correlated with the methylene protons of C$^4$ at δ 2.06, and 2.17 ppm.

### FTIR

Figure 5 shows FTIR spectra of pure and acid-treated ENR-50. Generally, the FTIR spectra of the ring-opened products via acid treatment showed the characteristic of ENR-50 and OH peaks. The additional acetate and ester peaks were shown for acid-treated ENR-50. In the acid-treated ENR-50 [Figure 5(a)], a broadband at 3451 cm$^{-1}$ corresponded to OH, intra- and intermolecular hydrogen bonds.[30,34] OH was attached at (↓) which later interacted with the carbonyl (C═O) of the acetate group of the vicinal carbon. This produced intramolecular hydrogen bonds in the similar polymer chain. The interaction of the OH and C═O amongst other polymer chains produced intermolecular hydrogen bonds (i.e., 3400–3200 cm$^{-1}$). The peak at 2960, 2926, 2862, 1447, 1373, and 1243 cm$^{-1}$ belonged

to C─H of ENR-50.[34,35] The peak at 3028 cm$^{-1}$ corresponded to C═C─H while, at 1656, 835 cm$^{-1}$ belonged to C═C of ENR-50.[30,34,35] The epoxide group was shifted to the lower wavenumber region at 869 cm$^{-1}$ as compared to purified ENR-50. This may be due to the intermittent presence of acetate within the polymer chains. The C═O functionality was observed as a sharp and intense peak at 1732 cm$^{-1}$ and ester peak at 1243 cm$^{-1}$ and asymmetric and symmetric vibrations of the C─O─C group of the ester were at 1143, 1067 cm$^{-1}$, respectively.[9,34,36] Comparison of the spectra of purified ENR-50 [Figure 5(a)] with the spectrum of acid treated ENR-50 [Figure 5(b)] indicates that there was a reduction in the epoxide peak intensity after the reaction. The extent of the reaction was estimated using eq. (1) and the methyl peak at 1378–1373 cm$^{-1}$ was used as the internal standard of this work.[20] Based on this semi-quantitative FTIR approach, out of the original epoxide ring, 21.04% of the ring opening reaction has occurred in acid-treated ENR-50. This supports the earlier results obtained in $^1$H-NMR at 19.56% for acid treated ENR-50.

### Thermal Analysis

**TG/DTG Analyses.** TG and DTG thermograms of purified ENR-50 and acid-treated ENR-50 are shown in Figure 6. Generally, TG and DTG thermograms of ENR-50 showed a single step degradation range at 331–493 °C with maximum temperature degradation ($T_{max}$) at 408 °C.[37,38] Meanwhile, acid-treated ENR-50 showed three steps of degradations over a temperature range studied. The temperature range for acid-treated ENR-50 was at 235–338, 338–523, 523–627 °C with $T_{max}$ at 292, 442, and 591 °C respectively. The first step of acid-treated ENR-50 represented the removal of water molecules that originated from the ring open structure of ENR-50, i.e., hydroxyl groups. Theoretically, the amount of hydroxyl present in the acid-treated ENR-50 was 10.58%wt and the experimental amount was 7.5%wt. This reveals that part of the hydroxyl groups of the acid-treated ENR-50 degraded during the second degradation curve. The second step was the pyrolysis of the polymer chains that

included polymer breakdown of the main and side chains such as the acetate groups.[39–42] These degradations occurred at wider temperature range than the purified ENR-50. This was due to the presence of polymer chains mixture, i.e., ring-opened and intact epoxide of ENR-50. The third step represents the rearrangement of carbonaceous materials from the polymer chain degradation as an aromatic carbon which was later presented as char residue.[39–43]

**DSC.** DSC thermograms of purified ENR-50 and acid-treated ENR-50 are shown in Figure 7. The purified ENR-50 and acid-treated ENR-50 showed a single glass transition ($T_g$) at $-17.7$ and 24.6 °C, respectively. The acid treated ENR-50 has higher ring-opened epoxide than the pure ENR-50. Thus, the $T_g$ increased with the increase in the epoxide ring opening. Typically, a single $T_g$ in the polymer indicated a good miscibility amongst the ring-opened and intact epoxide within the ENR-50.[44,45] This is due to similar polymer backbone that derived the ring-opened product. The attached acetate group to the ring-opened epoxide produced a rigid polymer at high temperature. The acetate group was able to restrict the motion of the polymer chains via filling more void and holes amongst the polymer chains. Furthermore, the presence of hydrogen bonding in the acid-treated ENR-50 contributed to this phenomenon.[46]

## CONCLUSIONS

The epoxide ring opening reaction of ENR-50 with acetic acid suggested the fixation of acetate group to the epoxide carbon via ester linkage and formation of hydroxyl groups in the polymer chains. The reaction in acid-treated ENR-50 formed a mixture of ring-opened products at the ($\uparrow$) and ($\downarrow$) positions of the epoxide carbon and was successfully assigned using 2D NMR; HMQC, HMBC, COSY techniques. ^{1}H-NMR revealed that 19.56% of the ring opening reaction has occurred in the acid-treated ENR-50. 13C-NMR proved the location of acetate group in the polymer chains. FTIR analysis showed the additional acetate and ester peaks for acid-treated ENR-50. Both experienced inter- and intramolecular hydrogen bonding in the polymer chains. The types of the alkyl group attached to the ring-opened epoxide influenced the thermal stability of the treated ENR-50. This agreement with the DSC profiles was where acetate group was able to restrict more motions of the polymer chains than the isopropyl group.

## ACKNOWLEDGMENTS

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