

CHAPTER 4

REACTIONS BETWEEN EPOXIDIZED NATURAL RUBBER AND PALM OIL-BASED MEDIUM-CHAIN-LENGTH POLYHYDROXYALKANOATES

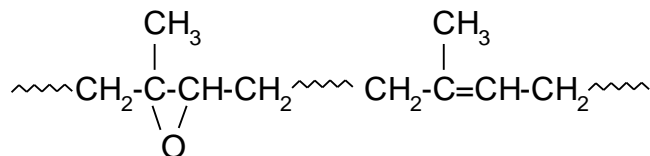
Medium-chain-length polyhydroxyalkanoates (mcl-PHAs) are bacterial polyesters which are produced in nature by a wide variety of Gram-negative bacteria, mainly the *Pseudomonas*. They have attracted research and commercial interests because of their chirality, biodegradability and elastomeric properties and have the potential for applications as environmentally biodegradable polymers and functional biomaterials for medical and industrial applications^{196,197}. Of the microorganisms capable of producing mcl-PHAs *Pseudomonas oleovorans* has been investigated most extensively¹⁹⁸⁻²⁰³. *P. putida* has also been reported for the production of mcl-PHAs²⁰⁴. Recent results in our laboratory have demonstrated that *P. putida* can produce mcl-PHAs from palm oil derivatives²⁰⁵.

Recently, we have investigated the incorporation of low levels of palm oil based mcl-PHA into ENR rubber compounds which were cured at 170 °C for 3 to 40 minutes^{206,207}. At 2 to 10 parts of mcl-PHA per hundred parts of ENR, the mcl-PHA could improve the vulcanization efficiency of ENR compound and significantly suppress the reversion of the vulcanized rubber.

Hence, the aim of the present work is to investigate the reaction of similar level of the palm oil-based mcl-PHA with ENR at conditions comparable to that of the rubber vulcanization, i.e. at 170 °C for 30 minutes.

4.1 Thermal degradation of ENR

ENR 50 contains equimolar amounts of epoxy and cis-1,4-polyisoprene units, as shown below, randomly distributed in the rubber molecules.



Since the formula weights of the rubber epoxy and isoprene units are 84 and 68 respectively, 152 g of ENR 50 would contain 1 mol of the epoxy group, hence the initial epoxy content of the ENR is 1 mol/152 g or 6.58 mmol g⁻¹.

Figure 4.1 shows the ¹H-NMR spectra of NR and ENR 50. As shown, these spectra are identical except the peaks (a) and (d) that appeared at 1.3 ppm and 2.7 ppm which are due to the methyl and methine protons on the epoxy ring. Three peaks (b), (c), (e) appear at 1.7 ppm, 2.0 ppm and 5.1 ppm represent the methyl, methylene and vinylic protons on the isoprene unit in both NR and ENR; while, the peak at 7.2 ppm is attributed to the CHCl₃ in the CDCl₃ solvent.

It is worthy to note that the presence of carbon-carbon double bonds renders rubbers susceptible to attack by oxygen, ozone and also thermal degradation²⁰⁸; whilst the epoxy groups can be ring-opened at acidic conditions and elevated temperature²⁷. In this study, thermal degradation of ENR upon heating at elevated temperature was investigated. Any thermal degradation of ENR would lead to a decrease in molecular weight, which could be seen from the intrinsic viscosity measurement.

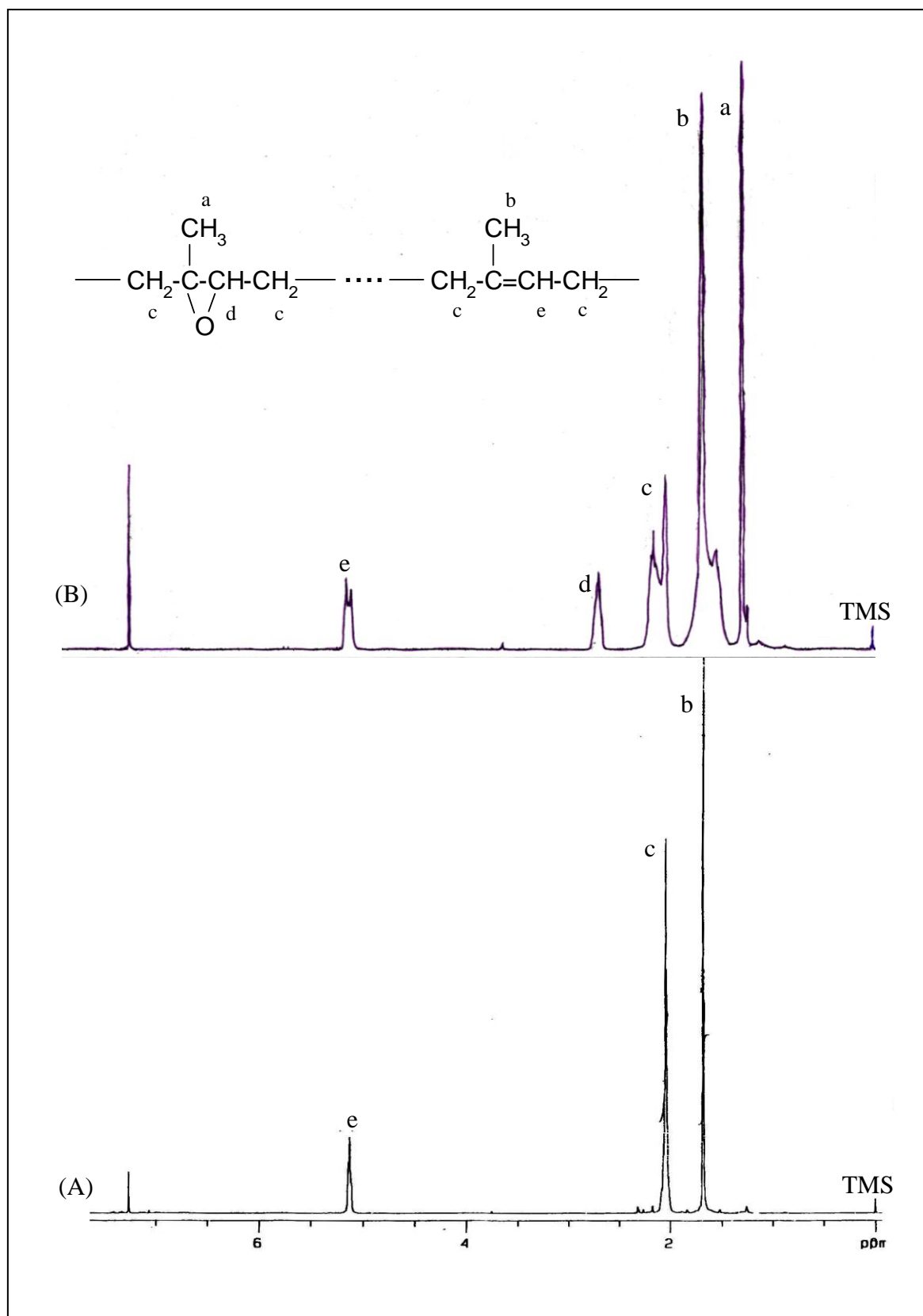


Figure 4.1 The ^1H -NMR spectra of NR (A) and ENR 50 (B).

4.1.1 Intrinsic viscosity measurement

In this method, the viscosity of a dilute polymer solution is measured as the relative viscosity, η_r which is defined as the ratio of the viscosity of a polymer solution, η to the viscosity of the solvent, η_0 . This value was used to compute the molecular weight of the degraded rubber. Other solution viscosity definitions used in this method are tabulated in the following Table 4.1.

Table 4.1
Solution viscosity definitions

Viscosity	Relative	Specific	Reduced	Inherent
Definition	$\eta_r = \frac{\eta}{\eta_0}$	$\eta_{sp} = \eta_r - 1$	$\eta_{red} = \frac{\eta_{sp}}{c}$	$\eta_{inh} = \frac{\ln \eta_r}{c}$

where, the specific viscosity is the fractional increase in viscosity from a series of dilute solutions; reduced viscosity is to account the concentration effect; inherent viscosity is use as an approximate indication of molecular weight since viscosities are determined at a single concentration.

Since the viscosity is concentration dependent, any changes in the solution viscosity (both reduced and inherent viscosities) with higher concentration could be expressed using the Huggins²⁰⁹ and Kraemer²¹⁰ equations as shown in equation [4.1] and [4.2] respectively.

$$\frac{\eta_{sp}}{c} = [\eta] + k_1[\eta]^2 c \quad [4.1]$$

$$\frac{\ln \eta_r}{c} = [\eta] - k_1'[\eta]^2 c \quad [4.2]$$

where, k_1 and k_1' are the Huggins and Kraemer constants respectively.

The Huggins constant, k_1 is related to the molecular structure and the degree of association of the polymer chains in the solvent. Hence, the two equations [4.1] and [4.2] would converge to intercept at the y-axis to the same intrinsic viscosity $[\eta]$, as follows,

$$k_1 + k'_1 = \frac{1}{2} \quad [4.3]$$

By plotting graphs of η_{sp}/c and $\ln \eta_r/c$ vs. c , the values of intrinsic viscosity $[\eta]$ could be obtained when both the linear experimental plots were extrapolated to zero concentration or to infinite dilution condition.

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} = \lim_{c \rightarrow 0} \frac{\ln \eta_r}{c} \quad [4.4]$$

The relation between intrinsic viscosity and molecular weight of a polymer is then given by the Mark-Houwink equation,

$$[\eta] = K(M_v)^a \quad [4.5]$$

where $[\eta]$ is the intrinsic viscosity, M_v is the viscosity average molecular weight, K and a are constants for a specific polymer and are dependent on the temperature and solvent.

In this study, the changes in viscosity average molecular weight, M_v during thermal degradation of ENR were determined. ENR solution was first prepared at concentration of about 1 g/100 mL of toluene and the viscosities were measured using an Ubbelohde type of viscometer. The flow time of a certain volume of solution through a capillary of fixed length of the viscometer was measured. The concentration of the solution was then reduced four times by adding 2-3 mL of toluene each time directly into the viscometer. Since the viscosity was temperature-dependence, all measurements were carried out in a water bath at

a constant temperature of 30 °C. The measurements of solvent flow time for toluene and solution flow time for ENR solutions are tabulated in Table 4.2 and Table 4.3.

Table 4.2

Solvent flow time for toluene

Solvent flow time, t_0 / s					
1	2	3	4	5	Average
124.0	123.3	124.0	123.7	124.0	123.8

Table 4.3

Solution flow time for ENR before and after heated at 170°C

Heating at 170°C	Concentration/ g dL ⁻¹	Solution flow time, t_s / s					
		1	2	3	4	5	Average
Before	0.9984	521.8	522.0	521.7	522.0	521.7	521.8
	0.8558	443.4	444.1	441.0	440.5	442.7	442.3
	0.7488	387.4	388.5	389.9	386.1	386.0	387.6
	0.6656	348.1	347.0	347.5	347.5	347.6	347.5
	0.5990	318.4	318.0	318.2	318.3	318.1	318.2
After 30 minutes	1.0040	467.7	459.9	460.3	459.8	459.5	461.4
	0.8606	394.9	393.9	394.0	393.4	393.8	394.0
	0.7530	349.5	348.5	349.8	349.0	348.2	349.0
	0.6693	316.6	316.5	315.6	316.3	316.1	316.2
	0.6024	292.0	291.7	292.0	291.7	291.7	291.8

The average values of both solvent and solution flow times were subsequently used to calculate the relative, specific, reduced and inherent viscosities, as shown in Table 4.4.

Table 4.4

The relative, specific, reduced and inherent viscosities* of ENR

Heating at 170°C	Concentration, c/ g dL ⁻¹	η_r	η_{sp}	η_{red}	η_{inh}
Before	0.9984	4.2149	3.2149	3.2200	1.4409
	0.8558	3.5727	2.5727	3.0063	1.4879
	0.7488	3.1309	2.1309	2.8457	1.5242
	0.6656	2.8069	1.8069	2.7148	1.5506
	0.5990	2.5703	1.5703	2.6213	1.5759
After 30 minutes	1.0040	3.7270	2.7270	2.7161	1.3104
	0.8606	3.1826	2.1826	2.5362	1.3452
	0.7530	2.8191	1.8191	2.4158	1.3764
	0.6693	2.5541	1.5541	2.3219	1.4010
	0.6024	2.3570	1.3570	2.2527	1.4233

* where, η_r was the ratio of the respective flow time of the solution (t_s) and solvent (t_0),

which was $\eta_r = \frac{t_s}{t_0}$. The η_{sp} , η_{red} and η_{inh} were calculated with reference to the formulae

as listed in Table 4.1.

The values of reduced (η_{sp}/c) and inherent ($\ln \eta_r/c$) viscosities from Table 4.4 are used to plot against concentration (c) for ENR before and after heated at specified reaction time. The plots are illustrated in Figure 4.2 and Figure 4.3, respectively.

From Figure 4.2 and Figure 4.3, the intercepts of the straight lines give the values of intrinsic viscosity $[\eta]$ for ENR. From the figure, the values of $[\eta]$ decreases slightly from 1.77 dL g^{-1} to 1.58 dL g^{-1} after heating at elevated temperature and this was an indication of thermal degradation in ENR.

As shown in Figure 4.2, from the plot of the reduced viscosity (η_{sp}/c) vs. concentration and with reference to equation [4.1], the Huggins constant k_1 can be evaluated from the slope of the plot, which is $(1.51) / (1.72)^2$, i.e. 0.51. From the plot of inherent viscosity ($\ln \eta_r/c$) vs. concentration and with reference to equation [4.2], the Kraemer constant k_1' can be evaluated from the slope of the plot, which is $(0.34) / (1.78)^2$, i.e. 0.11. When both k_1 and k_1' values were added, the total value was $0.51 + 0.11$, i.e. 0.62, which was closed to theoretical value of about 0.5, as estimated in the equation [4.3].

Using the same method, the k_1 was calculated from Figure 4.3 and the value was $(1.15) / (1.55)^2$, i.e. 0.48; while the Kraemer constant k_1' was $(0.28) / (1.59)^2$, i.e. 0.11. The total value of k_1 and k_1' was $0.48 + 0.11$, i.e. 0.59 and this was closed to the theoretical value in equation [4.3] of about 0.5.

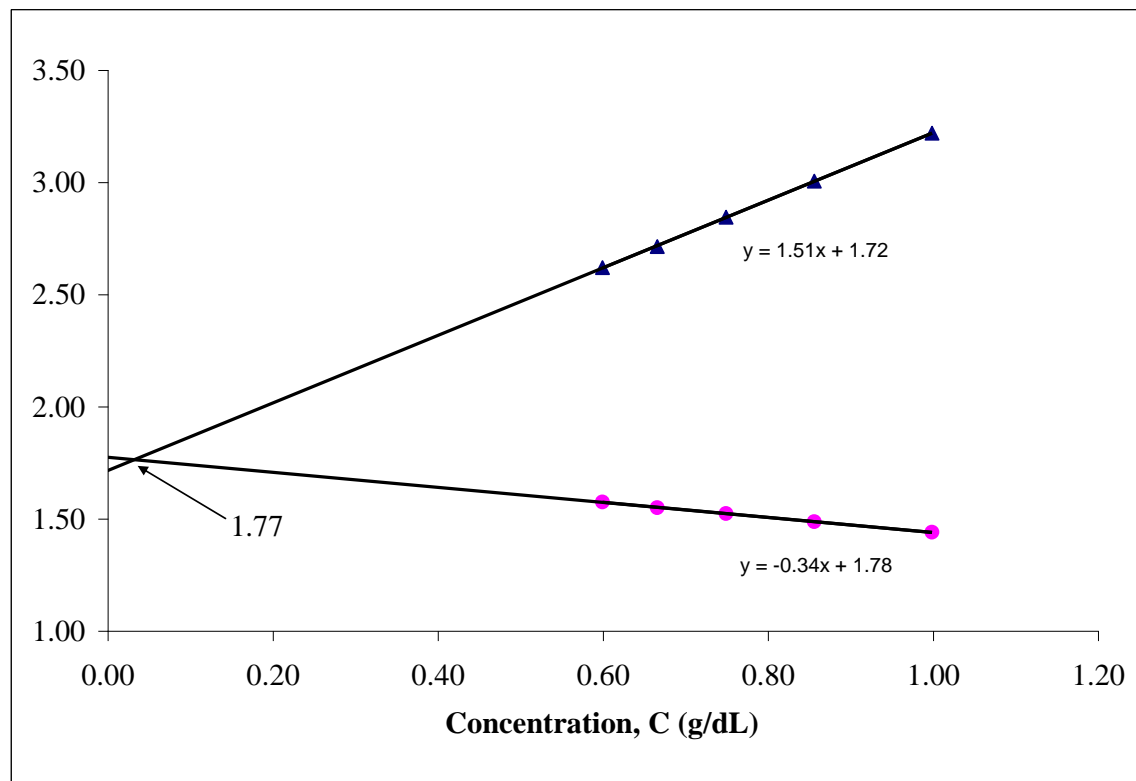


Figure 4.2: The reduced (η_{sp}/c) and inherent ($\ln \eta_r/c$) viscosities vs. concentration (c) for ENR before heated at 170°C for

30 minutes: ▲ values of η_{sp}/c ; ● values of $\ln \eta_r/c$.

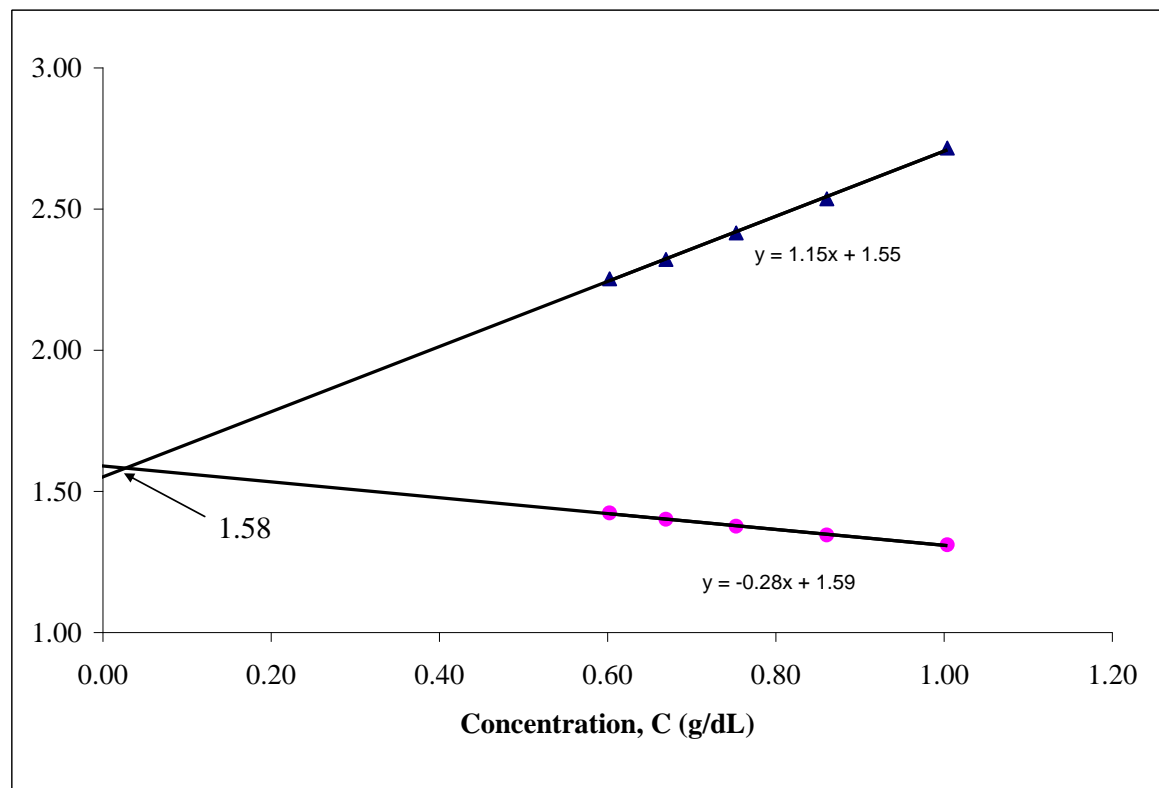


Figure 4.3: The reduced (η_{sp}/c) and inherent ($\ln \eta_r/c$) viscosities vs. concentration (c) for ENR after heated at 170°C for 30

minutes: ▲ values of η_{sp}/c ; ● values of $\ln \eta_r/c$.

The viscosity average molecular weight, M_v of ENR could be approximated with reference to equation [4.5] by assuming the constants for ENR is approximately the same as that of natural rubber in toluene at 30°C. Values of $K = 5.02 \times 10^{-4} \text{ dL g}^{-1}$ and $a = 0.667$, as reported by Carter *et al.*²¹¹. The work of Bloomfield²¹² has shown that the molecular weight calculated from these values gives good correlation with the \overline{M}_n values from the osmotic data for fractionated samples of fresh rubber. The calculated M_v values are tabulated in Table 4.5.

Table 4.5

Property changes in ENR before and after heated at 170°C

Property	Heating at 170°C	
	Before	After 30 minutes
Intrinsic viscosity*/ dL g ⁻¹	1.77	1.58
Viscosity average molecular weight, M_v	2.1×10^5	1.8×10^5

* Intrinsic viscosity was determined in toluene solution at 30 °C.

As shown in Table 4.5, the slight decrease in M_v provides evidence that ENR can undergo thermal degradation, which may be due to main chain scission at the $-\text{C}=\text{C}-$ bonds.

On the other hand, Poh *et al.* have suggested that ENR could undergo slow epoxy ring opening by homolytic bond scission after prolonged heating at about 155°C^{213,214} to generate free radicals with structures as follows.

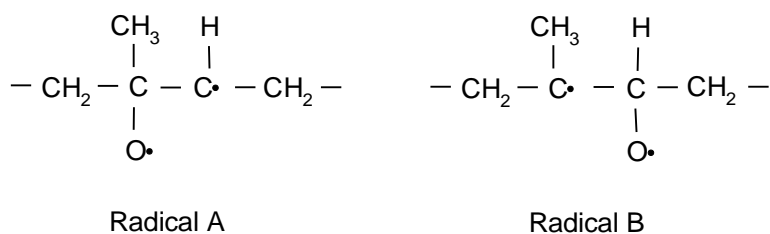


Figure 4.4 shows the overlaid $^1\text{H-NMR}$ spectra of ENR before and after heating at 170°C for 30 minutes. From this figure, both NMR spectra have very similar appearances, except spectrum (B) shows two very small peaks that occur at 3.6 ppm and 3.8 ppm. These peaks were due to the ring-opening of some epoxy groups presumably caused by the attack of trace moisture on the epoxy group. The percentage of epoxy groups in ENR sample could be calculated from the following equation.

$$\% \text{ epoxy group} = \frac{I_{2.7\text{ppm}}}{I_{2.7\text{ppm}} + I_{5.1\text{ppm}}} \times 100 \quad [4.6]$$

where, $I_{2.7\text{ppm}}$ and $I_{5.1\text{ppm}}$ are the integrations of the peaks occur at 2.7 ppm and 5.1 ppm, respectively.

With reference to equation [4.6], the calculated epoxy contents of ENR are listed in Table 4.6.

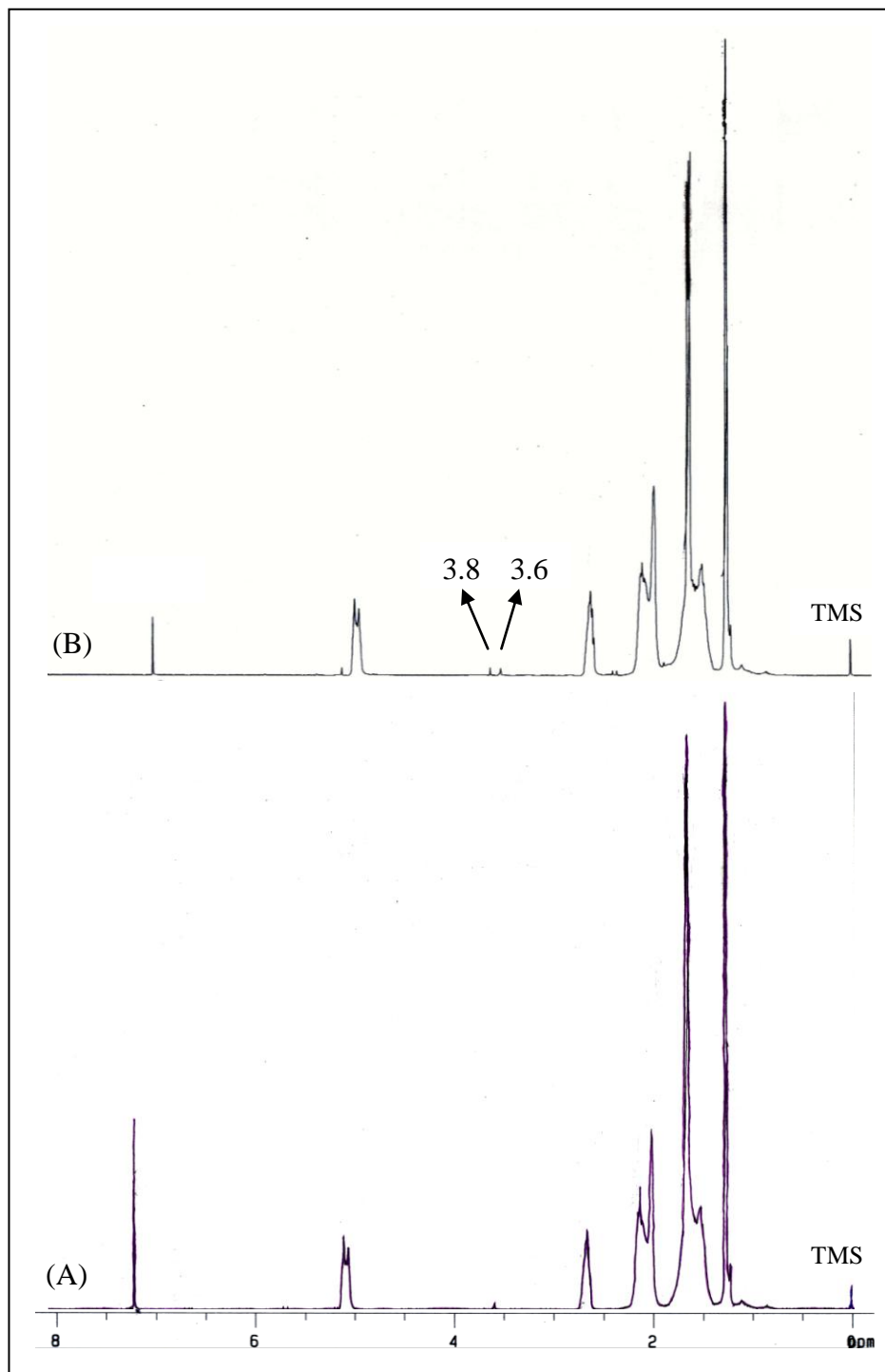


Figure 4.4 The overlaid ¹H-NMR spectra of ENR at ambient temperature (A) and heated at 170°C for 30 minutes (B).

Table 4.6**Epoxy contents of ENR before and after heating at 170°C**

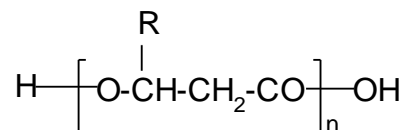
Heating at 170°C	Integration		% Epoxy group in ENR
	I _{2.7ppm}	I _{5.1ppm}	
Before	1.06	1.00	51.46
After 30 minutes	1.05	1.00	51.22

From Table 4.6, there is no significant change in the percentage of epoxy groups in ENR 50 heated at 170 °C for a short interval of 30 minutes. This finding is not in good agreement with the mechanism proposed by Poh *et al.* since such mechanism would lead to a significant decrease in epoxy content.

Further examination on the amount of swelling of ENR in toluene was carried out in the dark at ambient temperature for 20 hours. The absence of gel fraction indicated that there was no noticeable crosslinking reaction in ENR which might be due to some re-combinations of radicals from epoxy ring opening. In addition, the re-combinations of some radicals as in the mechanism proposed by Poh *et al.* were expected to increase the molecular weight. Apparently, this mechanism appears to be in conflict with the decrease in molecular weight as reported in Table 4.5. Based on the result, it seems apparent that the slight decrease in M_v was more in line with the thermal degradation of ENR through the main chain scission at the $-C=C-$ bonds.

4.2 Thermal degradation of mcl-PHA

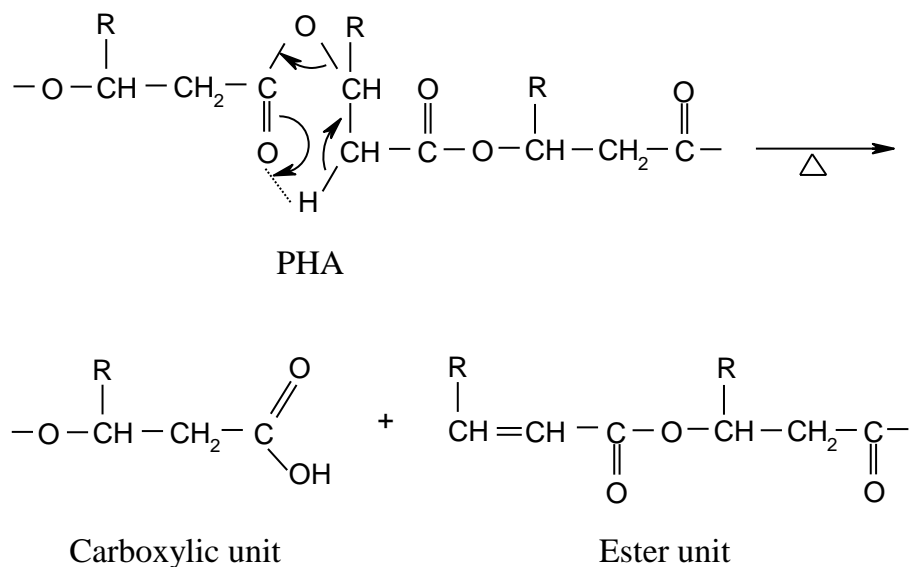
The mcl-PHA used in this study was a biopolymer produced by *P. putida* using oleic acid (C_{18:1}) as the carbon substrate. It can be represented by the following structure, where each molecule of the mcl-PHA has one hydroxyl and one carboxylic terminal group.



where R stands for an aliphatic group with 3,5,7,9, or 11 carbons.

The mcl-PHA is thermally unstable at temperatures above its melting point and tends to degrade to shorter chains^{215,216}. Doi revealed that the molecular weights of most PHA are not appreciably reduced for 20 minutes²¹⁷. In a previous paper, Grassie *et al.* found that the thermal degradation of PHA in the temperature range of 170-200°C was a random chain scission process at the ester linkages²¹⁸. This process occurred by random chain scission at ester groups^{218,219} which leads to the formation of shorter chains with carboxylic end groups, as presented in Figure 4.5.

In this study, thermal degradation reaction of mcl-PHA was investigated at 170°C for 30 minutes. The number average molecular weight of mcl-PHA was determined from the end group analysis.



where, R = Aliphatic group

Figure 4.5 Random chain scission at ester groups in PHA.

4.2.1 End group analysis

The mcl-PHA is suitable for this end group analysis as its free carboxylic groups appear at the chain end of this linear polymer and the carboxylic terminal can be titrated directly when dissolved in selected non-aqueous solvents, such as a solvent mixture of ethanol and toluene in ratio 1:2. Titration results for the standardization of KOH solution and the acid number of mcl-PHA solution are tabulated in Table 4.7 and Table 4.8, respectively.

Table 4.7**Standardization of KOH solution**

	First titration	Second titration
Weight of potassium acid phthalate/ g	0.5151	0.5053
KOH solution required/ mL	51.30	50.20
Molarity*	0.0492	0.0493
Average Molarity/ M	0.0493	

* where, Molarity was calculated using the equation [2.4] as mentioned in Section 2.8.1, Chapter 2.

Table 4.8**The acid number titration results of mcl-PHA with standardized KOH solution**

	Heating at 170°C			
	Before		After 30 minutes	
	First titration	Second titration	First titration	Second titration
Weight of mcl-PHA/ g	1.5165	1.5199	1.4978	1.4963
KOH solution required for titration of the sample/ mL	12.60	12.65	25.45	25.45
KOH solution required for titration of the blank/ mL	0.20	0.20	0.20	0.20
Acid number/ mg KOH g ⁻¹	22.61	22.66	46.62	46.67
Average acid number/ mg KOH g ⁻¹	22.64		46.64	

* where, acid number was calculated using the equation [2.5] as mentioned in Section 2.8.2, Chapter 2.

As shown in Table 4.8, the amount of $-\text{COOH}$ group has doubled after heating at 170°C for 30 minutes. This result indicated that thermal degradation in mcl-PHA followed the mechanism of random chain scission at ester groups as presented in Figure 4.5, where this mechanism leads to the formation of shorter chains with carboxylic end groups.

From Table 4.8, the acid number of mcl-PHA before thermal degradation is $22.6 \text{ mg KOH g}^{-1}$, indicating that the initial mcl-PHA contains $(22.6 \text{ mg KOH g}^{-1}) / 56100$, i.e. $4.03 \times 10^{-4} \text{ mol g}^{-1}$ of $-\text{COOH}$ group. Since one mcl-PHA chain has one carboxylic group, the number average molecular weight, M_n of the mcl-PHA is $1/(4.03 \times 10^{-4} \text{ mol g}^{-1})$, which is $2.48 \times 10^3 \text{ g mol}^{-1}$.

After it was heated at 170°C for 30 minutes, the acid number increased, thus giving $(46.6 \text{ mg KOH g}^{-1}) / 56100$, i.e. $8.31 \times 10^{-4} \text{ mol g}^{-1}$ of $-\text{COOH}$ group in mcl-PHA with M_n of $1.20 \times 10^3 \text{ g mol}^{-1}$. Results of calculation are then summarized in Table 4.9.

Results in Table 4.9 shows that the M_n of mcl-PHA is reduced by half with an increase in the amount of $-\text{COOH}$ group, which has doubled after heating at 170°C for 30 minutes. It was found that the solubility of the mcl-PHA in polar solvent such as ethanol and methanol, has greatly improved in line with the reduction of molecular weight.

Since lower molecular weight chains would have more terminal groups per unit volume than long chains, the thermal degraded polymer was expected to have a higher free volume and lower T_g . However, a slight increase in T_g , from 203.4 K to 206.1 K was observed. This could be attributed to an increase in the amount of carboxylic groups in the bulk, where the presence of these bulky pendant groups would provide steric hindrance to bond rotation in the bulk and thus raise the T_g of the polymer. There might also be more hydrogen bonding due to higher amount of polar $-\text{COOH}$ groups.

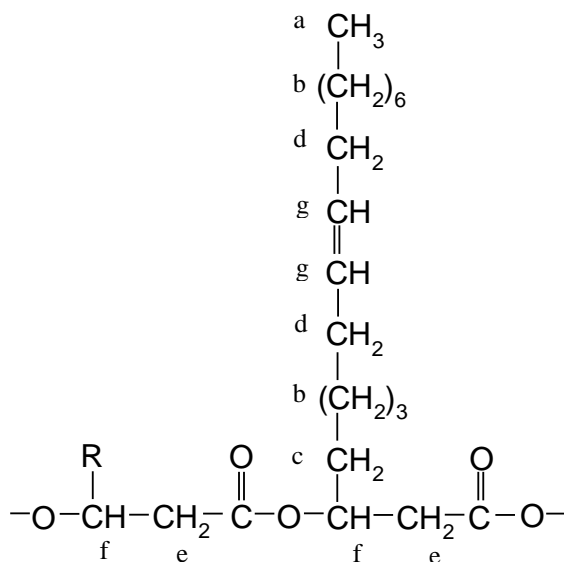
Table 4.9

Property changes in mcl-PHA before and after heated at 170°C

Property	Heating at 170°C	
	Before	After 30 minutes
Acid number/ mg KOH g ⁻¹	22.6	46.6
-COOH terminal concentration/ mol g ⁻¹	4.03 x 10 ⁻⁴	8.31 x 10 ⁻⁴
Number average molecular weight/ M _n	2.48 x 10 ³	1.20 x 10 ³
Glass transition temperature/ K	203.4	206.1

4.2.2 ¹H-NMR spectroscopy

Figure 4.6 shows the actual molecular structure of the mcl-PHA as could be determined from the NMR measurement shown in Figure 4.7.



where, R = Aliphatic group with 3,5,7,9,11 carbons

Figure 4.6 Molecular structure of mcl-PHA as could be determined from ¹H-NMR spectrum

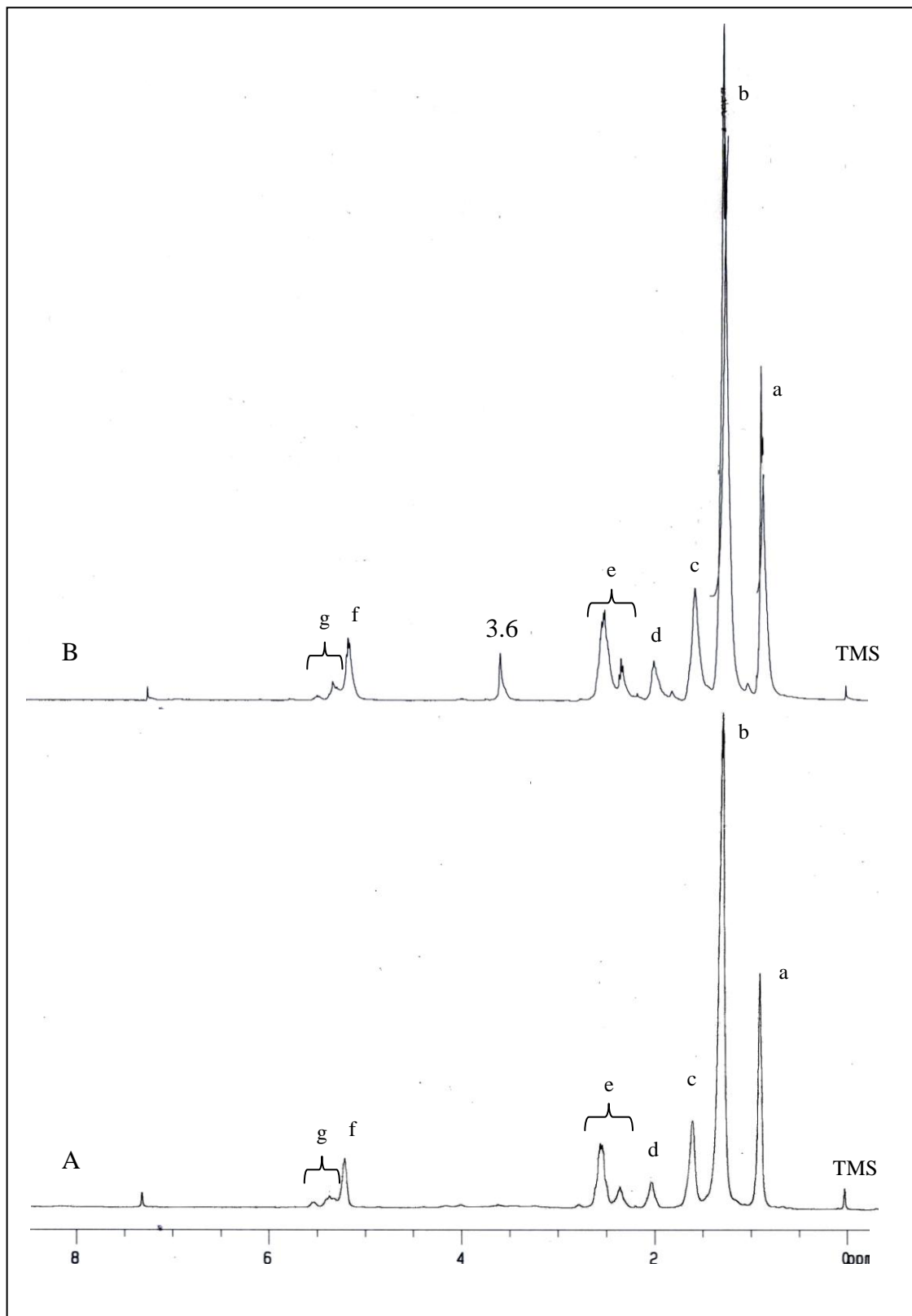
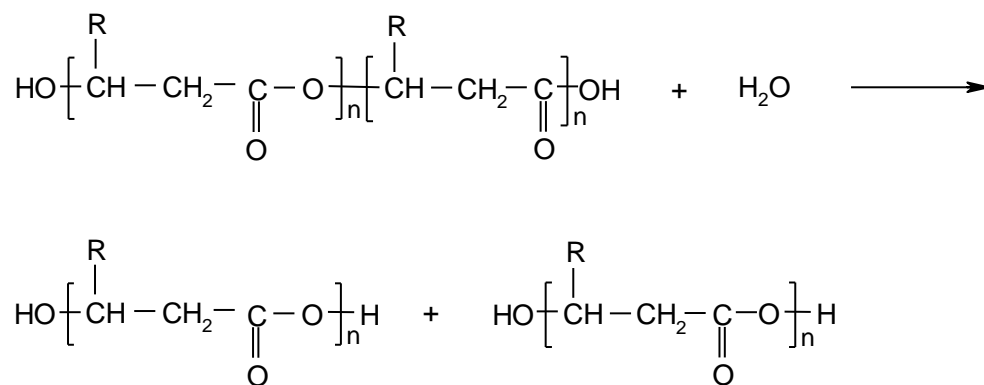


Figure 4.7 $^1\text{H-NMR}$ spectrum of mcl-PHA derived from oleic acid: at ambient temperature (A) and heated at 170°C for 30 minutes (B).

From Figure 4.7, the peak (a) at 0.9 ppm is due to the methyl protons at the side chain terminal. The strong resonances (b) at 1.3 ppm and (c) at 1.6 ppm are due to the methylene protons; while, the weak resonance (d) at 2.0 ppm is assigned to the methylene protons adjacent to the vinyl group. The peak (e) of methylene protons adjacent to ester group has a lower field shift to around 2.5 ppm. The methine protons adjacent to ester group are detected at peak (f) of 5.2 ppm. Peaks (g) around 5.3 ppm and 5.5 ppm represent the vinylic proton in the mcl-PHA. The peak at 7.2 ppm is due to the CHCl_3 in the CDCl_3 solvent.

As shown in Figure 4.7, both spectra (A) and (B) have very similar appearances, except spectrum (B) shows one distinct peak at 3.6 ppm. This peak indicates that hydrolysis of polymer chain occurred during thermal degradation of mcl-PHA, which led to the formation of shorter chains with hydroxyl end groups, as shown in the following Figure 4.8. Therefore, this peak is assigned to the tertiary proton of the carbon adjacent to the hydroxyl group in the shorter chain structure.



where, R = Aliphatic group

Figure 4.8 Hydrolysis in mcl-PHA.

4.3 Reactions of ENR and mcl-PHA

The reactions of ENR and mcl-PHA were studied in a blend containing 10 parts of mcl-PHA per hundred parts of ENR, which was coded as P₁₀. This P₁₀ was prepared by mixing 1 mL of mcl-PHA solution (41 % w/v in toluene), containing 0.41 g mcl-PHA, with 35 mL of ENR solution (11 % w/v in toluene), containing 3.85 g of ENR. In the initial mixture, the 0.41 g of mcl-PHA contain $0.41 \text{ g} \times 4.03 \times 10^{-4} \text{ mol g}^{-1}$ of –COOH group (i.e. $1.65 \times 10^{-4} \text{ mol}$); and 3.85 g of ENR 50 would then contain $3.85 \text{ g} \times 6.58 \times 10^{-3} \text{ mol g}^{-1}$ of epoxy group (i.e. $2.53 \times 10^{-2} \text{ mol}$). The initial amount of –COOH group in P₁₀ was less than 1 % of the epoxy group. After the specified reaction time, the reacted ENR was precipitated with methanol and the sample was analyzed by FTIR and ¹H-NMR.

4.3.1 FTIR spectroscopy

Fourier Transform infrared spectroscopy (FTIR) was used to characterise the structure of polymers within the mid-infrared region of 4000 cm^{-1} to 600 cm^{-1} . Sample was dissolved in chloroform and thin film was cast from the solution for the FTIR analyses. The moieties in the polymer would then absorb and emit radiation at frequencies which were characteristic of their chemical structure. Skeletal bond transitions due to chemical modification could also be detected in the infrared spectrum.

The FTIR spectra of ENR and mcl-PHA are shown in Figure 4.9 and Figure 4.10 respectively. The assignments of peaks are presented in Table 4.10 for ENR and Table 4.11 for mcl-PHA. In order to compare the changes that occurred in P₁₀, Figure 4.11 shows the overlaid FTIR spectra of ENR, mcl-PHA and P₁₀.

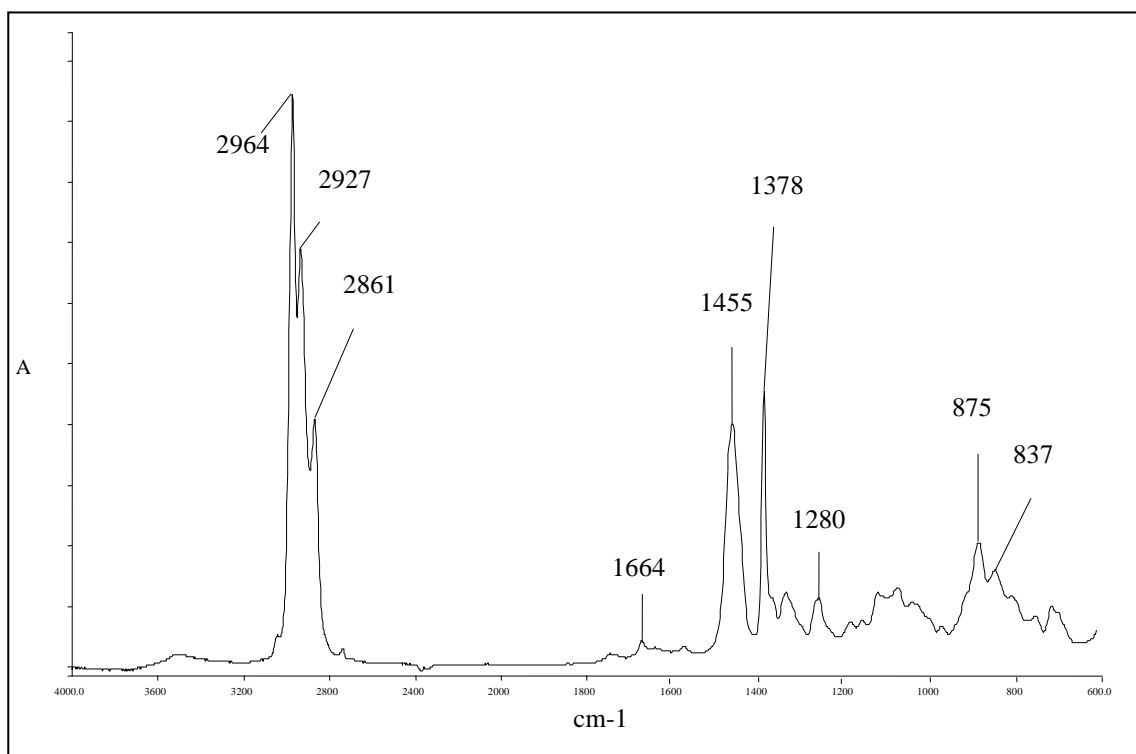


Figure 4.9: FTIR spectrum of ENR

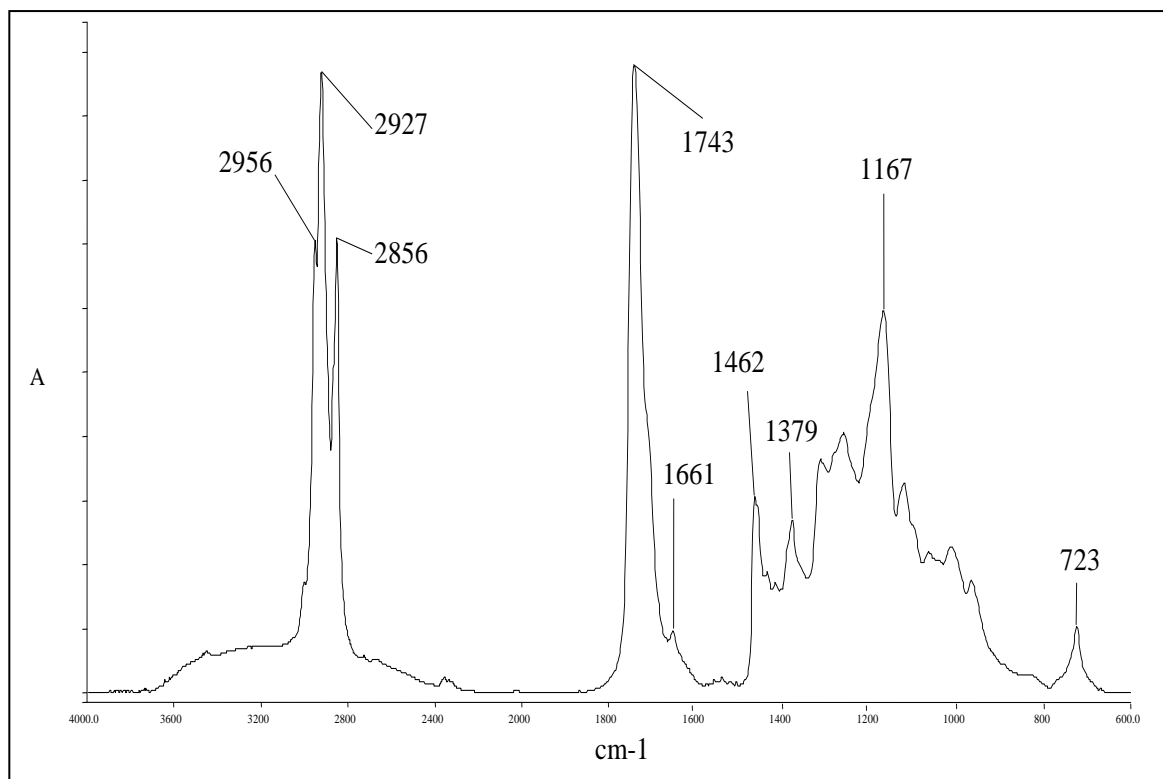


Figure 4.10: FTIR spectrum of mcl-PHA

Table 4.10**Major absorption peaks of ENR**

Wavenumber/ cm^{-1}	Bonding
837	C-H bending of C=C
875	Symmetric epoxy ring deformation
1280	Epoxy ring stretching (breathing mode)
1378	C-H bending of $-\text{CH}_3$
1455	C-H bending of $-\text{CH}_2$
1664	C=C stretching
2861	C-H stretching of $-\text{CH}_2$
2927, 2964	C-H stretching of $-\text{CH}_3$

Table 4.11**Major absorption peaks of mcl-PHA**

Wavenumber/ cm^{-1}	Bonding
723	C-H rocking of $-\text{CH}_2$
1167	C-O stretching of $-\text{COOH}$ overlapped with C-O stretching of ester
1379	C-H bending of $-\text{CH}_3$
1462	C-H bending of $-\text{CH}_2$
1661	C=C stretching
1743	C=O stretching of $-\text{COOH}$ overlapped with C=O stretching of ester
2856	C-H stretching of $-\text{CH}_2$
2927, 2956	C-H stretching of $-\text{CH}_3$

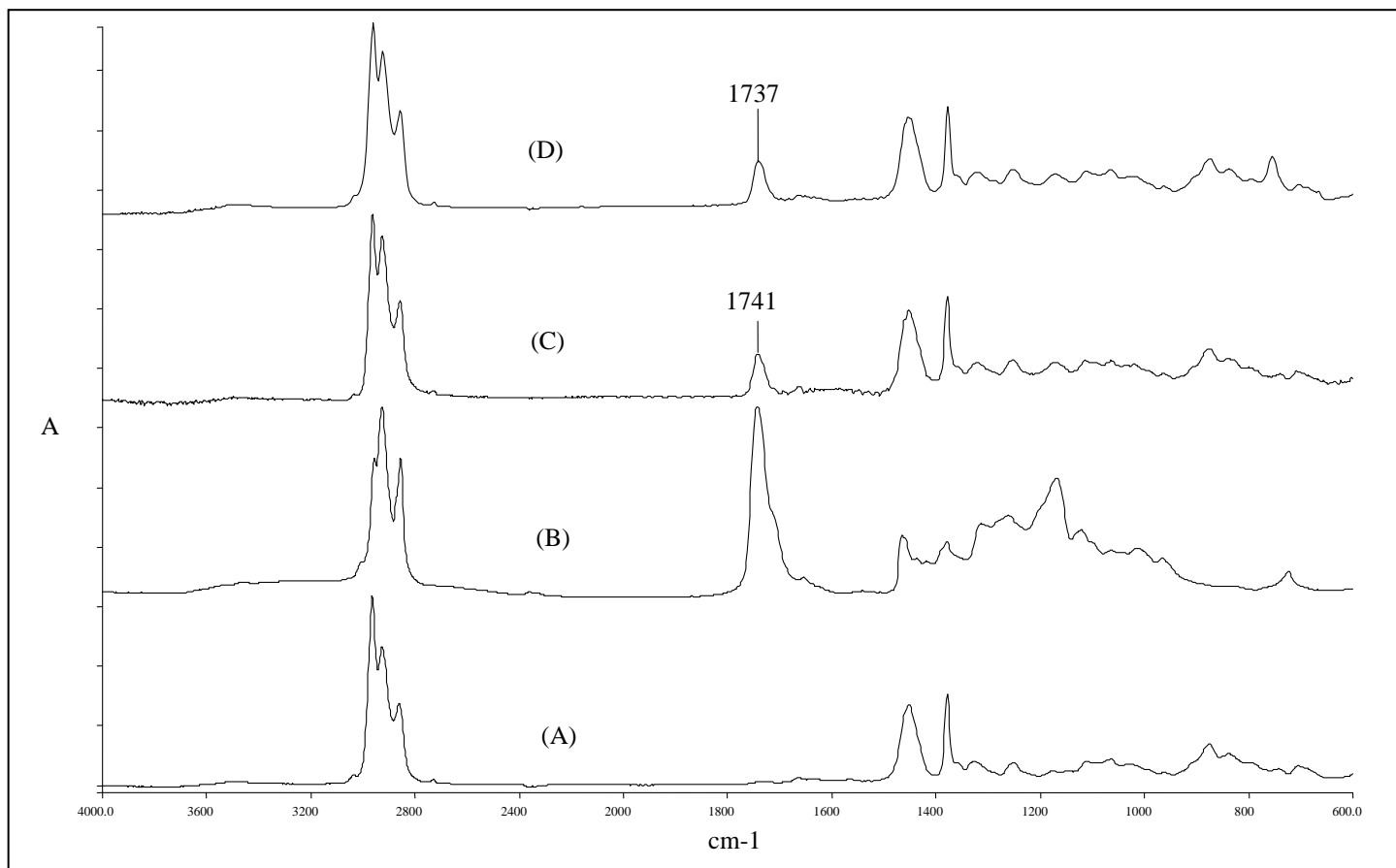


Figure 4.11 FTIR spectra of ENR (A); mcl-PHA (B); P₁₀ blend at ambient temperature (C), and after reacting at 170 °C for 30 minutes (D).

With reference to Figure 4.11, spectra (C) and (A) are almost identical except for the small peak at 1741 cm^{-1} which could be attributed to the carbonyl of the free carboxylic group of the mcl-PHA. This is consistent with the fact that the P₁₀ sample contained only approximately 10 parts mcl-PHA to 100 parts ENR, thus the weaker peaks of mcl-PHA have been overshadowed by the stronger peaks of ENR, except for the carbonyl peak at 1741 cm^{-1} which was exclusive to the mcl-PHA. Spectrum (D) shows that after the reaction at 170°C for 30 minutes, the carbonyl peak has shifted to 1737 cm^{-1} . This provides evidence that mcl-PHA has chemically reacted with ENR molecules with the formation of ester linkages. However, there is no noticeable reaction in P₁₀ at ambient temperature for short reaction time.

A more extensive examination of the effect of reaction temperature and duration on the reaction between ENR and mcl-PHA was then carried out. The effect of temperature was investigated by heating P₁₀ at 50°C , 70°C , 100°C , 130°C , 150°C and 170°C , each for 30 minutes. The FTIR results showed that all spectra were identical except for peak shifting detected at the carbonyl stretching region around 1600 cm^{-1} to 1800 cm^{-1} . The expanded scale of the infrared spectra at this region is illustrated in Figure 4.12.

As shown, the carbonyl peak in (G) has shifted from 1741 cm^{-1} to 1737 cm^{-1} . This indicates that the reaction between ENR and mcl-PHA could occur only at 170°C within short interval of 30 minutes.

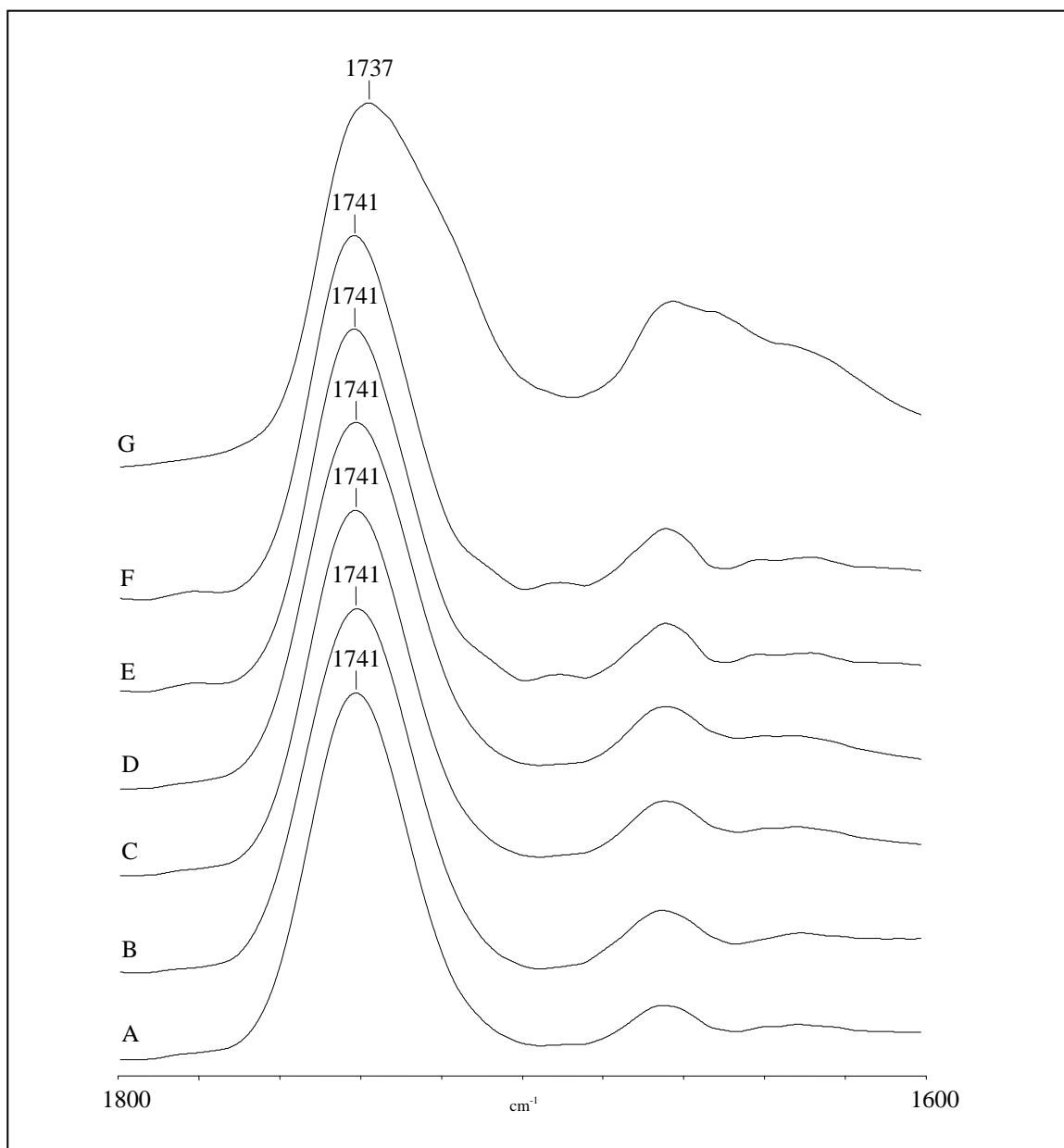


Figure 4.12 FTIR spectra of P₁₀ reacted 30 minutes at different temperatures: 30°C (A); 50°C (B); 70°C (C); 100°C (D); 130°C (E); 150°C (F), and 170°C (G).

The next study was to investigate the effect of reaction duration on P₁₀ when it was heated at 170°C for 10, 20 and 30 minutes. The IR spectra again indicates that no significant differences except for peak shifting around 1600 cm⁻¹ to 1800 cm⁻¹. From Figure 4.13, it is obvious that only carbonyl peak in (C) shifted to 1737 cm⁻¹. This suggests that the ester linkages would have formed in the blend after 20 to 30 minutes at 170 °C.

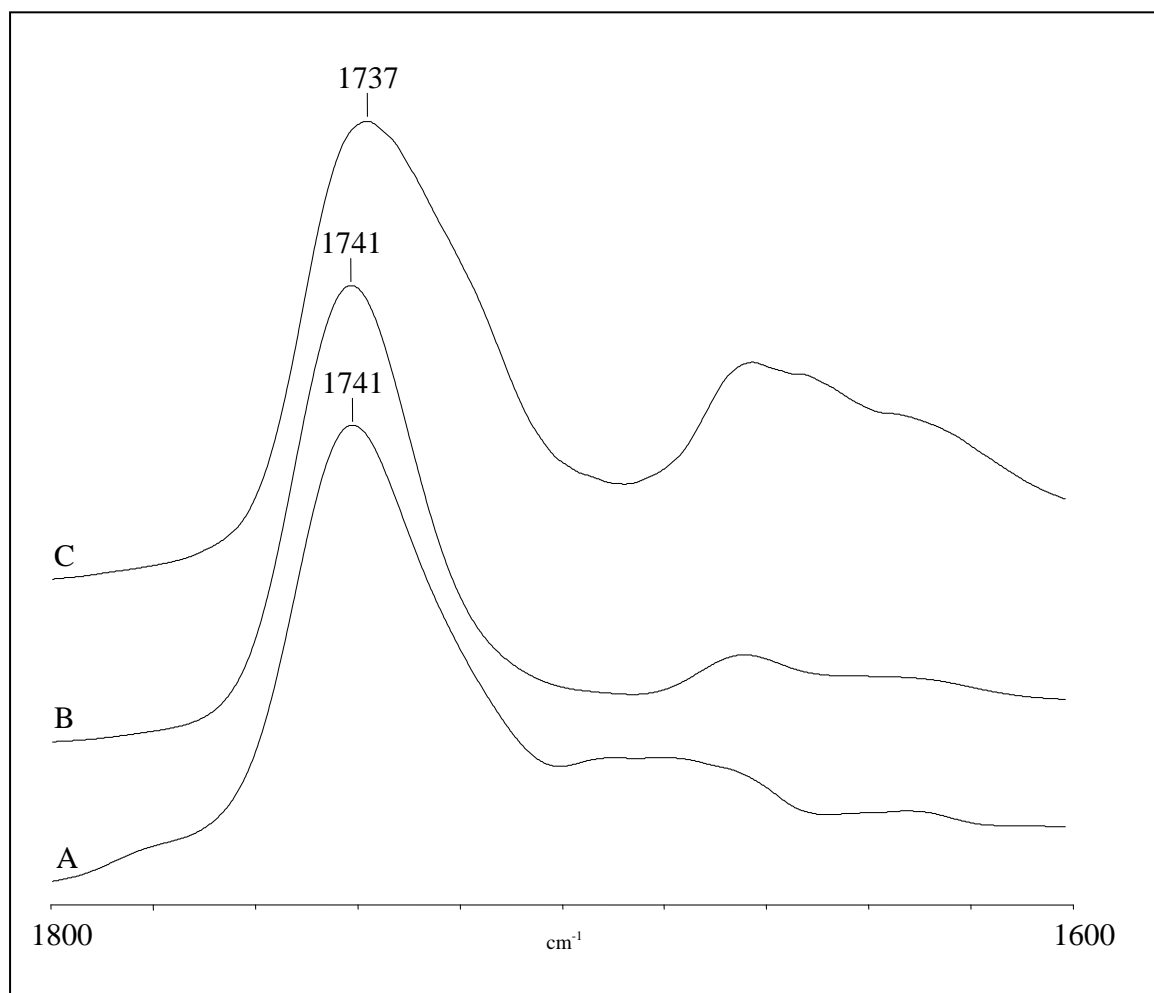


Figure 4.13 FTIR spectra of P₁₀ reacted at 170°C under different heating durations: 10 minutes (A); 20 minutes (B); 30 minutes (C).

4.3.2 ^1H -NMR spectroscopy

In proton Nuclear Magnetic Resonance (^1H -NMR) spectroscopy, protons resonate at characteristic frequencies (e.g. chemical shift) depending on their chemical environment, and therefore the specific nature of the proton can be identified. In this study, P₁₀ was dissolved in deuterated chloroform to form a solution of approximately 4 % w/v for the ^1H -NMR measurement. The overlaid ^1H -NMR spectra for the P₁₀ before and after reaction for 30 minutes at 170°C are shown in Figure 4.14.

In Figure 4.14, the small peaks appear at 0.9 ppm and 2.3-2.8 ppm region indicate the presence of mcl-PHA in the blend. The peak at 0.9 ppm is due to the methyl protons and the typical peak splitting pattern around 2.3-2.8 ppm is due to the methylene protons adjacent to ester group.

From Figure 4.14, although the two NMR spectra have very similar appearances due to the very low level of mcl-PHA in ENR, the expanded region at 2.0-4.0 ppm of spectrum (B) shows two distinct peaks at 3.5 and 3.6 ppm, which are due to the ring-opening of the epoxy group by the carboxylic terminal group of mcl-PHA. The plausible epoxy ring-opened structures are shown in Figure 4.15.

With reference to both Figure 4.14(B) and Figure 4.15, the different chemical shifts for the ring-opened structures are due to the shielding effect of the adjacent carbon atoms to which the hydroxyl protons were attached. The peak of -OH group in the epoxy ring-opened structure (I) is found at lower chemical shift value, i.e. 3.5 ppm since this hydroxyl proton is attached to a carbon atom adjacent to a methyl group which then shielded the hydroxyl proton. While, the peak at 3.6 ppm is assigned to the -OH of the epoxy ring-opened structure (II) where this hydroxyl proton is slightly deshielded by the adjacent -CH group and thus shift to a lower field.

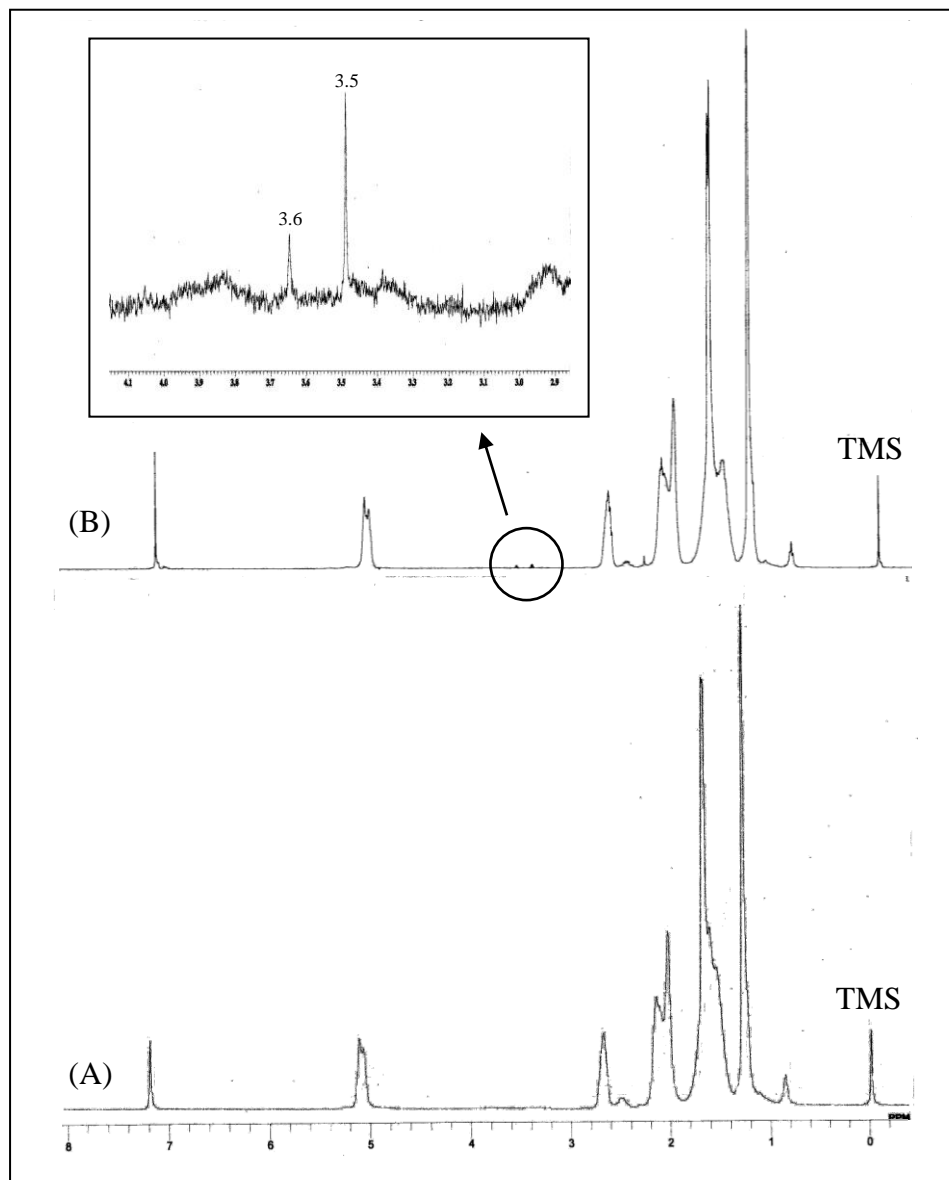


Figure 4.14 The overlaid ¹H-NMR spectra of P₁₀ blends, reacted for 30 minutes at:
ambient temperature (A) and 170°C (B).

Table 4.12**Composition of initial ENR/PHA mixture**

ENR/PHA	Volume of solution/ mL*		Dry solid/ g		Total dry solid/ g	Amount of functional groups in the mixture/ mol		Ratio of initial -COOH to epoxy groups
	ENR	PHA	ENR	PHA		Epoxy	-COOH	
P ₁₀	34	1	4.42	0.45	4.87	2.91×10^{-2}	1.81×10^{-4}	0.006
P ₃₀	26	3	3.38	1.35	4.73	2.22×10^{-2}	5.44×10^{-4}	0.025
P ₅₀	19	6	2.47	2.70	5.17	1.63×10^{-2}	1.09×10^{-3}	0.067
P ₇₀	11	8	1.43	3.60	5.03	9.41×10^{-3}	1.45×10^{-3}	0.154
P ₉₀	4	10	0.52	4.50	5.02	3.42×10^{-3}	1.81×10^{-3}	0.529

* where, the concentrations of mcl-PHA and ENR solutions were 45 % w/v in toluene and 13 % w/v in toluene, respectively.

4.4.1 FTIR spectroscopy

All blends were subjected to FTIR analysis. The FTIR spectra of all blends were similar to the spectrum of P₁₀ as shown previously in Figure 4.11 (D), except for the peak at 1737 cm⁻¹ that appears around carbonyl region. Figure 4.16 shows the expanded scale of the FTIR spectra at this region.

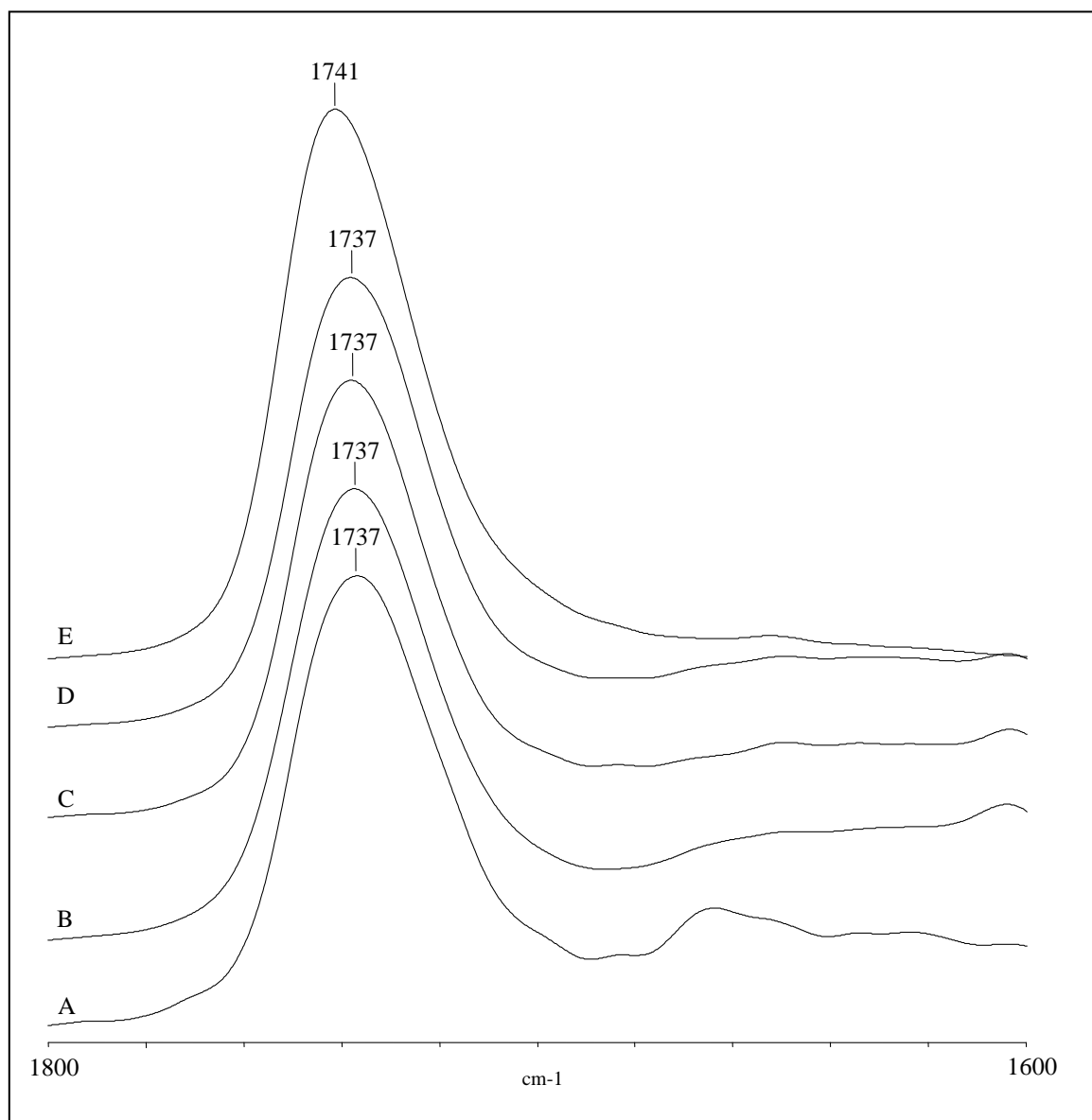


Figure 4.16 FTIR spectra of ENR/PHA blends of varied mcl-PHA composition: P₁₀ (A); P₃₀ (B); P₅₀ (C); P₇₀ (D), and P₉₀ (E).

From Figure 4.16, all blends except P₉₀ show carbonyl peak at 1737 cm⁻¹, which is due to the carbonyl stretching of the carboxylate group from the reaction of mcl-PHA with epoxy group. Since P₉₀ contained high ratio of the initial -COOH to epoxy groups, some of the excess and unreacted mcl-PHAs were not removed by methanol and thus remained in the system. This causes the overshadowing of the carboxylate group (1737 cm⁻¹) by the free unreacted carboxylic group (1741 cm⁻¹) in mcl-PHA.

4.4.2 DSC analysis

Glass transition temperature (T_g) was measured in this study using a differential scanning calorimeter (DSC), where the T_g was obtained via heat capacity (C_p) changes, which was then identified as the onset temperature of segmental motion in the amorphous regions of polymers. This value would cause a change in the slope of plot measured as a function of temperature and T_g was attained from the intersection of the extrapolated baseline with the tangent of the maximum slope.

Figure 4.17 shows an example of DSC thermogram of P₁₀. In fact, the DSC thermograms of all ENR/PHA blends exhibit only one T_g , which occur at the temperature intermediate between those of the pure components of the blends. This suggests that the blends are miscible over the whole composition ranges upon reacted at 170°C for 30 minutes. This result is consistent with the observation that the mcl-PHA formed clear dilute solutions with ENR during the preparation of the blends.

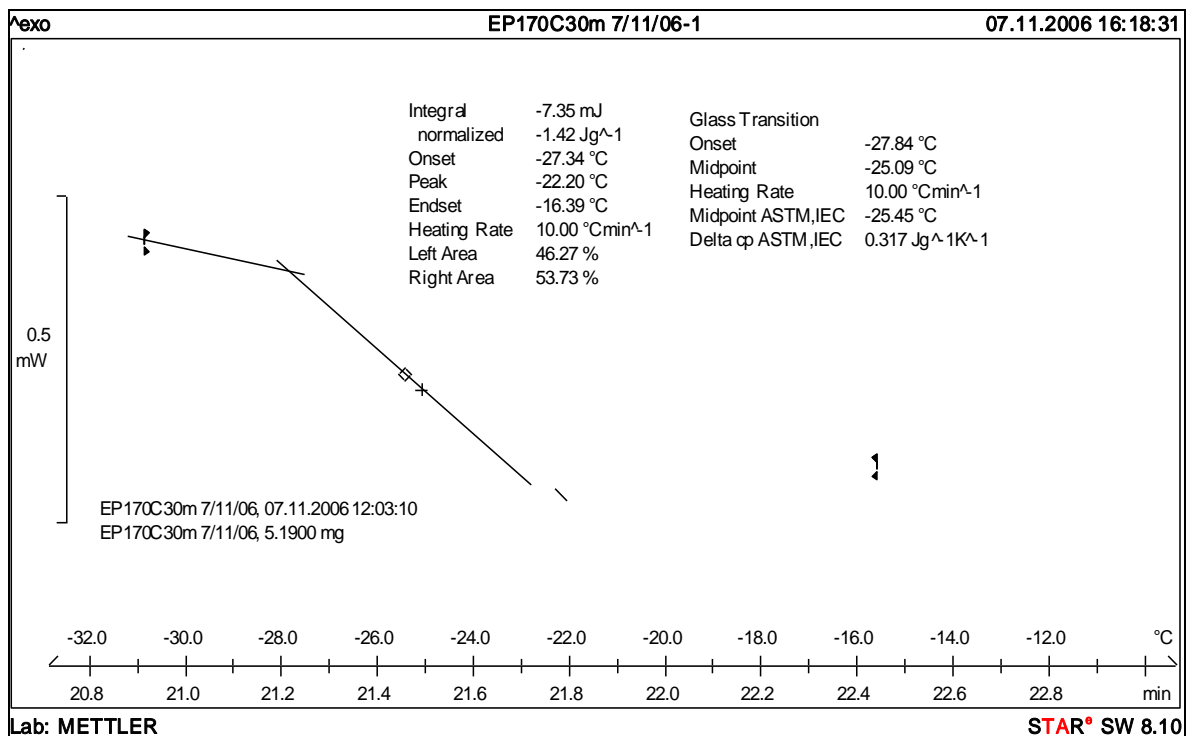


Figure 4.17 DSC thermogram for P₁₀ reacted at 170°C for 30 minutes

An example of calculation using Fox equation [3.9] to determine the T_g (theory) of P₁₀ is shown as follows:

$$\frac{1}{T_{gb}} = \frac{0.9}{247.1} + \frac{0.1}{203.4}$$

$$T_{gb} = 241.9\text{K}$$

where, T_{g1} and T_{g2} are 247.1 K and 203.4 K by assuming the components 1 and 2 in P₁₀ as ENR and mcl-PHA, respectively; and the W_1 and W_2 are 0.9 and 0.1; T_{gb} refers to the T_g (theory) of P₁₀.

The calculated glass transition temperatures of the T_g (theory) together with the T_g (onset) that obtained from DSC measurement are then tabulated in Table 4.13.

Table 4.13**Glass transition temperatures of ENR/PHA**

Blend	Glass transition temperature/ K	
	T_g (onset)*	T_g (theory)
P ₁₀	245.3	241.9
P ₃₀	237.9	232.1
P ₅₀	234.1	223.1
P ₇₀	231.0	214.8
P ₉₀	214.5	207.1

* where, the T_g (onset) of ENR and mcl-PHA are 247.1 K and 203.4 K, respectively.

From Table 4.13, the T_g (onset) decreases as the weight fractions of mcl-PHA in the blends increase from 10 to 90 parts of mcl-PHA per hundred parts of ENR. This suggests that the mcl-PHA has contributed plasticizing effect in the blends, in which the addition of this low molecular weight material will increase the free volume of the system and make the ENR more flexible. Therefore, as described in our Patent Application PI 20070672, only low level of mcl-PHA, preferable less than 10 parts per hundred parts of ENR, would be sufficient to improve the vulcanization of ENR compound and suppress the reversion of vulcanized rubber²⁰⁷.

On the other hand, the T_g (onset) of the blends is found to be lower than the the T_g (onset) of ENR, indicating that there is no crosslinking reaction in the blends. However, the T_g (onset) of all blends exhibits positive deviation from the T_g (theory). This could be attributed to the strong interpolymer interactions occurred between ENR and mcl-PHA. This result suggests that the presence of mcl-PHA in the ENR/PHA blends have

successfully modified the main chain structure of ENR through the formation of ester linkages.

4.5 Summary

The mcl-PHA was observed to undergo significant thermal degradation when subjected to heating at 170°C for 30 minutes. Significant reactions between ENR and mcl-PHA were detected at the same conditions of thermal degradation. This reaction was due to the increase of the amount of –COOH groups in mcl-PHA after thermal degradation. The reaction involved ring-opening of the epoxy groups in ENR by the carboxylic terminal of the mcl-PHA to form ester linkages in the blend.