CHAPTER 3

REACTIONS BETWEEN EPOXIDIZED NATURAL RUBBER AND PALM OIL-BASED ALKYDS

Alkyds are polyfunctional vegetable oil-modified polyesters, produced through esterification reaction between the natural oils containing fatty acids, polyols and polyacids. The versatile resin-forming reactions in alkyds have diversified the structural units connecting the ester groups. The properties of alkyds can be further modified either by physical or chemical blending with other polymers[73]. These reactions produced the finished resins with many potential applications in surface coating, labile biomedical matrices, liquid crystals, fibres and temperature resistant performance materials[68,80,87-89].

Recently, our laboratory had filed two applications of joint patents between UM and SRI in USA (2007/0100061A1) and Malaysia (PI 20070671) on the application of alkyd in the rubber composition for tyre and pneumatic tyre[184,185]. As described in these patents, alkyd was compounded as a tackifier in rubber composition and has shown an improvement in tackiness, hardness as well as lowered the rolling resistance of the tyre, compared with rubber composition compounding with a petroleum resin or a terpene resin. Alkyd has also shown good controls on reversion which is frequently observed when a rubber is vulcanized with sulfur for a short time at a high temperature.

This study aimed to investigate the chemical reactions between the palm oil-based alkyds and ENR.

3.1 Synthesis of palm oil-based alkyds

Figure 3.1 illustrates the overall preparation method of the three palm oil-based alkyds A1, A2 and A3.

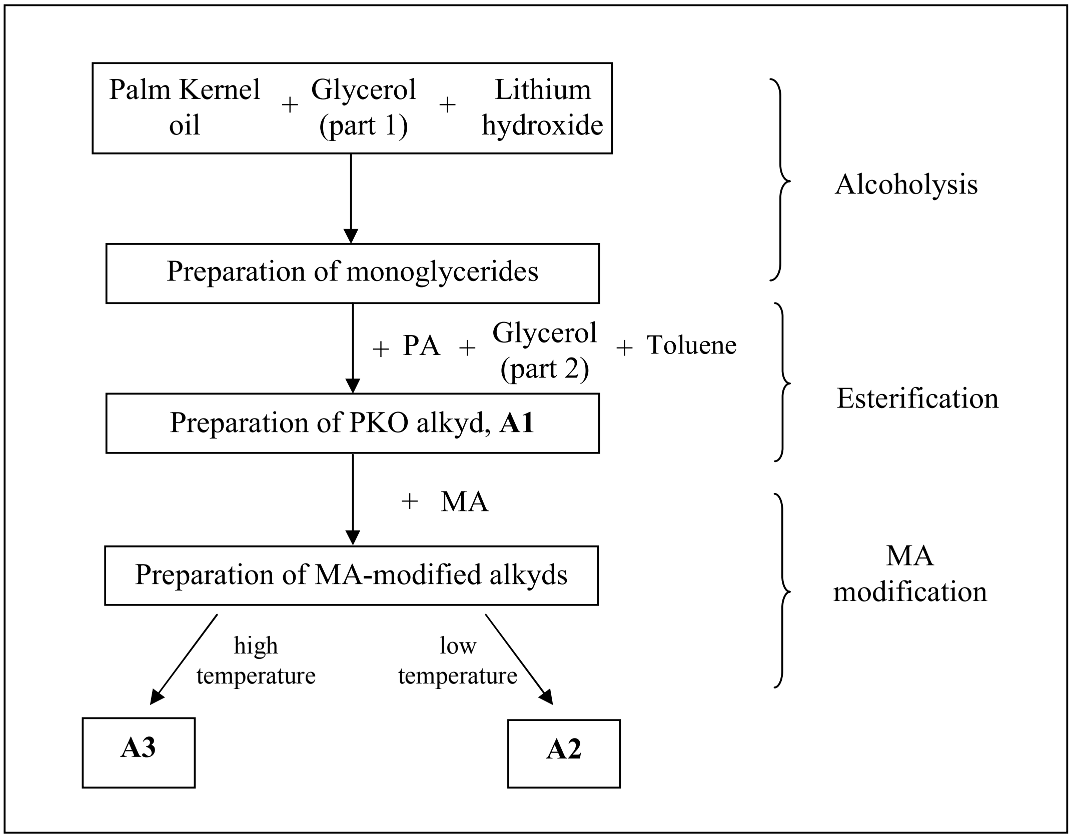


Figure 3.1: Preparation of PKO alkyds

In this study, a low molecular weight alkyd A1 was first synthesized with high hydroxyl number and low acid number. This alkyd was obtained by first performing the alcoholysis of palm kernel oil with glycerol to form predominantly monoglyceride, followed by reacting with PA and glycerol.

Then, two MA-modified alkyds having different proportions of the carboxylic and hydroxyl contents were prepared. This was done by treating A1 subsequently with MA at two different temperatures. In the case of using MA as a source of carboxylic functionality, a half-ester is first formed at lower temperature, which can then condense by further esterification at higher temperature to give longer chain polyesters. Therefore, alkyd A2 with higher carboxylic content than A1 was produced by reacting the anhydride with some of the hydroxyl groups of A1 to a half ester at 130°C. On the other hand, at 185°C the anhydride has reacted completely to produce alkyd A3 with similar carboxylic acid content as A1 but lower hydroxyl number than A1.

3.1.1 Synthesis of alkyd A1

A1 was synthesized from PKO, glycerol and PA. It was formulated according to Patton's gel point calculation, which was a practical alkyd formulating system to calculate the ratios of functional groups and the extent of reaction that can be reached while avoiding gelation. The theoretical calculation is shown in Table 3.1[182].

Table 3.1

An example of theoretical calculation for the formulation of alkyd A1[182]

Material	W (g)	E	e_A	e_B	F	m_0
PKO	241.5756	233.7	-	-	-	-
Glycerol from oil	-	-	-	1.034	3	0.345
Fatty acid from oil	-	-	1.034	-	1	1.034
Glycerine 99%	114.9452	31	-	3.708	3	1.236
PA	147.7656	74.1	1.994	-	2	0.997
Total	**504.2864**	**-**	**3.028**	**4.742**	**-**	**3.611**

where, W is weight; E is the equivalent weight (molecular mass divide by functionality); e_A is the number of acid equivalents; e_B is number of hydroxyl equivalents; F is functionality; m_0 is total moles present at the start of reaction. e_A, e_B and m_0 are calculated as follows:

$$e_A = \frac{W_{acid}}{\Sigma E}\ ; \qquad e_B = \frac{W_{hydroxyl}}{\Sigma E}\ ; \qquad m_0 = \frac{e_A}{F}\ or\ \frac{e_B}{F}$$

The most important concept in this Patton's gel point calculation is the alkyd constant K, derived based on Carother's classical theorem[186,187] with adaptation applying to alkyds[188]. The K is defined as the ratio of $\frac{\Sigma m_o}{\Sigma e_A}$ and should be larger than 1.00 so that gelation would not occur at 100 % reaction conversion. From Table 3.1, the K of A1 was (3.611 ÷ 3.028), i.e. 1.19 and thus A1 was expected to have no gelation at 100 percent of reaction.

On the other hand, the excess of hydroxyl group in A1 could be estimated from the ratio of $\frac{\Sigma e_B}{\Sigma e_A}$, i.e. (4.742 ÷ 3.028), or 1.57. This indicated that there was 57 %* of excess –OH groups available in the formulation. Since A1 was formulated with excess of hydroxyl groups, the expected hydroxyl value in the finished alkyd could be further estimated as follows:

$$\text{Expected hydroxyl value} = \frac{(\Sigma e_B - \Sigma e_A) \times 56100}{\Sigma W - \text{Water loss}}, \text{ where water loss is } e_A(\text{PA}) \times 9$$

$$= \frac{(4.742 - 3.028) \times 56100}{504.2864 - (1.994 \times 9)}$$

$$= 197.7 \text{ mg KOH g}^{-1}$$

From Table 3.1, A1 was formulated as a medium oil length alkyd with (100 × 241.5756 ÷ 504.2864), i.e. 47.9 parts per 100 parts resin, thus having a mixture of resin-like and oil-like properties, with more balance in its viscosity, tackiness and hardness, compared to short and long oil length alkyds.

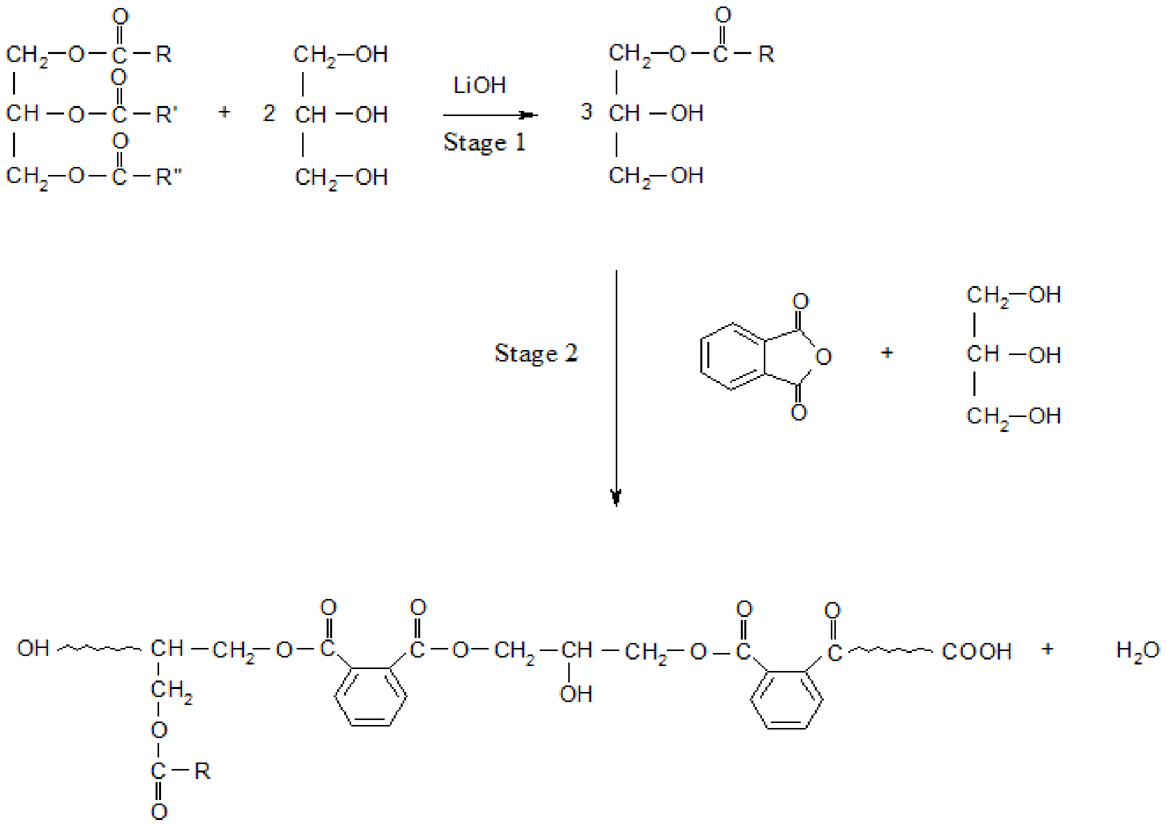
$$* \ \frac{(\Sigma e_B - \Sigma e_A)}{\Sigma e_A} \times 100 = \frac{(4.742 - 3.028)}{3.028} \times 100 = 57\ \%$$

As shown in Table 3.1, the amounts of glycerol and PA were (100 × 114.9452 ÷ 504.2864), i.e. 22.8 and (100 × 147.7656 ÷ 504.2864), i.e. 29.3 parts respectively per 100 parts resin. These amounts were maintained within the preferable range of polyhydric alcohol and polybasic acid in an alkyd formulation[184,185].

For polyhydric alcohol, if the amount is less than 5 % by weight, the molecular weight of the finished alkyd is difficult to be improved. However, if the amount exceeds 40 % by weight, there will be a lot of the unreacted polyhydric alcohols remained in the system and thus causing an excessive increase in hygroscopic property.

For polybasic acids, the favourable amount is 10-50 % by weight, where the condensation is difficult to proceed if the amount of ratio is less than 10 % by weight; while the tackiness of finished alkyd tends to be low if the amount ratio exceeds 50 % by weight. Furthermore, the excess amount of acid group may increase the extent of side reaction during synthesis which can cause gelation if the reaction proceeds at high temperature for longer time.

Figure 3.2 represents a plausible reaction mechanism in the preparation of A1. The first stage of reaction is alcoholysis, where the triglycerides of PKO were converted to monoglycerides through its reaction with the first portion of glycerol at 225-230°C**.** At this stage, etherification[87] tends to occur when there is a substantial excess of polyhydric alcohol, with the presence of an alkaline catalyst. This reaction would introduce an undesirable linkage to the polymer, which reduce the hydroxyl group and lead to the possibilities of gelation. Therefore, the total required amount of glycerol as stated in Table 3.1 was divided into two portions, where two moles of glycerol was calculated to be equivalent to one mole of triglycerides in alkyds, i.e. only 55 % of total glycerol (i.e. 63 g) was added at this stage. At the second stage of reaction, the resulting monoglycerides were converted to alkyd by esterification with PA and the second portion of glycerol in the toluene medium under reflux condition at 210-220°C.



Alkyd A1

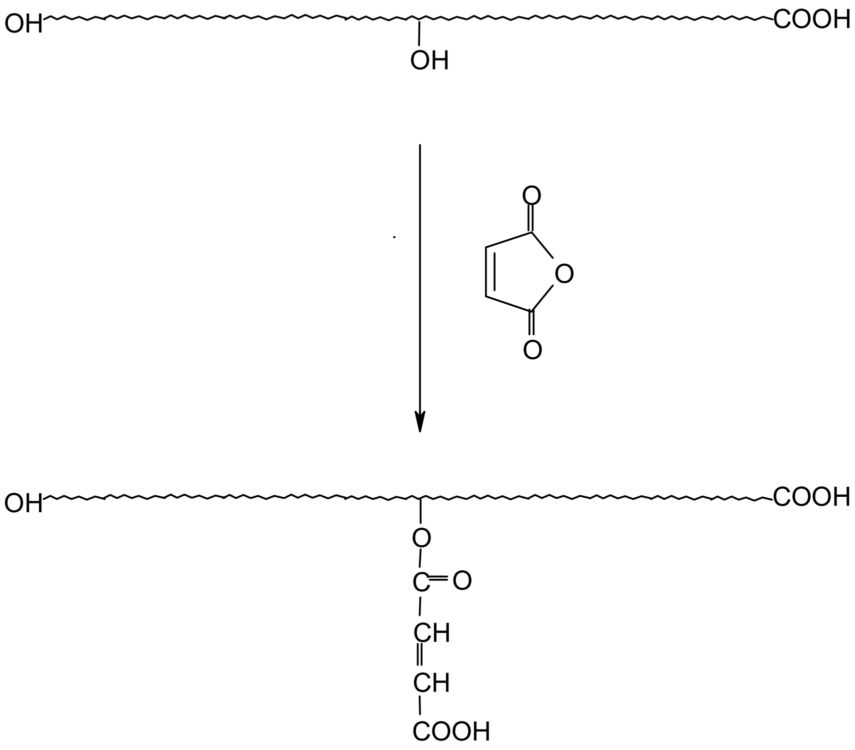
where, R, R', R" Fatty acid

Figure 3.2 A plausible reaction mechanism in the preparation of alkyd A1

On the other hand, an important factor that affects the rate of reaction at second stage is the rate of removal of water from the reactor since esterification is a reversible reaction. The water of reaction must be removed in order to prevent the occurrence of hydrolysis. Therefore, toluene was used as the reflux solvent to help the removal of water. However, only 10 % of toluene was used, since the reaction was carried out at the temperature far above the boiling point of toluene. This amount was found to be suitable for our set-up of an alkyd cooks as shown in Figure 2.2 in Chapter 2 as it was enough to reflux vigorously at high temperature. During the reaction, some of toluene was distilled off along with the water where the water was collected at a decanter side-arm and toluene was returned to the reactor.

3.1.2 Synthesis of alkyd A2

About 2.5 parts of MA was added to 100 parts of A1 to synthesize MA-modified alkyd A2. As MA is a dibasic acid, the anhydride is more reactive than the ring-opened carboxylic acid at lower reaction temperature. To produce half-ester A2, the reaction has to be carried out under controlled conditions of moderate temperature. It was found that when the reaction temperature was maintained around 140-143°C, water of reaction started to release after reacting for 20 minutes. The release of water indicated that further esterification could continue shortly after heating at this temperature range. However, when the anhydride reacted with the hydroxyl groups of A1 at 130-133°C, no water of reaction was released within 540 minutes of reaction. This indicated that half-esterification could have formed slowly at lower temperature. A plausible mechanism in the preparation of A2 is shown in Figure 3.3.



Alkyd A2
with some half-ester

Figure 3.3 A plausible reaction mechanism in the preparation of alkyd A2

3.1.3 Synthesis of alkyd A3

About 2.5 parts of MA was added to 100 parts of A1 to synthesize the second MA-modified alkyds, A3. The reaction of the MA with alkyd A1 was carried out at much higher temperature of 180°C, where all the anhydrides could react completely to form alkyd A3 and water of reaction was released. A plausible mechanism in the preparation of A3 is shown in Figure 3.4.

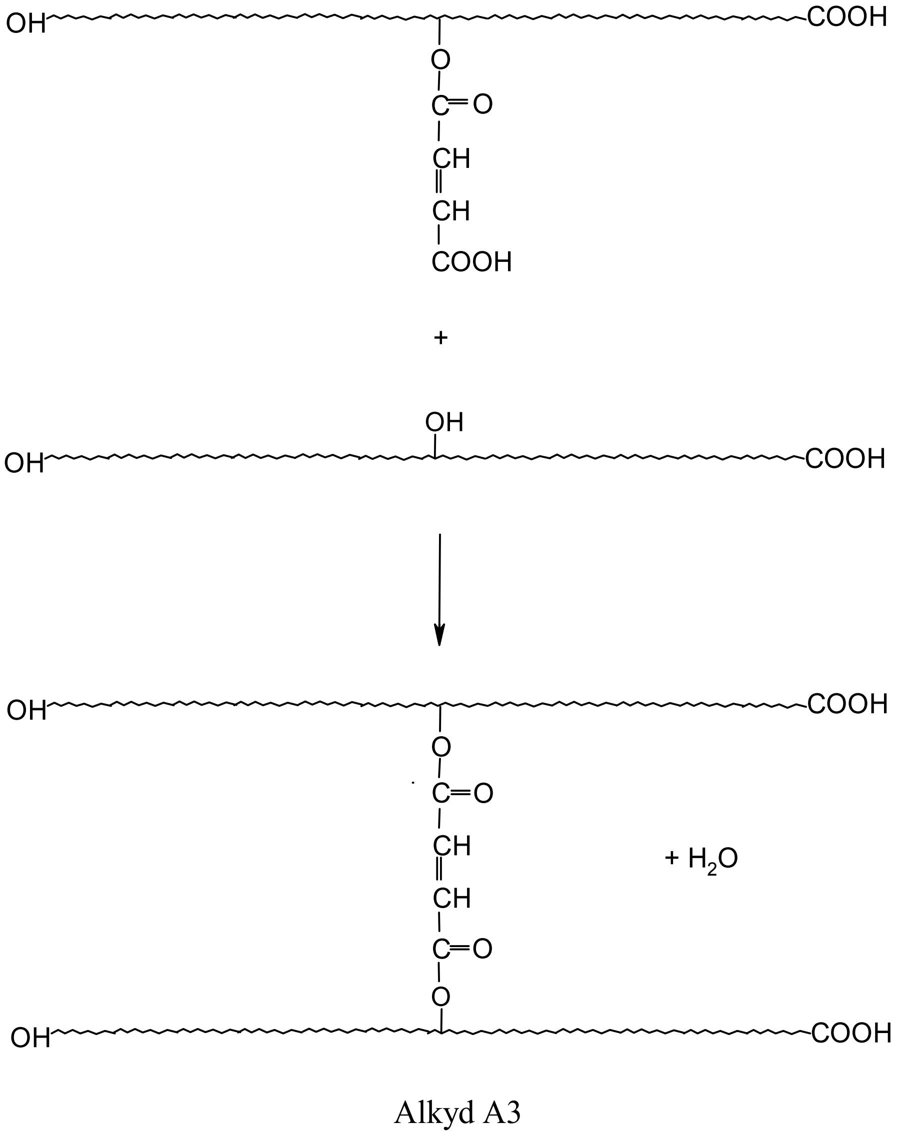


Figure 3.4 A plausible reaction mechanism in the preparation of alkyd A3

3.2 Changes in acid numbers during synthesis of alkyds

Acid number is defined as the number of milligrams of potassium hydroxide required to neutralize the acidity of 1 g of the alkyd resin. Any reaction which has consumed the carboxylic acid group would lead to a decrease in the acid number as determined by the titration of sample with standardized potassium hydroxide (KOH) solution.

3.2.1 Acid number of alkyd A1

In this study, the time when PA was added to the reaction mixture was recorded as the beginning of the esterification. The progress of reaction was then followed by periodically checking the acid number of the alkyd resin. The values of acid numbers determined during the synthesis of A1 are tabulated in Table 3.2.

Table 3.2

Acid numbers during synthesis of A1

Reaction time/ minutes	Acid number/ mg KOH g^{-1}
0*	221.8
70	81.7
120	43.4
155	19.1
200	4.9
220	1.8

* where, the initial acid number was calculated as $\dfrac{56100 \times e_A\,(PA)}{\Sigma W}$

$$\text{Initial acid number of A1} = \frac{56100 \times 1.994}{504.2864}$$

$$= 221.8 \text{ mg KOH g}^{-1}$$

From the above calculation, the initial acid number was calculated based on PA added at the beginning.

The percentage of conversion for alkyd A1 was determined from the calculation of [100 x (221.8 - 1.8) ÷ 221.8], i.e. 99.2 %. This calculated result indicated that esterification in A1 has almost achieved 100 % completion after reacting for 220 minutes.

An example of the acid number determination for A1 at 220 minutes was shown as follows, where the titration results for the standardization of KOH solution and the acid number determination are tabulated in Table 3.3 and Table 3.4, respectively

Table 3.3

Standardization of KOH solution

	First titration	**Second titration**
Weight of potassium acid phthalate/ g	0.5063	0.5080
KOH solution required/ mL	52.90	53.00
Molarity*	0.0469	0.0469
Average Molarity/ M	0.0469	

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

Table 3.4

Titration results of A1 with standardized KOH solution

	First titration	**Second titration**
Weight of A1 solution, W/ g	2.0011	2.0015
KOH solution required for titration of the sample, V/ mL	1.75	1.75
KOH solution required for titration of the blank, V_b/ mL	0.20	0.20
Acid number* / mg KOH g^{-1}	1.791	1.791
Average acid number/ mg KOH g^{-1}	1.79	

* where, acid number was calculated using the equation [2.5] as mentioned in Section 2.8.2, Chapter 2, with modification. Since the acid number was defined in dry weight basis and A1 solution contained 87.9 % of alkyd by weight, thus the formula became:

$$\text{Acid number} = \frac{0.879 \times 56.1 \times 0.0469 \times (\text{V - V}_\text{b})}{\text{W}}$$

The changes in acid numbers as a function of time for A1 are then plotted in Figure 3.5. As shown in Figure 3.5, acid numbers decreased consistently as the reaction proceeded and this indicated that PA has successfully incorporated to the hydrocarbon chain of alkyd resin, due to the disappearance of an acid group for every ester linkage formed.

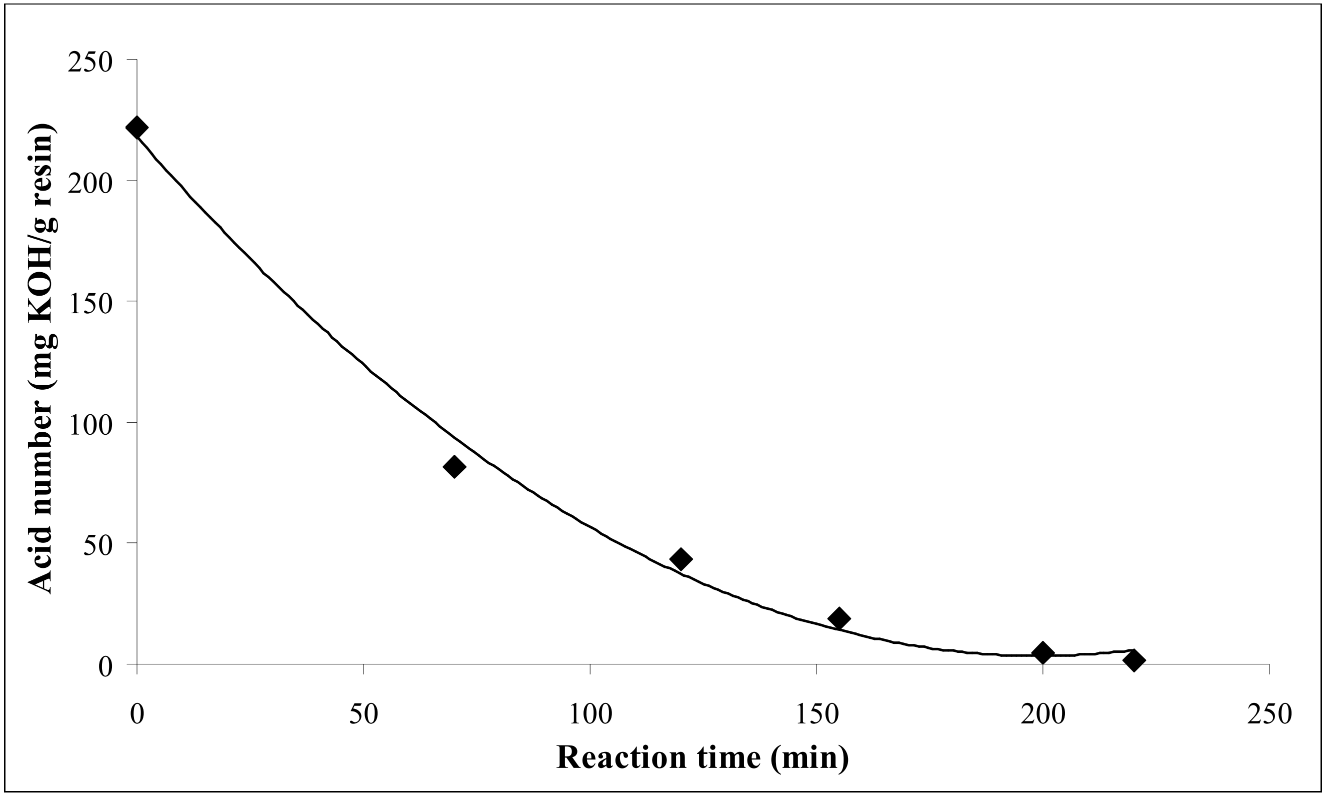


Figure 3.5 Changes in acid numbers with reaction time during the synthesis of alkyd A1

3.2.2 Acid number of MA-modified alkyds, A2 and A3

The addition of MA was taken as the start of the reaction. On the other hand, the values of acid numbers determined during the synthesis of A2 and A3 are tabulated in Table 3.5 and Table 3.6, respectively.

Table 3.5

Acid numbers during synthesis of A2

Reaction time/ minutes	Acid number/ mg KOH g^{-1}
0*	30.3
60	13.2
120	12.7
180	12.2
240	10.7
300	9.1
360	8.4
420	7.4
480	7.1
540	6.8

* where, Initial acid number $= \dfrac{56100 \times e_A(\mathrm{MA})}{\Sigma W} + \text{Final acid number of A1}$

$$= \frac{56100 \times 0.383}{753.5103} + 1.8$$

$$= 30.3\ \mathrm{mg\ KOH\ g^{-1}}$$

From Table 3.5, the percentage of conversion for alkyd A2 was calculated as [100 x (30.3 - 6.80) ÷ 30.3], i.e. 77.6 %. This implied that the esterification of MA with the hydroxyl groups in A1 was not totally completed, with about [100 x (6.8 ÷ 30.3)], i.e. 22 % of half-ester of anhydride still remained in A2.

Table 3.6 lists the acid number values at different reaction time during synthesis of A3. The percentage of conversion for A3 was [100 x (30.9 - 1.7) ÷ 30.9], i.e. 94.5 % and this implied that the anhydride has reacted almost completely to produce A3 with similar carboxylic acid content as A1.

Table 3.6

Acid numbers during synthesis of A3

Reaction time/ minutes	Acid number/ mg KOH g^{-1}
0*	30.9
60	14.0
80	10.8
100	9.8
120	8.4
140	5.6
160	3.0
180	2.8
200	1.7

* where, Initial acid number $= \dfrac{56100 \times e_A\,(\mathrm{MA})}{\Sigma W} + \text{Final acid number of A1}$

$$= \frac{56100 \times 0.264}{508.1837} + 1.8$$

$$= 30.9 \text{ mg KOH g}^{-1}$$

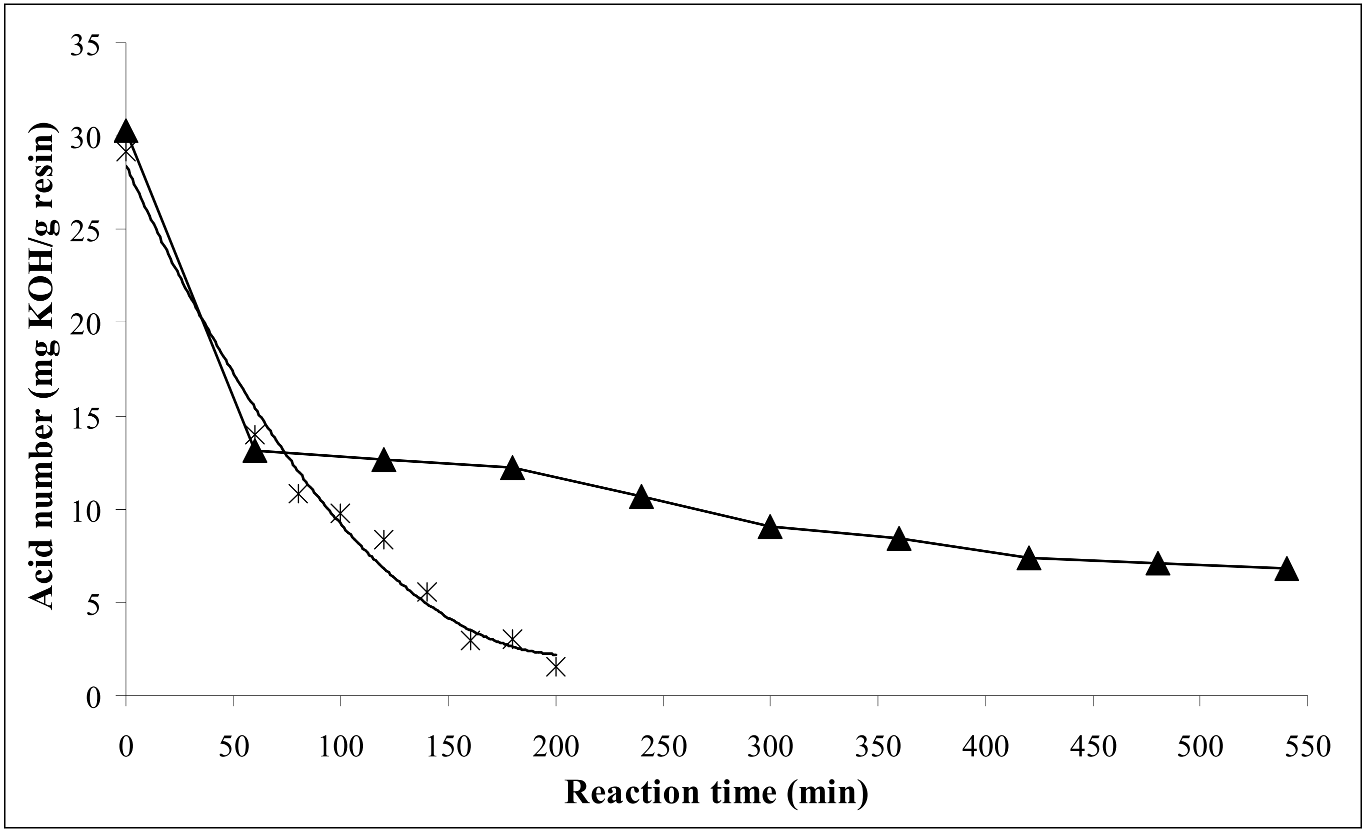


Figure 3.6 Changes in acid numbers with reaction time during the synthesis of alkyds: ▲, A2 prepared at 120-130°C; ∗, A3 prepared at 180°C.

The changes in acid numbers with reaction time during the synthesis of alkyds A2 and A3 are shown in Figure 3.6. In both cases, the reaction of MA with the hydroxyl groups of A1 has proceeded rapidly to form the half ester within 100 minutes. Then, for A2, the reaction of –COOH of the half ester of the anhydride with –OH was held at 130ºC at a slower rate in order to produce half-ester A2. The targeted acid number of around 7 mg KOH g^{-1} was achieved only after 540 minutes. However, for A3, the esterification continued on further heating to 180°C. Hence, the free –COOH could react with –OH at a much faster rate, and the acid number has dropped below 2 mg KOH g^{-1} within 200 minutes.

3.3 Characterization of alkyd synthesized

FTIR spectroscopy is one of the common techniques used to characterize the polymer structure by identifying the functional groups which vibrate and absorb typical frequencies within the infrared region. In this study, the functional groups that present in A1, A2 and A3 were characterized using the FTIR spectroscopy. The concentrations of both carboxylic and hydroxyl groups in alkyds were then determined quantitatively from the titration method.

3.3.1 FTIR spectroscopy

The overlay FTIR spectra of A1, A2 and A3 were shown in Figure 3.7; while, the assignments of peaks for these spectra were then presented in Table 3.7.

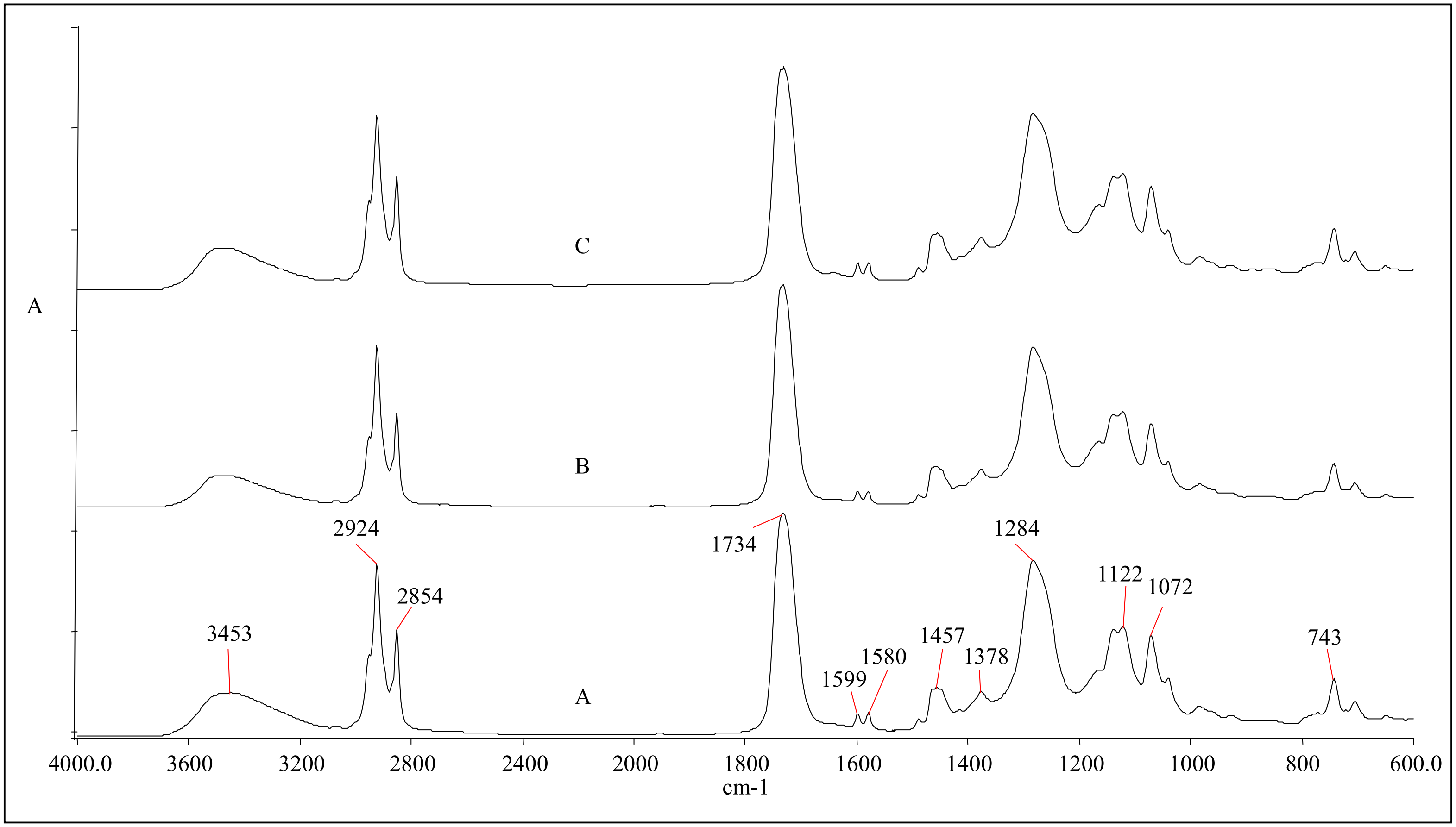


Figure 3.7 FTIR spectra of alkyds: A1 (A); A2 (B) and A3 (C).

As shown in Figure 3.7, the IR spectra for A1, A2 and A3 were almost identical, which was consistent with the fact that only 2.5 parts of MA was added to 100 parts of A1 to synthesize the MA-modified alkyds, A2 and A3. Thus, the weaker peaks of MA, were not observed in the IR spectra of A2 and A3.

Table 3.7

Major absorption peaks of alkyds

Wavenumber/ cm^{-1}	Bonding
743	Aromatic =C–H bending
1072, 1122, 1284	C–O stretching of –COOH overlapped with C-O stretching of ester
1378	C-H bending of CH_3
1457	C-H bending of CH_2
1580, 1599	Aromatic C=C stretching
1734	C=O stretching of –COOH overlapped with C=O stretching of ester
2854	C-H stretching of CH_2
2924	C-H stretching of CH_3
3466	O–H stretching

3.3.2 Characterization of alkyd

Basically, the finished alkyds A1, A2 and A3 have three fundamental functional groups, i.e. hydroxyl, carboxylic and olefinic groups. It was postulated that only the hydroxyl and carboxylic groups in alkyds might react with the epoxy groups of ENR at ambient temperature. Hence, it was important to determine the free hydroxyl and carboxylic groups remained in those alkyds prior to the investigation of the reaction between ENR and alkyds. Both the free hydroxyl and carboxylic groups could be determined from the hydroxyl number and acid number titrations, respectively.

3.3.2.1 Hydroxyl number determination

In the hydroxyl number determination, the free hydroxyl groups in the sample were first esterified with PA and the hydroxyl number was then determined from the amount of KOH required to neutralize the unreacted PA remained in the sample.

Before the titration was carried out, the sample size of alkyd A1 must be first determined by substituting the expected hydroxyl number (as calculated in Section 3.1.1) into equation [2.2] (as mentioned in Section 2.7.2, Chapter 2). Therefore, the sample size was (561 ÷ 197.7), i.e. 2.8 g. An example of titration results for the standardization of KOH solution and the hydroxyl number of A1 are tabulated in Table 3.8 and Table 3.9, respectively.

Table 3.8

Standardization of KOH solution

	First titration	**Second titration**
Weight of potassium acid phthalate/ g	4.9998	4.9892
KOH solution required/ ml	49.10	49.00
Molarity*	0.4987	0.4986
Average Molarity/ M	0.4987	

* where, Molarity was calculated using the equation [2.1] as mentioned in Section 2.7.1, Chapter 2.

Table 3.9

Titration results of A1 with standardized KOH solution

	First titration	**Second titration**
Sample saiz/ g	2.8411	2.8427
KOH solution required for titration of the sample/ mL	94.65	94.85
KOH solution required for titration of the blank/ mL	114.30	114.55
Hydroxyl number* / mg KOH g^{-1}	193.50	193.88
Average hydroxyl number/ mg KOH g^{-1}	193.7	

* where, hydroxyl number was calculated using the equation [2.3] as mentioned in Section 2.7.2, Chapter 2.

3.3.2.2 Properties of alkyds

Table 3.10 summarizes the hydroxyl numbers and the acid numbers of the three alkyds as determined from the titration method, together with the estimation of the properties for A1, A2 and A3, which are calculated from the titration results.

From Table 3.10, the estimated hydroxyl number of A1 was 193.7 mg KOH g^{-1}, which differed about 2.0 % from the calculated hydroxyl number (197.7 mg KOH g^{-1}) as calculated in Section 3.1.1.

Table 3.10

Hydroxyl and acid numbers of alkyd resins

Property	**Alkyd resin**		
	A1	**A2**	**A3**
Hydroxyl number/ mg KOH g^{-1}	193.7	166.4	161.3
Acid number/ mg KOH g^{-1}	1.8	6.8	1.7
–OH concentration* / mol g^{-1}	3.5×10^{-3}	3.0×10^{-3}	2.9×10^{-3}
–COOH concentration* / mol g^{-1}	3.2×10^{-5}	1.2×10^{-4}	3.0×10^{-5}
Ratio of –OH to –COOH	109	25	97

* where,

$$\text{- OH concentration} = \frac{\text{Hydroxyl number}}{56100}; \text{- COOH concentration} = \frac{\text{Acid number}}{56100}.$$

Among the three alkyds, A2 contained 1.2×10^{-4} mol g^{-1} of –COOH groups, which was about 73 % more than A1 and 75 % more than A3. This implied that there were more free carboxylic acids which remained in the hydrocarbon chain of A2 as compared to A3, when the grafting of MA was carried out at 130°C during the synthesis of A2. Although A1 had similar carboxylic content as A3, A1 still contained 17 % more –OH groups than A3. From the ratio of –OH to –COOH, all alkyds were invariably formulated with excess hydroxyl groups.

3.4 Reactions of ENR and alkyd

In this study, ENR was reacted with different alkyds (A1, A2 and A3) where ENR/A1, ENR/A2 and ENR/A3 denote the reaction product of ENR with A1, A2 and A3 respectively. These blends contained 50 parts of alkyds per hundred parts of ENR and were all reacted at ambient temperature. The reacted ENR was subsequently precipitated by methanol and the sample was analysed by FTIR and swelling test in toluene.

3.4.1 Preparation of ENR/Alkyd blends

The reactions of ENR and A1 were studied in a blend containing 50 parts of A1 per 100 parts of ENR, which was coded as ENR/A1. This blend was prepared by mixing 26.6 mL of ENR solution (12 % w/w in toluene), which contained approximately 3.19 g ENR, with 3.7 mL of A1 solution (88 % w/w A1 in toluene), which contained 3.26 g of A1. Since ENR 50 contains equimolar amounts of epoxy and isoprene units with the formula weights of 84 and 68 respectively, 152 g of ENR 50 would contain 1 mol of epoxy group and there are (1 mol ÷ 152 g) or 6.58×10^{-3} mol g^{-1} of epoxy groups available in ENR. In the initial mixture, the 3.19 g of ENR 50 contained 3.19 g x 6.58×10^{-3} mol g^{-1} of epoxy group (i.e. 2.10×10^{-2} mol); while, 3.26 g of A1 had 3.26 g x 3.2×10^{-5} mol g^{-1} of –COOH group (i.e. 1.04×10^{-4} mol) and 3.26 g x 3.5×10^{-3} mol g^{-1} of –OH group (i.e. 1.14×10^{-2} mol). The ratio of initial –COOH to epoxy group in ENR/A1 was 0.005; while, the ratio of initial –OH to epoxy group in ENR/A1 was 0.543.

The ENR/A2 refers to a blend containing 50 parts of A2 per hundred parts of ENR. It was prepared by blending 28.4 mL of ENR solution (12 % w/w in toluene), which contained approximately 3.41 g ENR, with 3.9 mL of A2 solution (89 % w/w A2 in toluene), which contained 3.47 g of A2. In the initial mixture, the 3.41 g of ENR 50 would contain 3.41 g x 6.58 x 10^{-3} mol g^{-1} of epoxy group (i.e. 2.24 x 10^{-2} mol); while, 3.47 g of A2 would contain approximately 3.47 g x 1.2 x 10^{-4} mol g^{-1} of –COOH group (i.e. 4.16 x 10^{-4} mol) and 3.47 g x 3.0 x 10^{-3} mol g^{-1} of –OH group (i.e. 1.04 x 10^{-2} mol). The ratio of initial –COOH to epoxy group in ENR/A2 was 0.019; while, the ratio of initial –OH to epoxy group in ENR/A2 was 0.464.

The blend of ENR and A3 was coded as ENR/A3, containing 50 parts of A3 per hundred parts of ENR. About 28.2 mL of ENR solution (12 % w/w in toluene), which contained 3.38 g ENR, mixed with 3.7 mL of A3 solution (92 % w/w A3 in toluene), which contained 3.40 g of A3. In the initial mixture, the 3.38 g of ENR 50 contained 3.38 g x 6.58 x 10^{-3} mol g^{-1} of epoxy group (i.e. 2.22 x 10^{-2} mol); while, 3.40 g of A3 would contain 3.40 g x 3.0 x 10^{-5} mol g^{-1} of –COOH group (i.e. 1.02 x 10^{-4} mol) and approximately 3.40 g x 2.9 x 10^{-3} mol g^{-1} of –OH group (i.e. 9.86 x 10^{-3} mol). The ratio of initial –COOH to epoxy group in ENR/A3 was 0.005; while, the ratio of initial –OH to epoxy group in ENR/A3 was 0.444. The amount of functional groups in the initial ENR/Alkyd mixtures was summarized in Table 3.11.

Table 3.11

Amount of functional groups in the initial ENR/Alkyd mixture

ENR/Alkyd	Amount of functional groups in the mixture (mol)			Ratio of initial –OH to epoxy group	Ratio of initial –COOH to epoxy group
	Epoxy	–OH	–COOH		
ENR/A1	2.10×10^{-2}	1.14×10^{-2}	1.04×10^{-4}	0.543	0.005
ENR/A2	2.24×10^{-2}	1.04×10^{-2}	4.16×10^{-4}	0.464	0.019
ENR/A3	2.22×10^{-2}	9.86×10^{-3}	1.02×10^{-4}	0.444	0.005

3.4.2 FTIR spectroscopy

While both ENR and alkyds are soluble in toluene, ENR is insoluble in methanol whereas the low molecular weight alkyds (A1, A2 and A3) are miscible with methanol. Initial mixing of the ENR solution with the alkyds solution, has produced a freely flowable solution. The blend was then reacted at ambient temperature (27 ± 2°C).

The reaction between ENR and alkyds could be observed visually from the progressive increase in viscosity of the mixture, and a jelly-like material was formed after 7 days at ambient temperature of around 28°C. At the end of the specified time, methanol was added to precipitate the ENR and this help to remove any unreacted alkyd. Figure 3.8 shows the overlaid FTIR spectra of the initial ENR, alkyd A1 and ENR/A1; Figure 3.9 shows the overlaid FTIR spectra of the initial ENR, alkyd A2 and ENR/A2; Figure 3.10 shows the overlaid FTIR spectra of the initial ENR, alkyd A3 and ENR/A3.

From Figure 3.8, Figure 3.9 and Figure 3.10, it is apparent that many characteristic peaks of the alkyds are seen in the reacted ENR which signified that these alkyds have been chemically incorporated into the ENR molecules.

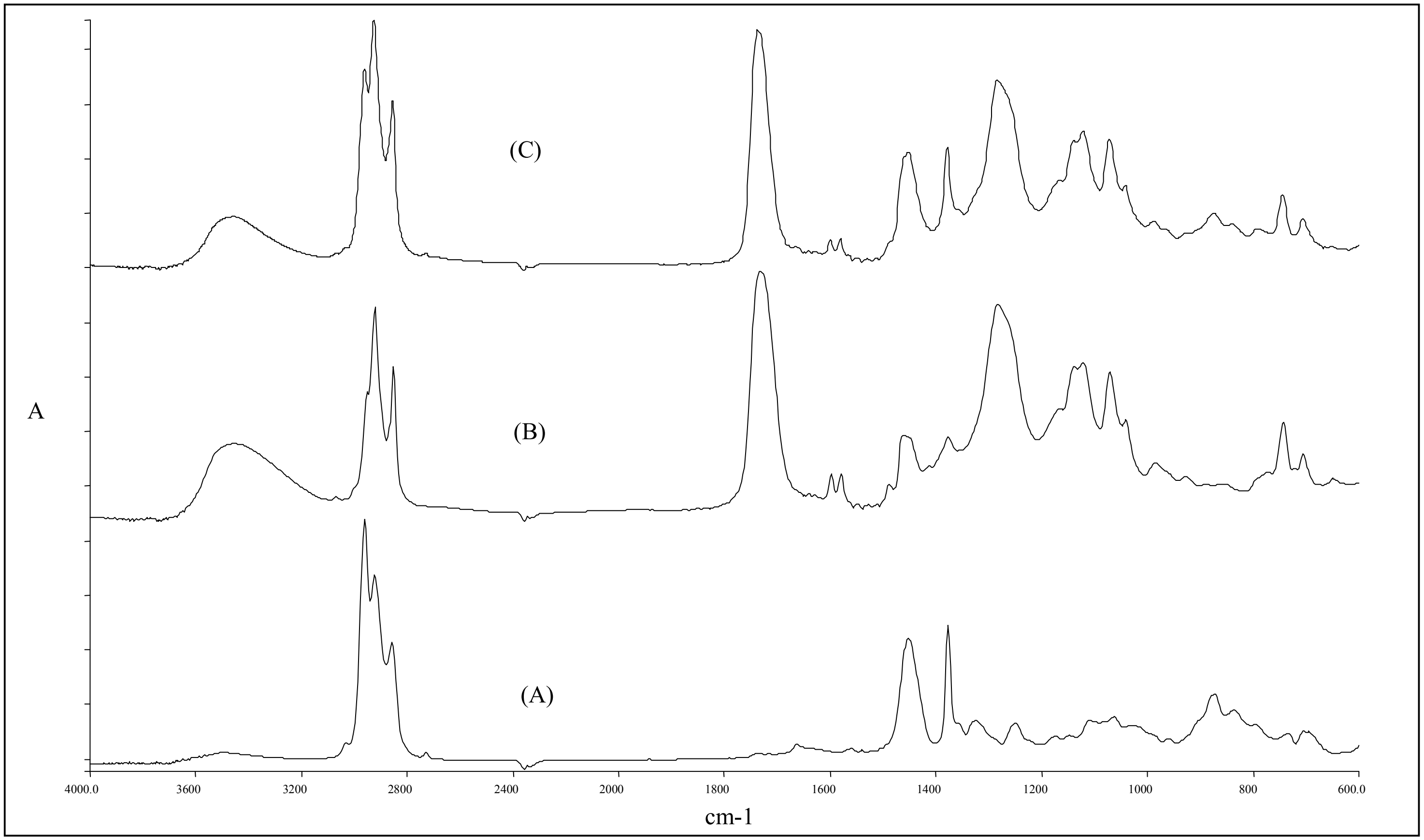


Figure 3.8 FTIR spectra of the initial ENR (A); alkyd A1 (B) and ENR/A1 (C).

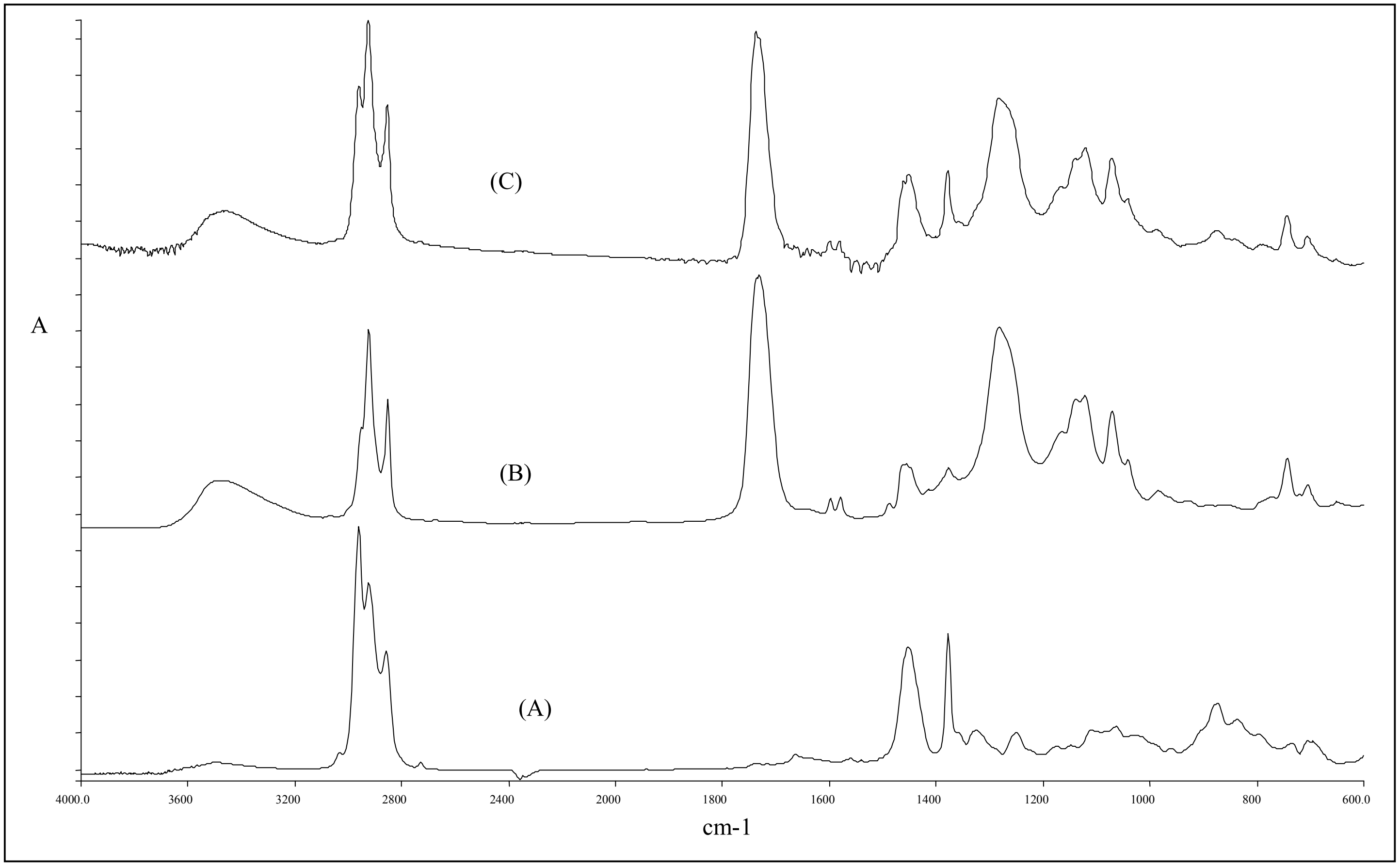


Figure 3.9 FTIR spectra of the initial ENR (A); alkyd A2 (B) and ENR/A2 (C).

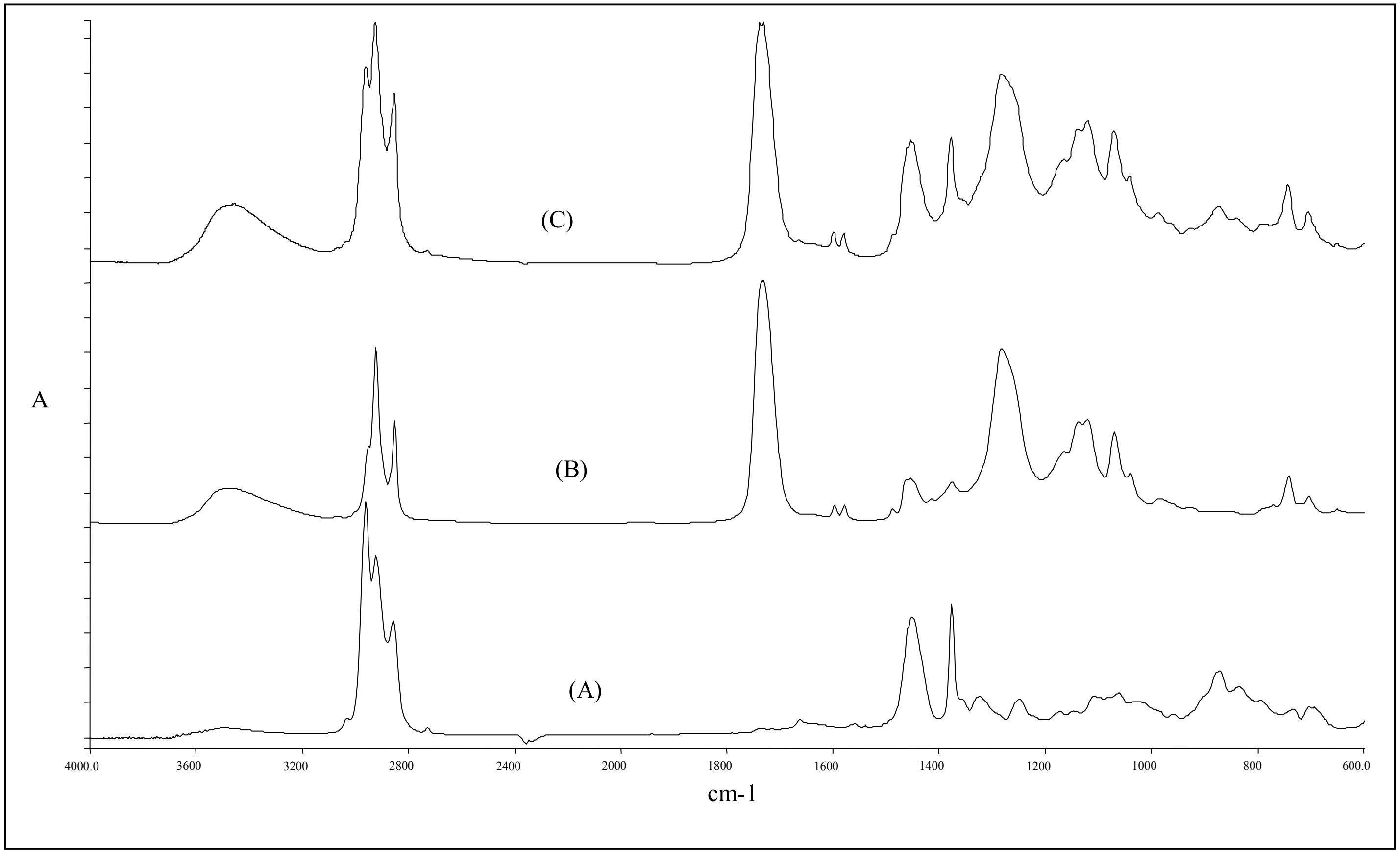


Figure 3.10 FTIR spectra of the initial ENR (A); alkyd A3 (B) and ENR/A3 (C).

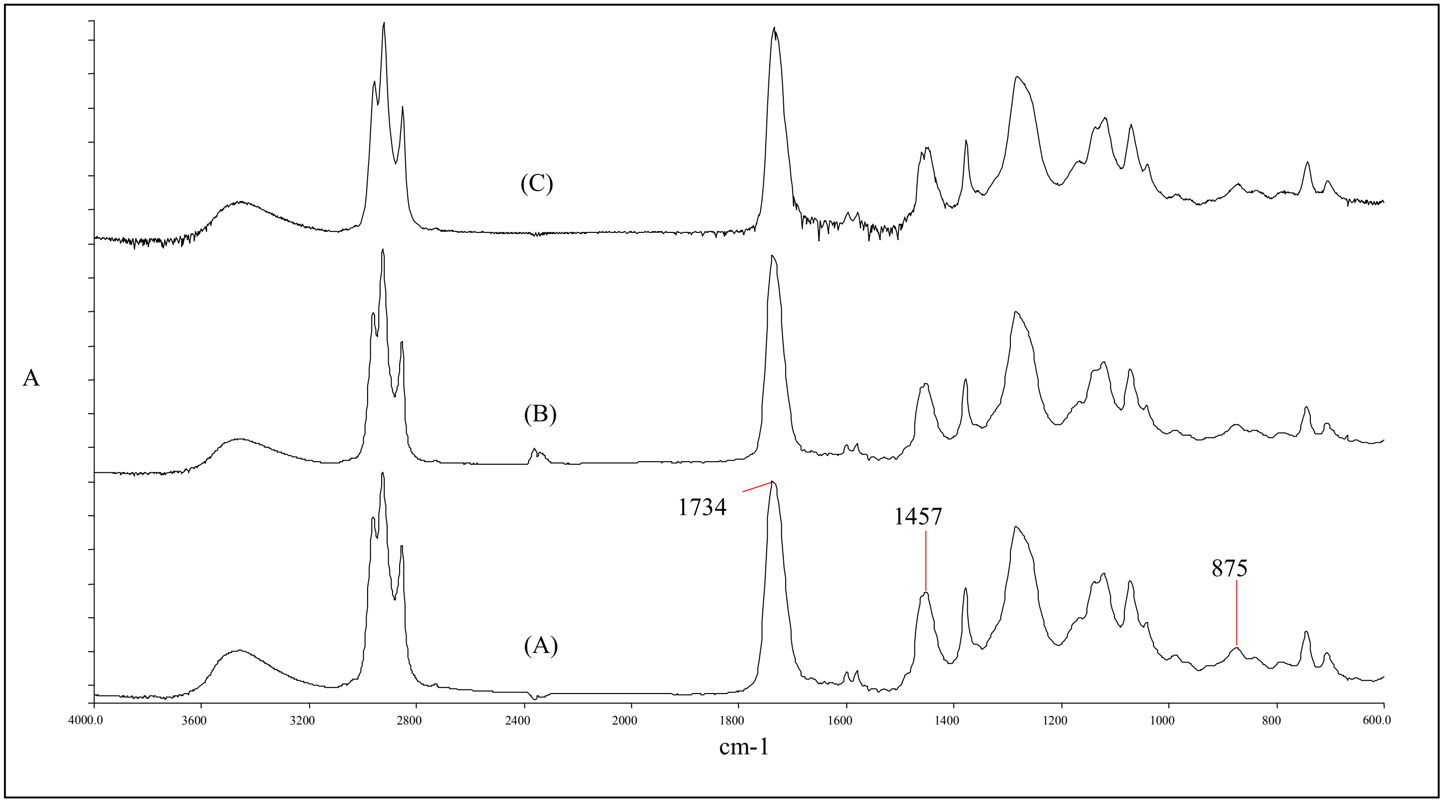


Figure 3.11 FTIR spectra of the ENR/A1 at different reaction time: 1 week (A); 1 month (B) and 3 months (C).

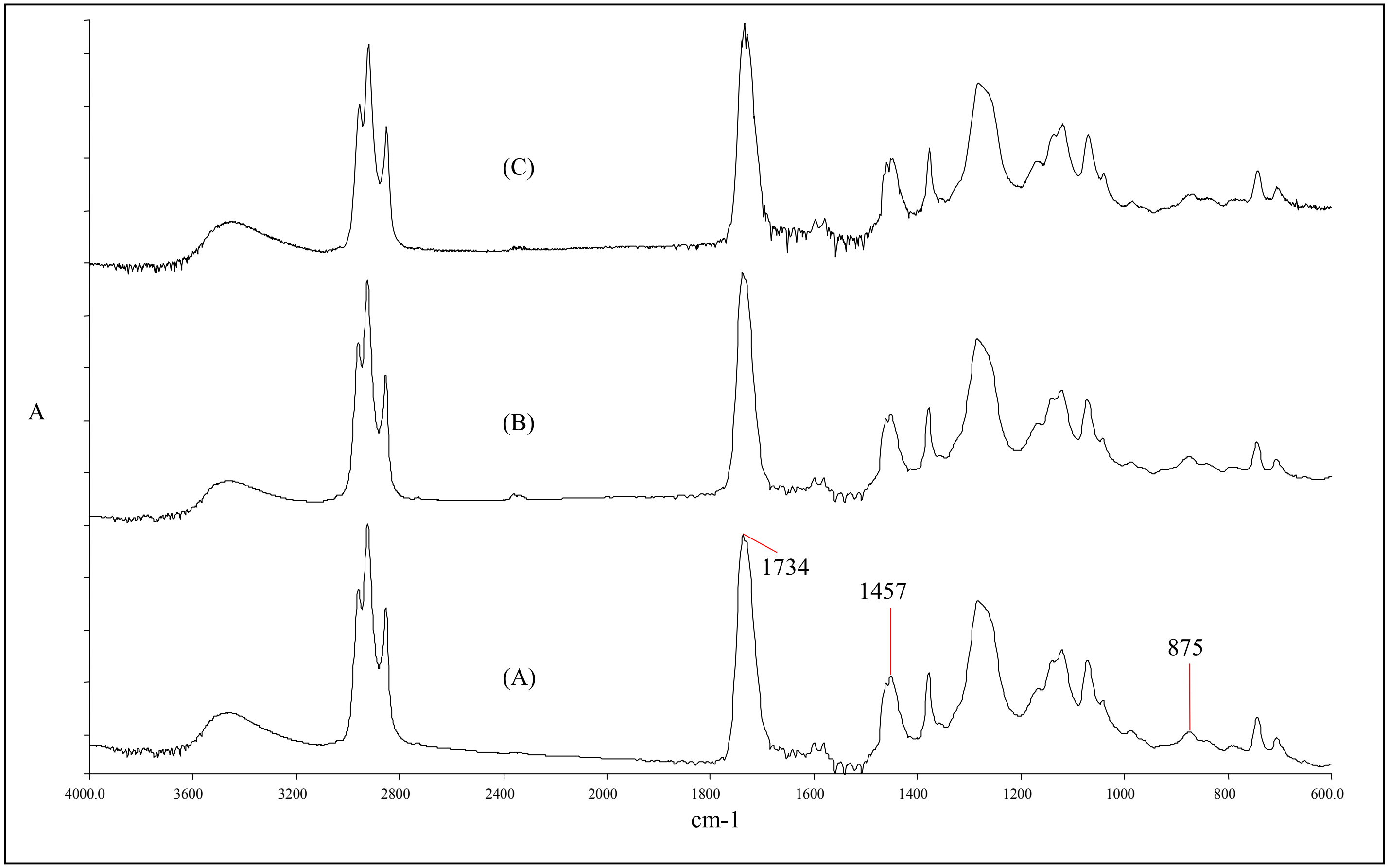


Figure 3.12 FTIR spectra of the ENR/A2 at different reaction time: 1 week (A); 1 month (B) and 3 months (C).

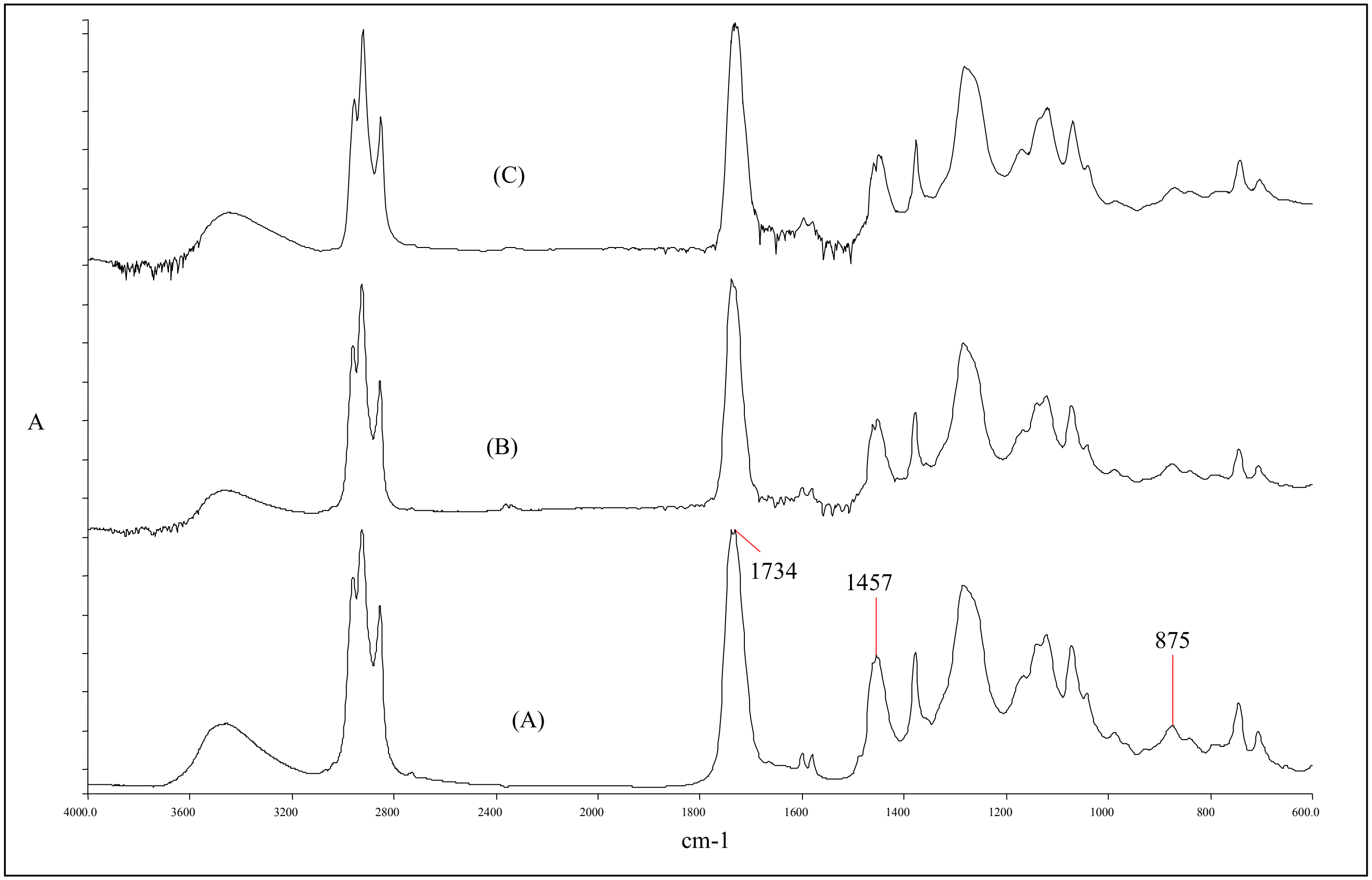


Figure 3.13 FTIR spectra of the ENR/A3 at different reaction time: 1 week (A); 1 month (B) and 3 months (C).

The FTIR spectra of ENR/A1, ENR/A2 and ENR/A3 taken at various reaction times are shown in Figure 3.11, Figure 3.12 and Figure 3.13, respectively. From these figures, it seems obvious that the intensity of the peak assigned to symmetric epoxy ring deformation at 875 cm^{-1} has decreased after prolonged reaction duration. However, other peaks did not show any significant changes.

It is worthy to note that as the reaction progressed, the concentration of the reactive functional groups in ENR/Alkyd changed. By measuring the changes in absorbance of specific functional group periodically, the course of reaction in the blends could be followed. This could be done by further calculation on the ratio of the absorbance of a selected peak to the reference peak so as to reflect the concentration of the functional groups in the ENR/Alkyd blends. The peak at 1457 cm^{-1} was taken as the reference because the C-H bending of $–CH_2$ was not expected to undergo any change during the reaction.

Table 3.12, Table 3.13 and Table 3.14 show the calculated ratio of the absorbance at 1734 cm^{-1} and 873 cm^{-1} during the reaction time of ENR/A1, ENR/A2 and ENR/A3 at different reaction times.

Table 3.12

Absorbance ratio of A_{873}/A_{1457} and A_{1734}/A_{1457} for ENR/A1 at different reaction times

Reaction time	A_{873}/A_{1457}	A_{1734}/A_{1457}
1 week	0.5142	2.4181
1 month	0.5023	2.5298
3 months	0.4241	2.8521

Results in Table 3.12 indicates that the absorbance ratio of C=O stretching at 1734 cm^{-1} increased about 1.2 times from the initial amount after ENR/A1 has reacted at ambient temperature for three months. This shows good correlation with a decrease in the absorbance ratio of symmetric epoxy ring deformation at 875 cm^{-1}, which is about also 1.2 times from the initial amount within the same reaction duration. This similar trend was also observed in ENR/A3.

Table 3.13

Absorbance ratio of A_{873}/A_{1457} and A_{1734}/A_{1457} for ENR/A2 at different reaction times

Reaction time	A_{873}/A_{1457}	A_{1734}/A_{1457}
1 week	0.6339	1.9257
1 month	0.3981	3.0546
3 months	0.3249	3.6244

Table 3.14

Absorbance ratio of A_{873}/A_{1457} and A_{1734}/A_{1457} for ENR/A3 at different reaction times

Reaction time	A_{873}/A_{1457}	A_{1734}/A_{1457}
1 week	0.4069	2.6449
1 month	0.3733	3.0791
3 months	0.3030	3.4848

For ENR/A3, the absorbance ratios of epoxy groups as shown in Table 3.14 decreased consistently with the increase of the C=O stretching, where the difference from the initial amount was about 1.3 times. With reference to Table 3.13, ENR/A2 reacted to generate about twice the amount of C=O groups and show good correlation with the amount of decrease in the epoxy group.

In the comparison of the changes in the absorbance ratio at 1734 cm^{-1}, it seems apparent that more ester linkages are formed in ENR/A2 among the three blends. In fact, the peak at 1734 cm^{-1} owing to the C=O stretching of –COOH overlapped with the C=O stretching of ester in which the C=O stretching of –COOH group was not expected to undergo any changes during the reaction of ENR and alkyd.

Furthermore, A1 had 17% more –OH group than A3 and yet showed similar reactivity due to their similar carboxylic content; while A2 was more reactive than A1 or A3 toward rubber epoxy group due to its higher carboxylic content. Therefore, the formation of ester linkages in ENR/Alkyd blends was more likely due to the predominant reaction of the carboxylic groups with rubber epoxy rather than the hydroxyl groups with rubber epoxy at ambient temperature.

3.4.3 Percentage of swelling in toluene

Upon drying, the reacted ENR could not be redissolved in toluene, and it formed a gel when soaked in toluene for 20 hours. The amount of crosslinking in the gel can be reflected from the amount of toluene it can hold per unit weight of the sample. The more crosslinked ENR would absorb less toluene and hence would have a smaller swelling capacity. The percentage of swelling of the reacted ENR is defined by the following equation.

$$\%\ \text{Swell} = \frac{\text{swollen weight - original weight}}{\text{original weight}} \times 100\% \qquad [3.1]$$

With reference to equation [3.1], the swelling results for ENR/A1, ENR/A2 and ENR/A3 were calculated and shown in Table 3.15, Table 3.16 and Table 3.17, respectively. The calculated swelling capacities of the crosslinked ENR from the reaction with A1, A2 and A3, were then summarized in Table 3.18.

Table 3.15

% swelling of the crosslinked ENR/A1 in toluene

	Determinations		
	First	**Second**	**Third**
Original weight of ENR/A1/ g	0.4027	0.3961	0.3962
Weight of mesh + gel/ g	19.8115	19.0088	20.9971
Weight of mesh/ g	11.0407	10.2906	12.1957
Swollen weight* of ENR/A1/ g	8.7708	8.7182	8.8014
% Swell	2078	2101	2121
Average % Swell	2100		

* where, Swollen weight = (Weight of mesh + gel) – Weight of mesh

Table 3.16

% swelling of the crosslinked ENR/A2 in toluene

	Determinations		
	First	**Second**	**Third**
Original weight of ENR/A2/ g	0.3937	0.3923	0.4074
Weight of mesh + gel/ g	8.0307	7.2739	8.0333
Weight of mesh/ g	4.8906	4.2626	4.8814
Swollen weight* of ENR/A2/ g	3.1401	3.0113	3.1519
% Swell	698	668	674
Average % Swell	680		

* where, Swollen weight = (Weight of mesh + gel) – Weight of mesh

Table 3.17

% swelling of the crosslinked ENR/A3 in toluene

	Determinations		
	First	**Second**	**Third**
Original weight of ENR/A3/ g	0.4002	0.4015	0.4006
Weight of mesh + gel/ g	13.2630	13.1455	20.5108
Weight of mesh/ g	4.6587	4.4972	11.9146
Swollen weight* of ENR/A3/ g	8.6043	8.6483	8.5962
% Swell	2050	2054	2046
Average % Swell	2050		

* where, Swollen weight = (Weight of mesh + gel) – Weight of mesh

Table 3.18

Summary of the % swelling of the crosslinked ENR in toluene

Crosslinked ENR	% swelling
ENR/A1	2100
ENR/A2	680
ENR/A3	2050

As seen in Table 3.18, all alkyds have caused crosslinking in ENR. Among the three blends, ENR/A2 exhibited the lowest percentage of swelling, which implied that ENR/A2 had the highest degree of crosslinking where this highly crosslinked structure would have a smaller swelling capacity to absorb toluene. Owing to the higher carboxylic content, A2 showed higher reactivity towards the epoxy groups in rubber compared to A1 and A3.

On the other hand, the equilibrium degree of swelling for a swollen rubber network is related to the concentration of physical effective crosslink density[189]. Thus, the crosslink density in the blends can be determined from the Flory-Rehner equation[190],

$$- \ln (1 - V_r) - V_r - \chi V_r^2 = 2 \rho V_0 \eta_{phys} V_r^{1/3} \qquad [3.2]$$

where, V_r is the volume fraction of the rubber in the swollen gel, χ is the polymer-solvent interaction parameter, ρ is the density of rubber and V_0 is the molar volume of solvent.

It is worthy to note that when the rubber was brought into contact with toluene, two opposing forces were experienced, which caused the segment in between crosslink to swell[191-194]. The driving force for swelling was due to the decrease in Gibbs energy during the mixing of toluene with the polymer particles, while the elastic force in rubber had caused the extension of its particles to act against the swelling. At equilibrium, these two forces were balanced due to the enthalpy and entropy of mixing the solvent molecules and the polymer segments in the swollen network. This happened when the volume fraction of the polymer in the swollen gel reached a characteristics value of V_r. The modulus of swollen gel, G is described by the following equation.

$$G = \frac{RT\rho}{M_c \times V_r} \qquad [3.3]$$

where, R is the gas constant (i.e. 8.314 J K^{-1} mol^{-1}), T is the temperature at 25°C (or 298.15 K), ρ is the density of rubber, M_c is the number average molecular weight between crosslinks and V_r is the volume fraction of swollen rubber. Both M_c and V_r can be expressed in the following equations [3.4] and [3.5], respectively.

$$M_c = \frac{-\rho V_0 V_r^{1/3}}{\ln(1 - V_r) + V_r + \chi V_r^2} \qquad [3.4]$$

where, ρ is the density of rubber and V_0 is the molar volume of toluene (i.e. 106.11 mL mol^{-1}), the value of χ for rubber and solvent interaction is 0.42*.

$$V_r = \frac{1}{(1 + Q_m)} \qquad [3.5]$$

where, Q_m is the volume ratio of solvent in gel and can be expressed as follows

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*Orwoll, R. A.; Arnold, P. A. In Physical Properties of Polymer Handbook, Mark, J. E., Ed.; Springer: New York, 2006, Chap. 14.

$$Q_m = \frac{W_g - W_2 \big/ \rho'}{W_2 \big/ \rho} \qquad [3.6]$$

where, W_g and W_2 are the weights of swollen and original rubber respectively, ρ' is the density of toluene at 25°C (i.e. 0.867 g mL^{-1}) and ρ is the density of rubber. ρ can be expressed as follows

$$\rho = \frac{W_1}{V_1}, \text{g mL}^{-1} \qquad [3.7]$$

where, W_1 is the weight of the mixture of methanol and glycerol, V_1 is the volume of density bottle. V_1 is equal to the weight of water in density bottle during calibration, because density of water is always 1 g/mL.

Combining equations [3.2] and [3.4], we can obtain a relationship between the physical effective crosslink density, η_{phy}, and the number average molecular weight between crosslink, M_c as given in equation [3.8].

$$\eta_{phys} = \frac{1}{2M_c} \qquad [3.8]$$

Taking χ = 0.42 and by assuming the ENR-toluene interaction constant is approximately the same as that of natural rubber-toluene interaction constant, the rest of the volume fractions and densities could be measured experimentally. Table 3.19 shows the values of η_{phy} , M_c and G for the crosslinked ENR samples.

Table 3.19

Physical effective crosslink density, η_{phy}, number average molecular weight between crosslink, M_c, and modulus of swollen crosslinked ENR, G

Crosslinked ENR	η_{phy} / 10^{-6} mol $g^{-1}RH^{-1}$	M_c / 10^5 g mol^{-1}	G / J mL^{-1}
ENR/A1	1.85	2.70	0.25
ENR/A2	14.7	0.34	0.66
ENR/A3	2.15	2.32	0.26

With reference to Table 3.19, the physical effective crosslink density in ENR/A3 is similar to that of ENR/A1 (i.e. within 3 % experimental error) but that of ENR/A2 is significantly higher. However, the physical effective crosslink density of ENR/A3 is slightly higher than that of ENR/A1 and this could be attributed to the alkyd structure of A3 being more complex than A1, presumably causing more chain entanglements in ENR/A3.

On the other hand, the M_c for ENR/A2 is much smaller since the average molecular weight between crosslink, M_c is inversely proportional to the crosslink density. The G values of all the three samples are very low, several orders of magnitude smaller than the typical G value for vulcanized rubbers.

Overall, the above results show that A2 exhibited more extensive crosslinking reaction with rubber epoxy compared to A1 or A3. This could be attributed to the fact that A2 contained about four times the amount of carboxylic groups that of A1 and A3, despite A1 and A3 had higher ratio of –OH to –COOH. Therefore, it seems apparent that the hydroxyl groups did not react significantly with ENR at ambient temperature. Hence, for the ENR/Alkyd blends, the predominant crosslinking reaction could be represented as in Figure 3.14.

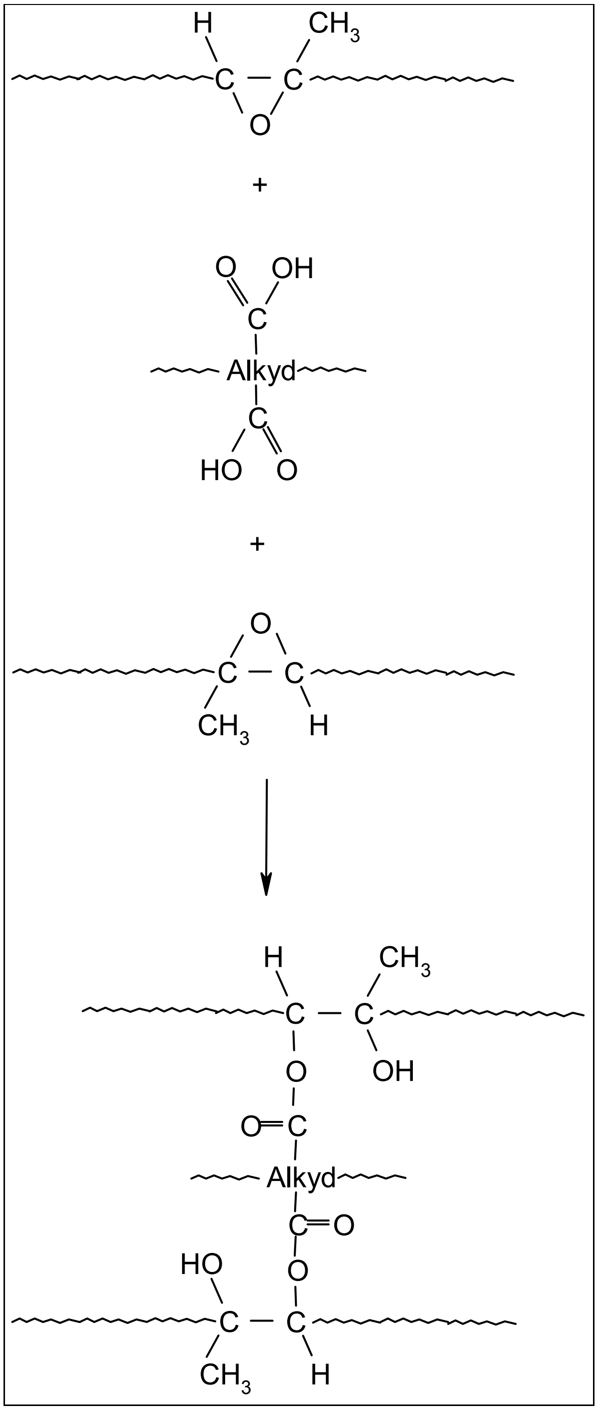


Figure 3.14 The predominant crosslinking reaction between ENR and alkyd

3.5 Reactions in the ENR/A4 blend

The subsequent investigation was to study the thermal properties and molecular structures of the ENR/alkyd blend using ^{1}H-NMR, FTIR and DSC. This could be done by synthesizing alkyd A4 incorporated with higher carboxylic acid content. This alkyd was then blended with ENR in which the blend was noted as ENR/A4. The blend was then reacted at ambient temperature and the reaction was expected to give significant results which are within the detection limit of the instruments.

3.5.1 Synthesis of alkyd A4

About 11.4 parts of MA was added to 100 parts of A1 to synthesize MA-modified alkyd, A4 at 130-133°C. Since this alkyd was prepared under the same reaction conditions as alkyd A2, the plausible mechanism in the preparation of A4 was expected to be similar as that of A2 as shown in the previous Figure 3.3.

3.5.1.1 Changes in acid numbers during synthesis of alkyd A4

The progress of reaction for A4 was followed by determining the acid number values during the synthesis of A4. Results of acid number titration are tabulated in Table 3.20 and the changes in acid number as the function of time for A4 are plotted in Figure 3.15.

With reference to Table 3.20, the percentage of conversion for A4 was calculated as [100 x (67.3 -28.9) ÷ 67.2], i.e. 57%. This indicates that although the reaction of MA with the hydroxyl groups of A1 has proceeded slowly, it was not completed [100 x (28.9 ÷ 67.3)], i.e. 43% of half-ester of the anhydride was still remained in A4.

Table 3.20

Acid number for A4 during synthesis

Reaction time/ minutes	Acid number/ mg KOH g^{-1}
0	67.3*
63	59.1
180	44.0
240	42.7
300	40.5
360	38.2
420	35.4
480	31.8
540	28.9

* where,

$$\text{Initial acid number} = \frac{56100 \times e_A\,(\text{MA})}{\Sigma W} + \text{Final acid number of A1}$$

$$\text{Initial acid number of A4} = \frac{56100 \times 0.410}{351.2999} + 1.8$$

$$= 67.3 \text{ mg KOH g}^{-1}$$

As shown in Figure 3.15, acid numbers decrease consistently as the reaction proceeded, indicating the successful incorporation of MA to the hydrocarbon chain of alkyd resin. There was no water of reaction produced and the reaction has reached the targeted acid number of about 28.9 mg KOH g^{-1} within 540 minutes.

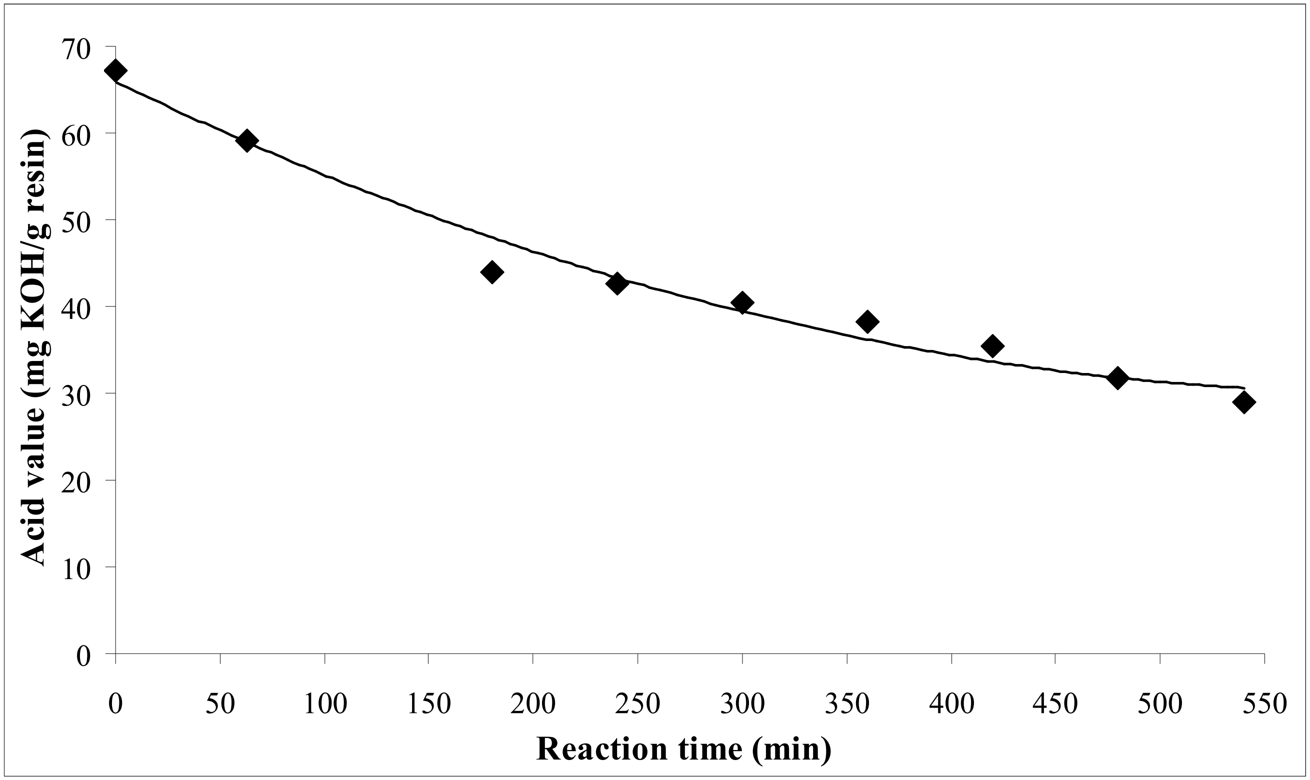


Figure 3.15 Changes in acid numbers with reaction time during the synthesis of alkyd A4.

3.5.1.2 Properties of alkyd A4

Table 3.21 summarizes the properties of A4 which was determined from the titration method, together with the estimated values calculated from the titration results.

Table 3.21

Properties of alkyd A4

Property	Value
Hydroxyl number/ mg KOH g^{-1}	84.3
Acid number/ mg KOH g^{-1}	28.9
–OH concentration* / mol g^{-1}	1.5×10^{-3}
–COOH concentration* / mol g^{-1}	5.2×10^{-4}
Ratio of –OH to –COOH	3
Percentage of conversion/ %	57.0

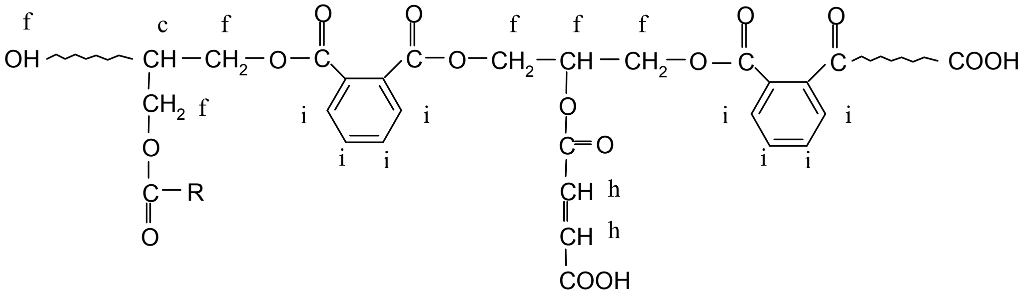
* where,

$$\text{- OH concentration} = \frac{\text{Hydroxyl number}}{56100}\text{; - COOH concentration} = \frac{\text{Acid number}}{56100}.$$

From Table 3.21, the titration of A4 with standardized potassium hydroxide solution shows that A4 contained 5.2×10^{-4} mol g^{-1} of –COOH groups, giving an acid number of 28.9 mg KOH g^{-1} and this carboxylic amount is about 77 % much higher than A2.

3.5.1.3 ^{1}H-NMR spectroscopy

The molecular structure of alkyd A4 as shown in Figure 3.16 could be determined from the NMR spectrum. Figure 3.17 shows the ^{1}H-NMR spectrum of A4.



where, R = Fatty acid which contains oleic acid, $C_{18:1}$ with

structure $CH_3(CH_2)_7CH{=}CH(CH_2)_6CH_2COOH$
a b g g b e

and linoleic acid, $C_{18:2}$ with structure

$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_6CH_2COOH$
a b g g d g g b e

Figure 3.16 Molecular structure of alkyd A4 as could be determined from ^{1}H-NMR spectrum

From Figure 3.17, the peak (a) appeared at 0.8 ppm is assigned to the methyl protons in the chain end of the free fatty acids. The strong resonance (b) at 1.2 ppm is due to the methylene protons of the free fatty acids; while the weaker resonance (c) at 1.5 ppm is assigned to the methine protons of the monoglyceride unit. The subsequent small peak (d) at 2.0 ppm is attributed to the methylene protons in a diallylic group which was found in the linoleic acid of the PKO free fatty acids. On the other hand, the peak (e) appeared at 2.3 ppm is due to the methylene protons adjacent to carbonyl group.

It was found that both methylene and methine protons on the glycerol unit which attaches directly to the oxygen atom of an ester group are deshielded due to the electronegativity of oxygen and thus appears together with the methine protons as a broad peak (f) shown at a lower field of 4.2-4.3 ppm. On the other hand, the peak (g) which appears at 5.4 ppm is attributed to the vinylic proton of the unsaturated oleic ($C_{18:1}$) and linoleic ($C_{18:2}$) acids which are found in the PKO free fatty acids. The peak (h) at 6.2 ppm is due to the methine protons of the ring-opened MA. The small peak at 7.2 ppm is assigned to the $CHCl_3$ in the $CDCl_3$ solvent; while the two peaks (i) locate at 7.5 ppm and 7.7 ppm represents the vinylic protons in the phthalate unit of PA.

3.5.1.4 FTIR spectroscopy

The overlaid FTIR spectra of A1 and A4 are shown in Figure 3.18. As shown in Figure 3.18, since A4 was incorporated with higher amount of MA, the weaker peaks of MA, particularly due to the aliphatic C=C double bonds stretching and =C-H out of plane bending modes, are observed at 1640 cm^{-1} and 820 cm^{-1} respectively in the IR spectrum of A4.

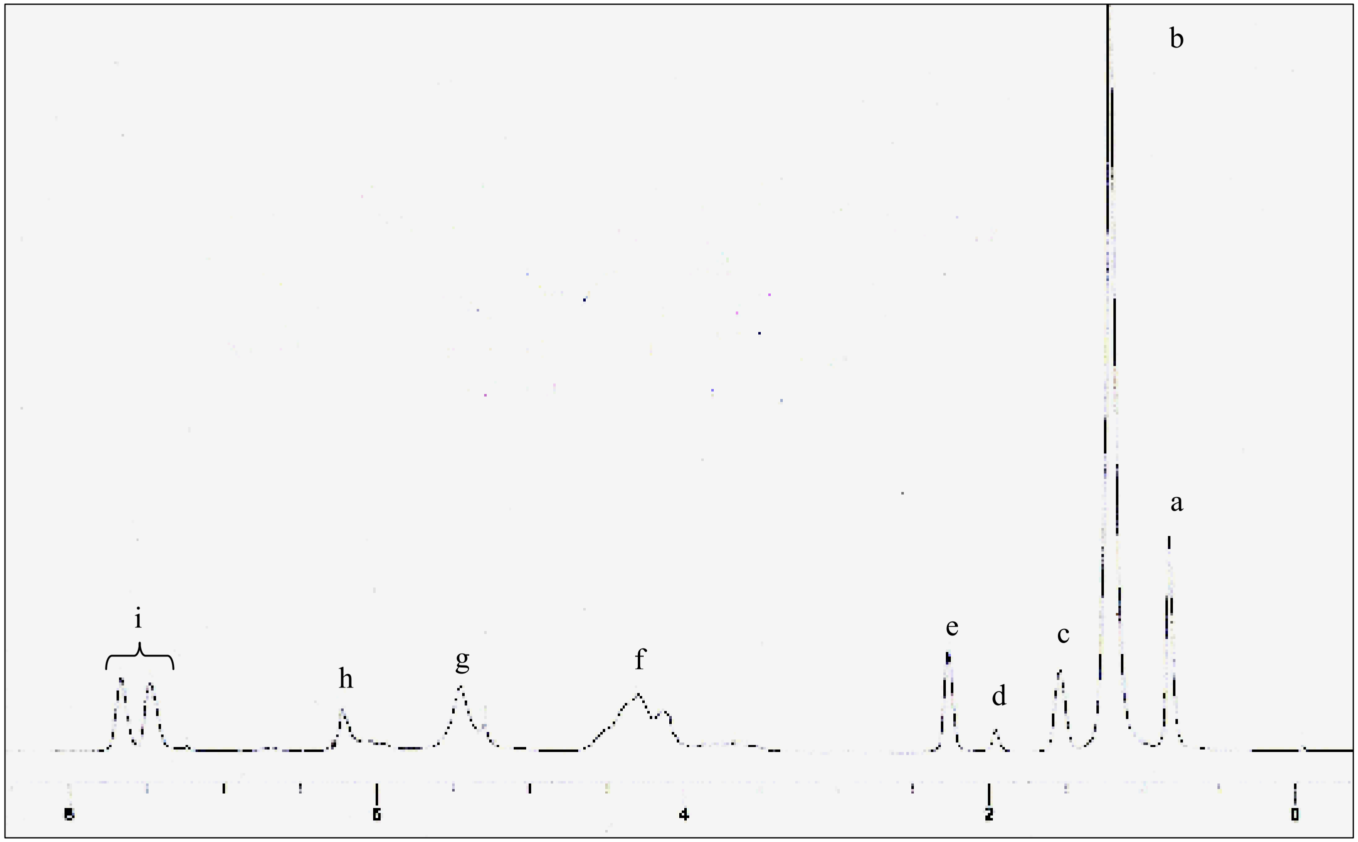


Figure 3.17 ^{1}H-NMR spectrum of alkyd A4

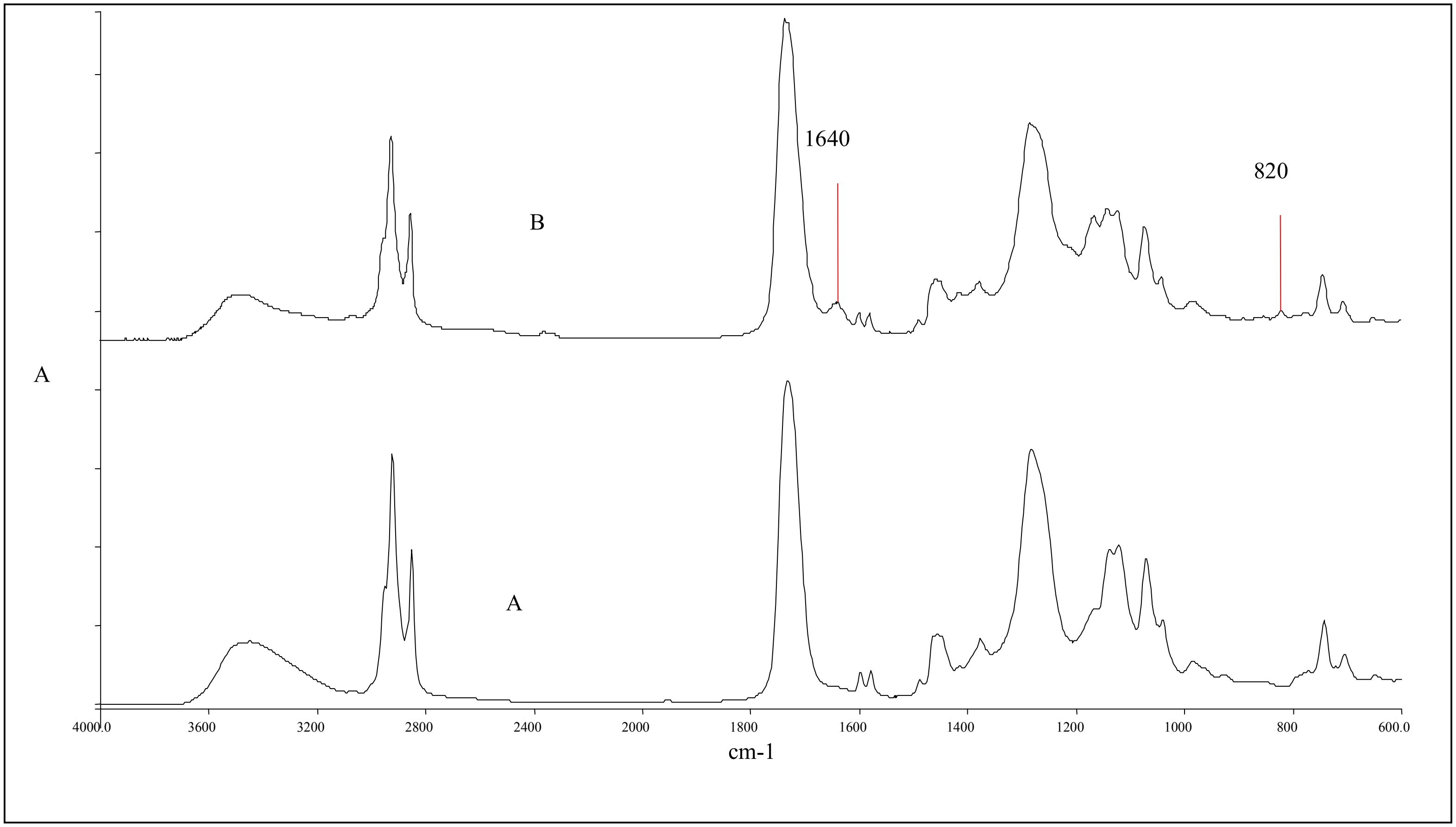


Figure 3.18 FTIR spectra of alkyds: A1 (A) and A4 (B).

3.5.2 Preparation of ENR/A4 blends

The initial mixing of ENR with A4 solutions has produced a freely flowable solution. The ENR reacted with A4 at ambient temperature and a progressive increase in viscosity of the mixture could be observed visually. A jelly-like material was formed within a few hours. After the specified reaction time, the reacted ENR was precipitated with methanol and the sample was analyzed by DSC, ^{1}H-NMR and FTIR.

3.5.2.1 DSC analysis

In this study, three ENR/A4 blends were prepared at different ratio of –COOH to epoxy groups in the mixture and the blends were coded as $A4_{0.5}$, $A4_{1.0}$ and $A4_{1.6}$, where the subscripts denoted the amount ratio of –COOH to epoxy groups in the mixture. These blends were then all reacted at ambient temperature. The reacted ENR was subsequently recovered by methanol precipitation and the sample was analyzed by DSC. The composition of these blends is shown in Table 3.22.

Table 3.22

Composition of initial ENR/A4 mixture

ENR/A4	Volume of solution (mL)*		Dry solid (g)		Amount of functional groups in the mixture (mol)		Ratio of initial –COOH to epoxy groups
	ENR	A4	ENR	A4	Epoxy	–COOH	
$A4_{0.5}$	32	37	3.84	25.16	2.53×10^{-2}	1.31×10^{-2}	0.5
$A4_{1.0}$	32	75	3.84	51.00	2.53×10^{-2}	2.65×10^{-2}	1.0
$A4_{1.6}$	19	66	2.28	44.88	1.50×10^{-2}	2.33×10^{-2}	1.6

* where, the concentrations of A4 and ENR solutions were 68 % w/v in toluene and 12 % w/v in toluene, respectively.

The preparation of $A4_{1.0}$ blend which contained equimolar ratio of –COOH to epoxy groups served as an example of calculation. $A4_{1.0}$ was prepared by mixing 32 mL of ENR solution (12 % w/v in toluene), which contained about 3.84 g of ENR mixed with 75 mL of A4 solution (68 % w/v in toluene), which contained 51.00 g of A4. In the initial mixture, the 3.84 g of ENR 50 contain approximately 3.84 g x 6.58 x 10^{-3} mol g^{-1} of epoxy group (i.e. 2.53 x 10^{-2} mol); while 51.00 g of A4 contained 51.00 g x 5.2 x 10^{-4} mol g^{-1} of –COOH group (i.e. 2.65 x 10^{-2} mol). The initial amount of –COOH and epoxy groups was in equimolar.

When ENR/A4 blends were subjected to DSC analysis, the DSC thermograms of all blends exhibited only one glass transition temperature (T_g) in the plot. This suggests that the blends are miscible over the whole composition ranges upon reacted at ambient temperature. This result is consistent with the observation that A4 has formed a clear dilute solution with ENR during the preparation of the blends.

The glass transition temperature of a binary blend could be estimated using the following Fox equation[195].

$$\frac{1}{T_{gb}} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \qquad [3.9]$$

where, T_{gb} is the theoretical glass transition temperature or T_g (theory); W_1 and W_2 are the weight fractions of the blending component 1 and 2, respectively; T_{g1} and T_{g2} are the glass transition temperatures or T_g (onset), of the blending component 1 and 2, respectively. This T_g (onset) was obtained from the DSC measurement.

An example of calculation to determine the T_g (theory) of $A4_{0.5}$ is shown as follows:

$$\frac{1}{T_{gb}} = \frac{0.135}{247.1} + \frac{0.865}{239.9}$$

$$T_{gb} = 240.8\text{K}$$

where, T_{g1} and T_{g2} are 247.1 K and 239.9 K by assuming the components 1 and 2 in $A4_{0.5}$ as ENR and A4, respectively; and the W_1 and W_2 are 0.135 and 0.865; T_{gb} refers to the T_g (theory) of $A4_{0.5}$.

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 3.23.

Table 3.23

Glass transition temperatures of ENR/A4 blends

Blend**	**Glass transition temperature, K**	
	T_g (onset)*	**T_g (theory)**
$A4_{0.5}$	255.6	240.8
$A4_{1.0}$	253.5	240.4
$A4_{1.6}$	241.8	240.2

* where, the T_g (onset) of ENR and A4 are 247.1 K and 239.9 K, respectively.

** All the blends were reacted at ambient temperature for 3 hours.

From Table 3.23, a decrease in T_g (onset) is observed when the amount ratio of –COOH to epoxy groups in the mixture increased from 0.5 to 1.6. This shows that the addition of alkyd A4 to the blend would induce plasticization effect which depressed the T_g (onset) of the blend.

On the other hand, the T_g (onset) of all blends exhibited positive deviation from the T_g (theory). This could be attributed to the strong interpolymer interactions that occurred between ENR and A4. This result suggests that the presence of A4 in the ENR/A4 blends had successfully modified the main chain structure of ENR through the formation of ester linkages.

However, the T_g (onset) of both $A4_{0.5}$ and $A4_{1.0}$ exhibited far more positive deviation than $A4_{1.6}$ from the T_g (theory). Among the three blends, only the T_g (onset) of $A4_{1.6}$ occurred at the temperature intermediate between those of the pure components of the blends. This result indicates that crosslinking reaction could occur in the ENR/A4 blends upon reacted for 3 hours at ambient temperature, provided that the blends contained equimolar of –COOH to epoxy groups ($A4_{1.0}$) or with the epoxy group in excess ($A4_{0.5}$). This produced crosslinked structures with more parts of chain tied closer together which subsequently caused a decrease in the free volume of mixture that might increase the chain stiffness, restrict the chain mobility in the mixture and thus increase the T_g (onset) of $A4_{0.5}$ and $A4_{1.0}$ significantly.

A more extensive examination of the effect of reaction time on the crosslinking reaction in $A4_{1.0}$ was carried out. The T_g (onset) of $A4_{1.0}$ obtained from DSC measurement is tabulated in Table 3.24.

From Table 3.24, the T_g (onset) of $A4_{1.0}$ deviates more positively from the calculated T_g (theory), i.e. 240.4 K with increased of reaction duration. Overall, these T_g (onset) values were not at the temperature intermediate between those of the pure components of the blends. It was apparent that the –COOH group in alkyd has reacted with the epoxy group in ENR at a rapid rate and thus crosslinking reaction has occurred in $A4_{1.0}$ after 1 hour or even less than 1 hour of reaction at ambient temperature.

Table 3.24

Glass transition temperature, T_g (onset), for $A4_{1.0}$ reacted at ambient temperature under different reaction times

Reaction time/ hour	T_g (onset)/ K
1	248.2
2	250.3
3	253.5
4	255.4
5	255.8
6	260.0

* where, the T_g (theory) of $A4_{1.0}$ is 240.4 K.

3.5.2.2 ^{1}H-NMR spectroscopy

NMR measurement was utilized to obtain further information about the molecular structure of the reacted ENR. However, ENR and A4 reacted rapidly at ambient temperature to form crosslinked structure which swelled in deuterated chloroform that made it difficult to be examined in liquid state. Therefore, the $A4_{2.0}$ blend was prepared where the subscripts denoted the amount ratio of –COOH was twice the amount of epoxy groups in the blend so that to avoid excessive crosslinking in the blend.

The $A4_{2.0}$ blend was prepared from 10 mL of ENR solution (12 % w/v in toluene), which contained 1.20 g of ENR mixed with 48mL of A4 solution (68 % w/v in toluene), which contained 32.64 g of A4. In the initial mixture, the 1.20 g of ENR 50 would contain 1.20 g x 6.58 x 10^{-3} mol g^{-1} of epoxy group (i.e. 7.90 x 10^{-3} mol); while, 51.00 g of A4 would contain 32.64 g x 5.2 x 10^{-4} mol g^{-1} of –COOH group (i.e. 1.70 x 10^{-2} mol). Thus, the ratio of initial –COOH to epoxy group in $A4_{2.0}$ was 2.2. After reacted for an hour, the blended polymer was precipitated by methanol and dissolved in deuterated chloroform ($CDCl_3$). It was found that the sample could dissolve in $CDCl_3$ and therefore was possible to record the NMR spectrum. Figure 3.19 shows the ^{1}H-NMR spectrum of the initial ENR; while Figure 3.20 shows the ^{1}H-NMR spectrum of the reacted ENR.

From Figure 3.19, the peaks (a) and (d) that appears at 1.3 ppm and 2.7 ppm are due to the methyl and methine protons on the epoxy ring. Three peaks (b), (c) and (e) appear at 1.7 ppm, 2.0 ppm and 5.1 ppm representing the methyl, methylene and vinylic protons on the isoprene unit; while, the peak at 7.2 ppm is attributed to the $CHCl_3$ in the $CDCl_3$ solvent.

From Figure 3.20, the two signals that appear at 3.6 ppm and 3.8 ppm are due to the ring opened structures of the epoxy group. Since the ratio of initial –COOH to epoxy group in $A4_{2.0}$ is more than 1.0 with the reaction time of only an hour, it is expected that the crosslinking reaction as shown in the previous Figure 3.14, has not occurred to a great extent in this blend. Therefore, it seems apparent that epoxy ring-opened structures in $A4_{2.0}$ have formed under the esterification and it should occur prior to crosslinking reaction. The plausible esterification reaction is shown in Figure 3.21.

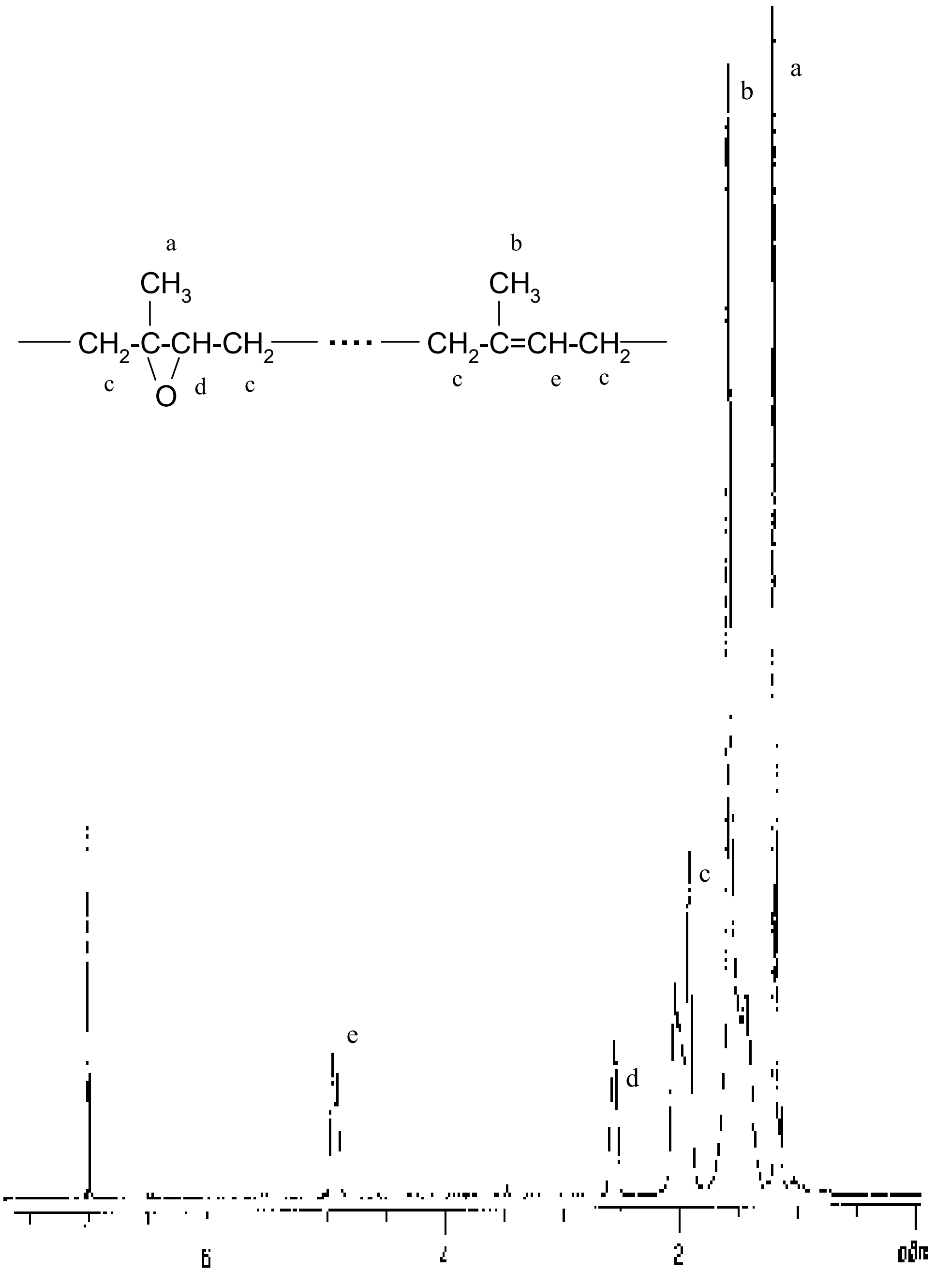


Figure 3.19 The ^{1}H-NMR spectrum of ENR.

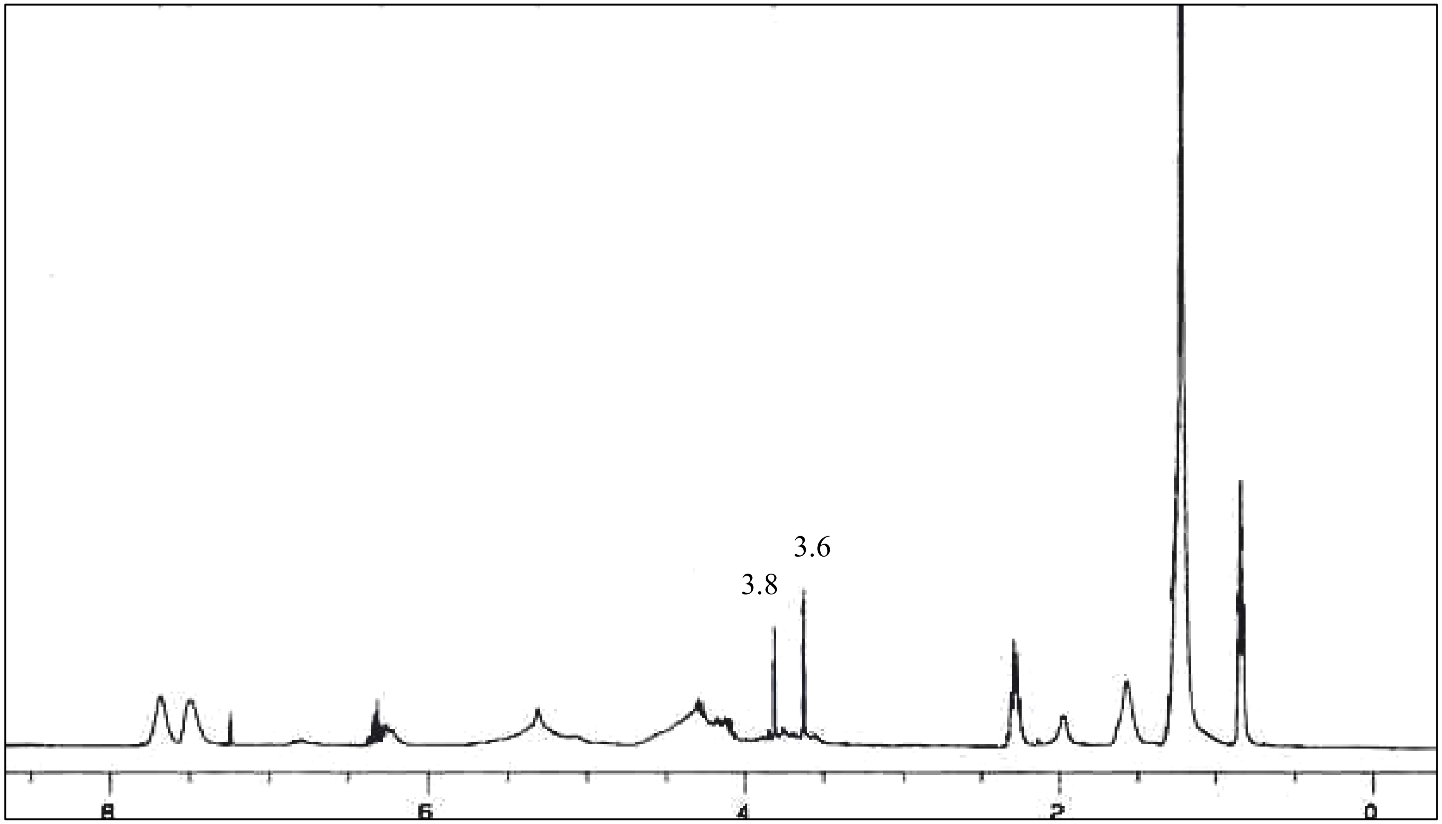
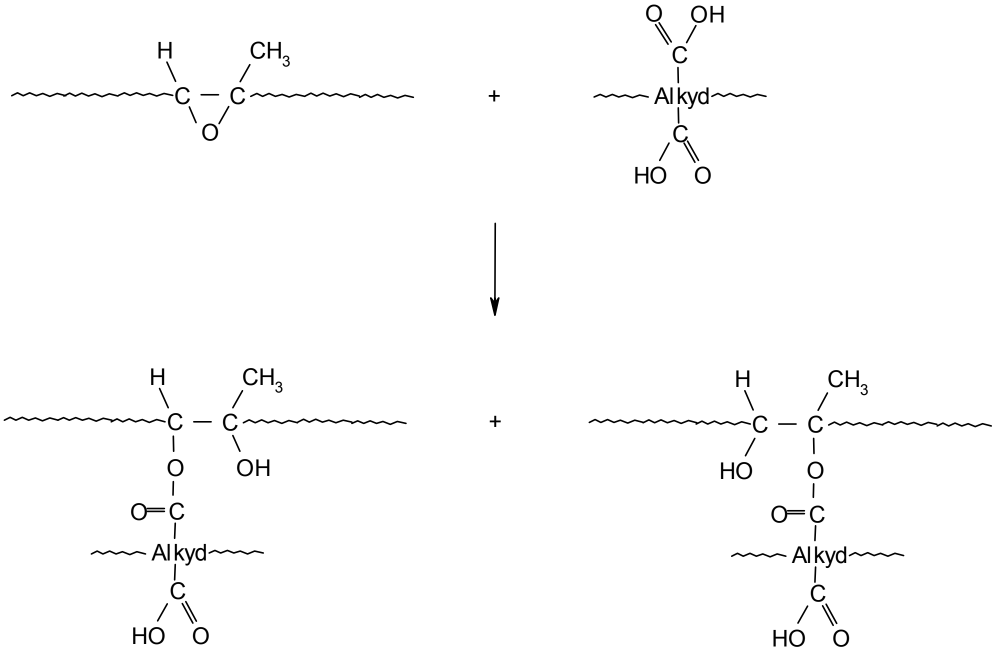


Figure 3.20 The ^{1}H-NMR spectrum of $A4_{2.0}$.



(I) (II)

Figure 3.21 A plausible esterification between ENR and alkyd

With reference to both Figure 3.20 and Figure 3.21, 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. 3.6 ppm since this hydroxyl proton attaches to a carbon atom adjacent to a methyl group which then shields the hydroxyl proton. While, the peak at 3.8 ppm was 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 shifts to a lower field.

3.5.2.3 FTIR spectroscopy

Further investigation of the effect of the reaction time on the $A4_{1.0}$ blend was carried out using the FTIR spectroscopy. Within a few hours of reaction at ambient temperature, it was observed that the viscosity of the blend has increased dramatically, followed by gradual formation of gel. Methanol was added to precipitate the ENR and to remove any unreacted alkyd at the end of the specified time.

FTIR measurement of $A4_{1.0}$ at different reaction times was carried out and the calculated ratios of the IR absorbance at 1731 and 877 cm^{-1} are tabulated in Table 3.25. It is found that within 6 hours of reaction, the absorbance ratio of epoxy groups decreases almost consistently with the increase of the C=O stretching, where the difference from the initial amount is about 1.0-1.3 times. Therefore, this result gives further evidence that esterification has occurred predominantly in $A4_{1.0}$ within 6 hours, where $A4_{1.0}$ contained equimolar of –COOH to epoxy groups.

Table 3.25

Absorbance ratio of A_{873}/A_{1457} and A_{1734}/A_{1457} for $A4_{1.0}$ at different reaction time

Reaction time/hour	A_{873}/A_{1457}	A_{1734}/A_{1457}
1	0.4167	1.2500
2	0.4103	1.3269
3	0.3906	1.6171
4	0.3853	1.6192
5	0.3701	1.6200
6	0.3636	1.6212

* where, the peak at 1457 cm^{-1} was taken as the internal reference peak.

3.6 Summary

The reactions between ENR and alkyds could occur at ambient temperature. The epoxy groups of ENR have reacted predominantly with the carboxylic groups of alkyds to form crosslinked structures. Alkyds with higher carboxylic content could be synthesized by reacting the anhydride of MA partially with the hydroxyl groups of A1 to produce half-esters at lower temperature range.