

## Blends of Phthalic Anhydride-Modified Palm Stearin Alkyds with High Carboxylic Acid Contents with Epoxidized Natural Rubber

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**ABSTRACT:** Solution blends comprised of alkyd having high carboxylic acid ( $-\text{COOH}$ ) content and epoxidized natural rubber (ENR 50, having nominally 50% of the isoprene units converted to epoxide groups) are self-crosslinkable at  $30^\circ\text{C}$  in toluene solution. Two modified palm stearin alkyds with different amounts of  $-\text{COOH}$  groups were synthesized by reacting phthalic anhydride with alkyd containing excess hydroxyl ( $-\text{OH}$ ) groups under controlled conditions, leading to the formation of different amounts of  $-\text{COOH}$  as side-chains. The crosslinking reactions between the alkyds and ENR 50 in toluene solutions were investigated using FTIR and DSC. The compatibility between ENR 50 and alkyd was indicated by the presence of a single glass transition temperature ( $T_g$ ) in the blend. Intercomponent crosslinking reactions have occurred between the epoxide groups of ENR 50 and  $-\text{COOH}$  groups of alkyd with the formation of ester linkages. The crosslink density is proportional to the amount of  $-\text{COOH}$  groups in the alkyd. As the  $-\text{COOH}$  content is increased, the blend produces higher percentage of gel insoluble in toluene. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 153–160, 2013

**KEYWORDS:** crosslinking; differential scanning calorimetry; polymer blends; spectroscopy; gels

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### INTRODUCTION

Blending of polymers has become a popular trend in the industry. This is driven by the aim to produce new material with desired properties to meet new requirements. In addition, blending of polymers benefits the manufacturers as it can be cost effective due to improved processability, product uniformity and scrap reduction.<sup>1</sup> The synergistic properties in the polymer blends are attributed to the miscibility of the components or the favorable chemical interactions between them. Polymers are miscible when there is significant interaction between the constituents resulting in negative free energy of mixing.<sup>2</sup> The various specific interactions responsible for miscibility may include hydrogen bonding, dipole–dipole interactions, ion–ion interactions, ion dipole interactions, or repulsive interactions.<sup>3</sup> Besides, the components in a blend could become miscible when there are chemical reactions between the reactive functional groups in the polymers.<sup>4</sup>

Epoxidized natural rubber (ENR) is a semisynthetic rubber with high commercial value due to its dual functionality of  $-\text{C}=\text{C}-$  and epoxide groups, which could be chemically manipulated for various purposes, such as the development of novel materials or enhancing the properties of rubber. While the  $-\text{C}=\text{C}-$  serves as the site for sulfur vulcanization,<sup>5</sup> the epoxide group allows

ENR to react with many other functional groups.<sup>6,7</sup> ENR could form self crosslinkable blends with a large number of polymers and chemicals. These include the blend of carboxylated nitrile rubber (XNBR)/ENR,<sup>8</sup> Hypalon/ENR,<sup>9,10</sup> PVC/ENR,<sup>11</sup> EPDM/ENR,<sup>12,13</sup> and dodecanedioic acid/ENR.<sup>14,15</sup>

This work focused on the synthesis of phthalic anhydride (PA)-modified palm stearin alkyds with different  $-\text{COOH}$  contents, and the crosslinking reactions between the modified alkyds and ENR 50. Results of this study reveals the potential usage of palm stearin alkyd having carboxylic acid side chains as crosslinking agent in rubber compounding and the blend of the modified alkyd with ENR 50 in toluene solutions was found to be self-vulcanizable at ambient temperature.

### EXPERIMENTAL

#### Materials

Details of the materials used are given in Table I. PA was purchased from DC Chemical Korea. Toluene, calcium hydroxide, potassium hydroxide (KOH) and potassium hydrogen phthalate are reagent grade chemicals from Merck and they were used as received.

#### Preparation of Alkyd 1

Alkyd 1 synthesis comprised of two stages. It started with alcoholysis process, where 385.3 g of palm stearin was allowed

**Table I.** Details of Materials Used

Materials	Description	Source
Epoxidized natural rubber (ENR 50) <sup>a</sup>	Epoxide content = 50 mol %	Rubber Research Institute of Malaysia (RRIM)
	Specific gravity = 1.03 g cm <sup>-3</sup>	
	Mooney viscosity ML(1 + 4) at 100°C = 72	
Palm stearin <sup>b</sup>	Iodine value = 34.2 g I <sub>2</sub> g <sup>-1</sup> oil	Emery Oleochemicals Malaysia Sendirian Berhad
	Nonvolatile content = 99.5%	
	Acid number = 1.0 mg KOH g <sup>-1</sup> oil	
Glycerol	Purity = 99.5%	Emery Oleochemicals Malaysia Sendirian Berhad

<sup>a</sup>Technical specifications of ENR 50 given by supplier.

<sup>b</sup>Iodine value obtained based on ASTM D5768.

to react with 155.8 g of glycerol at 210–220°C for 2 h with constant stirring at 220 rpm. During this stage, the triglycerides (in palm stearin) react with the glycerol to form a mixture of monoglycerides.<sup>16,17</sup> The completion of this process was confirmed by checking the solubility of the mixture in ethanol. The reaction mixture was then cooled below 140°C and 236.6 g of PA was added into the mixture before raising the temperature to 220–230°C for the polycondensation reaction between the glycerides and PA. The progress of the alkyd synthesis was monitored by measuring the acid number of the reaction mixture at 30 min interval for 5 h from the beginning of the evolution of water of reaction. The reaction was stopped when the acid number of the mixture fell below 15 mg KOH g<sup>-1</sup> alkyd.

#### Preparation of Alkyd 1A and Alkyd 1B

Alkyd 1 was used as the precursor to produce the PA-modified alkyds, Alkyd 1A and Alkyd 1B. Alkyd 1A was obtained by reacting 6.22 parts of PA with 100 parts Alkyd 1, while for Alkyd 1B, 11.42 parts of PA over 100 parts Alkyd 1 was used. The reaction was carried at temperature below 180°C and stopped when the acid number of the reaction mixture has dropped to approximately half of its initial value. PA reacts with hydroxyl group to form a half-ester and a free —COOH group without liberation of any water. Higher temperature would lead to further reaction of this —COOH with other hydroxyl group to form an ester linkage with liberation of water.

#### Characterization of alkyd

Acid number of the alkyd was determined according to the method described in ASTM D1639-90. Neutral solvent which composed of equal volume of isopropanol and toluene was used to dissolve a known weight of alkyd, followed by titration with standardized KOH solution, using phenolphthalein as the indicator. FTIR spectrum of the alkyd was recorded on a Perkin Elmer Spectrum 400 FTIR spectrometer. Gel Permeation Chromatography (GPC) was performed using a GPC instrument (Model: Waters 600) equipped with four styragel columns connected in series (dimension 4.6 × 300 mm), and calibrated with monodispersed polystyrene standards. 100 μL of sample (2% w/v of alkyd in tetrahydrofuran) was injected into the column at 30°C. The chromatograms and integrated data were recorded using Empower software.  $T_g$  of alkyd was determined using

Mettler Toledo Differential Scanning Calorimeter (Model No: DSC822e). <sup>1</sup>H-NMR analysis was performed on JEOL JNM-GSX 270 Fourier Transform (FT) NMR spectrometer using deuterated chloroform as solvent.

#### Preparation of ENR 50-Alkyd Solution Blend

Blending was carried out at room temperature (28–30°C). Six parts of 10% w/w of ENR 50 in toluene was mixed with 1 part of 60% w/w of alkyd in toluene, so that the ratio of ENR 50: alkyd in the blend would be 1 : 1 w/w. Two samples from each blend were taken at the second and twenty-fourth hour of blending. The samples were dried in fume hood at room temperature for 24 h before further dried in vacuum oven at 60°C for 24 h. ENR 50-Alkyd 1 blend, ENR 50-Alkyd 1A blend and ENR 50-Alkyd 1B blend were designated as E50-A1, E50-A1A, and E50-A1B, respectively.

#### FTIR Analysis on ENR 50-Alkyd Blend

The blend solution was applied as a thin layer on potassium bromide (KBr) cell, and the solvent was removed by hot air blower. The spectrum was recorded on FTIR spectrometer.

#### Gel Formation and Determination of Gel Content

A known weight of dried blend sample was soaked in toluene for 48 h at room temperature. If gel was formed, it was filtered out from the soluble part using a sieve (size = 20 Mesh) and dried in vacuum oven at 60°C. The dry weight of the gel fraction was recorded. The % of toluene soluble and insoluble portions of the blend was calculated.

#### DSC Analysis on ENR 50-Alkyd Blend

Dried blend sample (5–10 mg) was encapsulated in aluminum sample pan and the analysis was carried out in nitrogen atmosphere from –60 to 60°C at a scan rate of 20°C min<sup>-1</sup>.

## RESULTS AND DISCUSSION

#### Characterization of Alkyd

**Acid Number of Alkyd.** The initial and final acid numbers of the alkyds are reported in Table II, together with the amount of —COOH calculated from their final acid numbers. The decrease in the acid numbers of the PA-modified alkyds are due to the reaction of PA to form half ester with the free —OH group in Alkyd 1 chain.<sup>18</sup> This was in agreement with the experimental observation where no water was produced at this stage.<sup>18,19</sup>

**Table II.** Initial and Final Acid Number of Alkyds and Calculated Amount of —COOH groups

Alkyd	Initial Acid Number <sup>a</sup> (mg KOH g <sup>-1</sup> alkyd)	Final Acid Number <sup>b</sup> (mg KOH g <sup>-1</sup> alkyd)	Amount of —COOH groups <sup>c</sup> (10 <sup>-4</sup> mol g <sup>-1</sup> alkyd)
Alkyd 1	230.6	12.3	2.19
Alkyd 1A	56.9	29.0	5.17
Alkyd 1B	90.6	44.4	7.92

<sup>a</sup>Initial acid number = Number of acid equivalents × (56,100/total weight of reactants charged).

<sup>b</sup>Determined by titration.

<sup>c</sup>Amount of —COOH = Acid number/56,100 mg KOH mol<sup>-1</sup>.

Each half ester formed results in a free —COOH group in the alkyd chain. Alkyd 1A and 1B were cooked at controlled temperature (<180°C) until their final acid numbers have reduced to approximately half from their initials. This serves the purpose of preserving the free —COOH groups in the alkyd. Generally higher temperature will result in the polyesterification between the free —COOH and the other —OH groups in the alkyd.<sup>20</sup>

**FTIR Analysis on Alkyds.** FTIR absorbance spectra of Alkyd 1, Alkyd 1A and Alkyd 1B are shown in Figure 1, along with the calculated absorbance ratio at 3472 to 1457 cm<sup>-1</sup> ( $A_{3472}/A_{1457}$ ). The spectra are similar to each other as they were synthesized from the same raw materials but with different amount of PA.

The following peaks are observed in the spectrum: peak at 3472 cm<sup>-1</sup> corresponds to —OH stretching, 2854–2925 cm<sup>-1</sup> from the C—H stretching of methyl and methylene groups, peak at 1732 cm<sup>-1</sup> corresponds to C=O stretching of ester and carboxyl groups, and 1282 cm<sup>-1</sup> from the C—O of ester groups. The peak at 1457 cm<sup>-1</sup>, which corresponds to C—H bend of —CH<sub>2</sub> group was taken as the internal standard to overcome the effect of different film thickness during the analysis of the spectra. Alkyd 1 has relatively high  $A_{3472}/A_{1457}$  as it was formulated with excess of hydroxyl groups. The ratio however decreased after more PA was added into the alkyd to produce Alkyd 1A and Alkyd 1B, suggesting that the —OH group of Alkyd 1 has reacted with the PA.

**GPC Results.** Table III shows the number average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ), and poly-

**Table III.**  $M_n$ ,  $M_w$ , and Polydispersity Index (PI =  $M_w/M_n$ ) of Alkyd 1, 1A, and 1B

Sample	$M_n$ (g mol <sup>-1</sup> )	$M_w$ (g mol <sup>-1</sup> )	PI
Alkyd 1	1003	2787	2.78
Alkyd 1A	1030	2900	2.82
Alkyd 1B	1102	3128	2.84

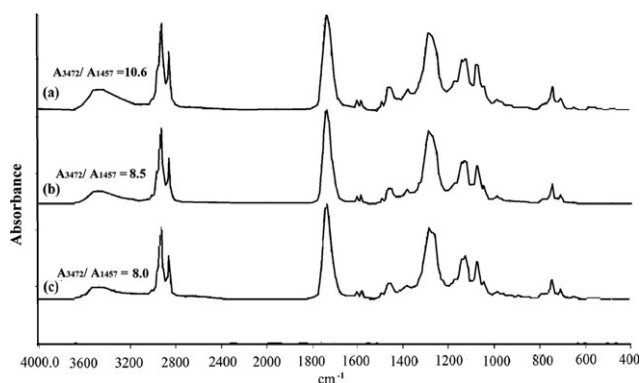
dispersity index (PI =  $M_w/M_n$ ) of the three alkyds.  $M_n$  and  $M_w$  of the modified alkyds are higher than Alkyd 1, suggesting that PA has been incorporated into Alkyd 1 to produce Alkyd 1A and Alkyd 1B. Between the two modified alkyds, Alkyd 1B has higher molecular weight, consistent with the higher amount of PA incorporated into the alkyd chain. The increase in molecular weight might also be due to small amount of condensation reaction between the —COOH and —OH groups of the alkyd molecules. It should be pointed out that the GPC was calibrated with monodispersed polystyrene standards, and thus the molecular weights obtained are not absolute.

**DSC Analysis.** Figure 2(a) shows the DSC thermograms of the alkyds. The  $T_g$  of Alkyd 1, Alkyd 1A, and Alkyd 1B were observed at -21.8, -20.4, and -17.4°C, respectively. Being a semicrystalline polymer,<sup>21,22</sup> alkyd also exhibited several endothermic peaks, which correspond to the melting transitions, observed after the  $T_g$  of the alkyd. The reappearance of the endothermic peaks when Alkyd 1A was cooled down and rescanned with DSC [Figure 2(b)] confirms that these endothermic peaks are indeed due to physical transition. Four distinct melting peaks were observed in the temperature range of 10–50°C, due to broad distribution of crystallites of various sizes. All the alkyds appear as semisolid at temperature below 10°C but became flowable viscous liquids around 30°C.

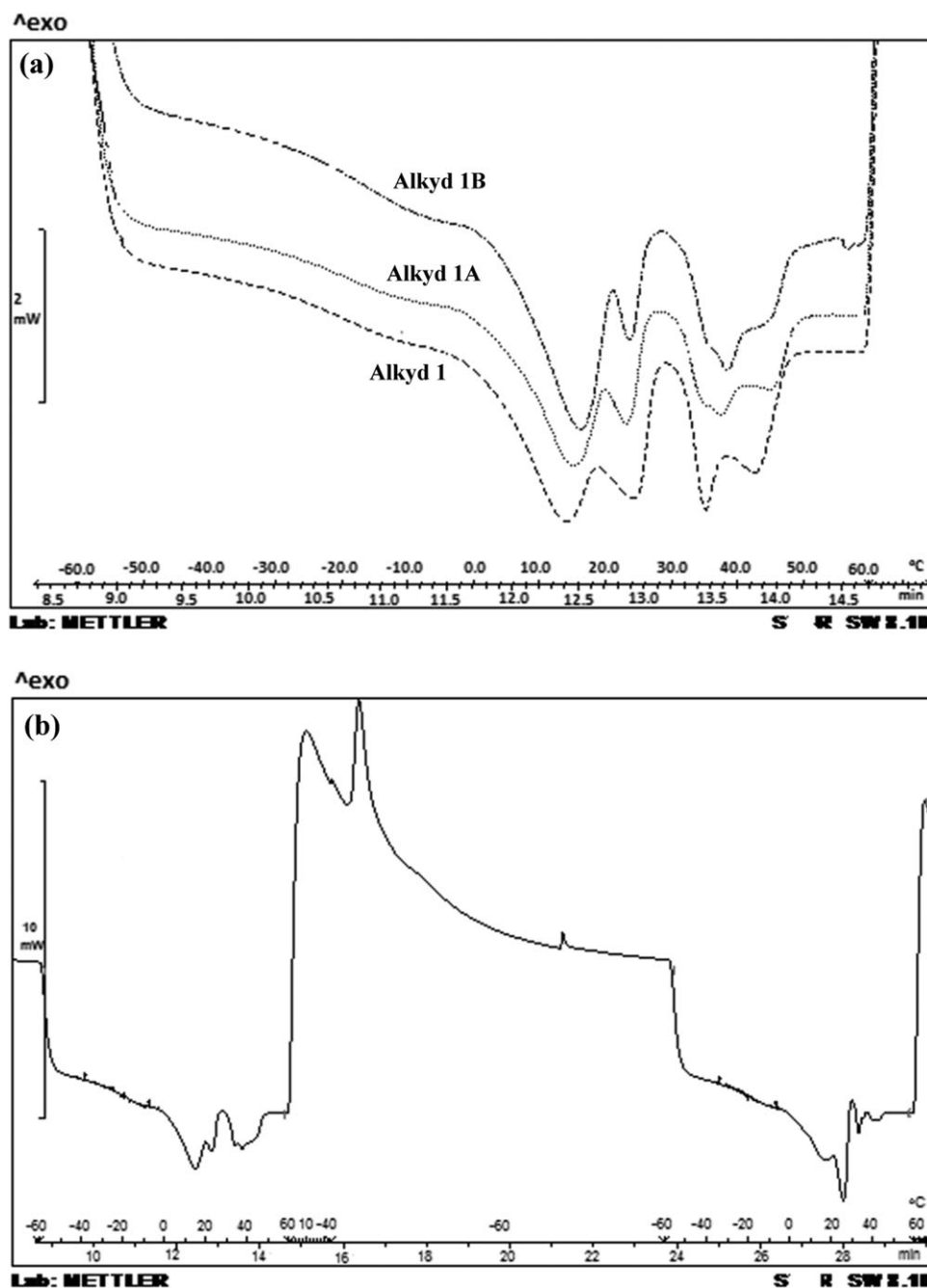
**<sup>1</sup>H-NMR Analysis.** Figure 3 shows the <sup>1</sup>H-NMR spectra of Alkyd 1 and Alkyd 1A. The assignments of the various protons were as shown in the figure. An obvious difference in the spectra is seen around 3.3 ppm, where there is a distinct peak present in Alkyd 1. The peak corresponds to the hydroxyl protons (—OH). However, after reaction with PA, the hydroxyl proton became significantly reduced. The amount of —OH group in the modified alkyd has reduced as the incorporation of PA took place via esterification reaction, which consumed the —OH group. A plausible reaction during the incorporation of PA into Alkyd 1 is shown in Figure 4.

### Reactions of ENR 50 and Alkyd

Blending of ENR 50 and alkyd was carried out via solvent casting technique using toluene. At the end of specified blending time, the solution was transferred into an open glass dish, where the solvent evaporated off quickly in the fume hood at room temperature. The thin solid film obtained was dried in vacuum oven at 60°C to trace solvent in the blend. According to Gan and Burfield,<sup>23</sup> the activation energy for the reaction involving ENR 50 with the —COOH of benzoic acid in solid form is quite high, ~70 kJ mol<sup>-1</sup>. Such reaction only occurred when ENR 50 and benzoic acid were heated at temperature at 160°C. Drying the solid film at 60°C only accelerates the removal of the



**Figure 1.** FTIR spectra of (a) Alkyd 1, (b) Alkyd 1A, and (c) Alkyd 1B.



**Figure 2.** (a) DSC thermograms of Alkyd 1, Alkyd 1A, and Alkyd 1B; (b) DSC thermogram of Alkyd 1A obtained through repeated heating and cooling.

trapped solvent but would not affect the extent of crosslinking in the blend.

#### Characterization of ENR-Alkyd Blend

**FTIR Analysis.** Figure 5 shows the FTIR spectra of ENR 50-Alkyd blends at 1060–1380  $\text{cm}^{-1}$  and 820–950  $\text{cm}^{-1}$  regions. The peaks in the spectra were normalized against peak at 1380  $\text{cm}^{-1}$  for comparison between the blends. Peak at 877  $\text{cm}^{-1}$  in the figure corresponds to the epoxy ring while the peak at 1282  $\text{cm}^{-1}$  is attributed to the C–O stretching of the ester group.

The decrease in the absorbance at 877  $\text{cm}^{-1}$  shows that epoxy group of the ENR 50 was consumed during the blending. Presumably, crosslinking between the ENR 50 and alkyd has taken place via ring opening of the epoxide group. A plausible reaction between carboxylated alkyd and ENR is proposed in Figure 6.<sup>19</sup> The supporting evidence comes from the reduction in the epoxide peak at 877  $\text{cm}^{-1}$ , followed by the increase in the ester peak at 1282  $\text{cm}^{-1}$ . The increase in the absorption at 1042, 1071, and 1122  $\text{cm}^{-1}$  are presumably due to the formation of secondary alcoholic group and ethers— both aliphatic and

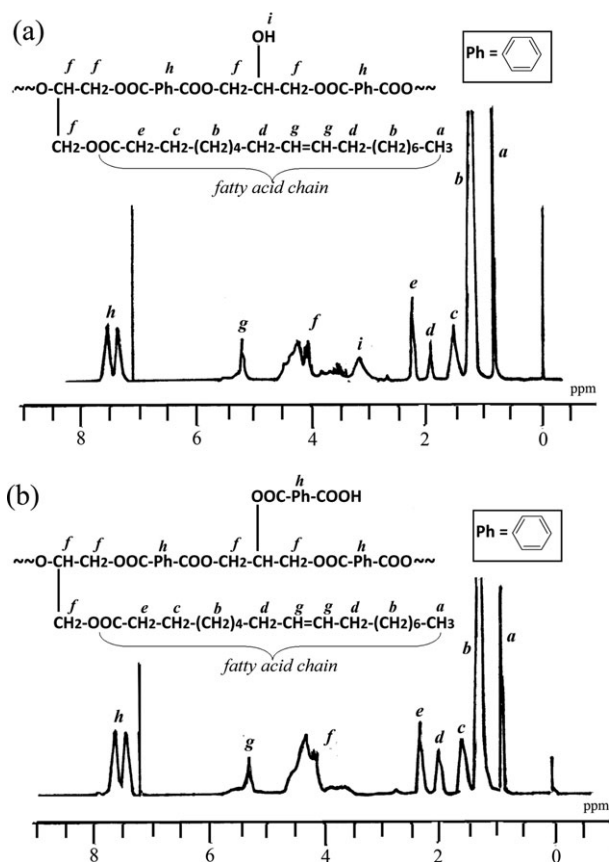


Figure 3.  $^1\text{H}$ -NMR spectra of (a) Alkyd 1 and (b) Alkyd 1A.

cyclic.<sup>24</sup> The change in the epoxide content ( $A_{877}/A_{1380}$ ) is summarized in Table IV.

**Gel Content.** The % of toluene soluble and insoluble fractions of ENR 50-Alkyd blends, ENR 50, and alkyds are tabulated in Table V. Individually, all the alkyds are completely soluble in toluene while ENR 50 recorded 98% solubility in toluene. However, after they were blended for 2 h, the product has lower solubility in toluene, where gel formation was observed due to significant crosslinking reactions between the blend components. The gel % in the blend has increased when the blending time was prolonged from 2 to 24 h, consistent with the increase in the amount of crosslinks in the system. E50-A1B has the highest

gel % attributed to the highest amount of  $-\text{COOH}$  present in the modified alkyd.

**DSC Analysis.** DSC analyses were conducted on two sets of samples. The first set is the ENR 50-Alkyd blends, while the second set is the dried gel of the toluene insoluble fraction of ENR 50-Alkyd blends. Their DSC thermograms are shown in Figure 7(a,b), respectively. The  $T_g$  was obtained from the midpoint of the inflection in the curve, and the results are tabulated in Table VI. The endothermic peaks ( $10$ – $50^\circ\text{C}$ ), which correspond to the melting transition of the alkyd components, were observed in the DSC thermograms of the whole sample of the ENR50-Alkyd blends [Figure 7(a)]. However, these endothermic peaks are no longer visible in Figure 7(b) as toluene soluble fraction in the blends has been extracted out during the 48 h of immersion in toluene. FTIR analysis on the toluene soluble fraction of the blend has confirmed the fraction consists of predominantly the unreacted alkyd. Removal of the unreacted alkyd has increased the  $T_g$  of the toluene insoluble fraction of the blend. For example, before the removal of unreacted alkyd, the  $T_g$  of E50-A1B after blended for 2 h was  $-19.6^\circ\text{C}$ , but after it was soaked in toluene and dried, its  $T_g$  has increased to  $2.6^\circ\text{C}$ .

All the blends, irrespective of blending time and type of alkyds, exhibited single  $T_g$ , indicating the compatibility of the components and the occurrence of intercomponent reaction between the blend constituents. This  $T_g$  is lower than that of the ENR 50 and the alkyd. Presumably, the final product is not a simple physical mixture, when Fox's equation can be applied. There is the ring-opening reaction of the epoxide group by the carboxylic acid to form a hydroxyl on the rubber chain, and an ester linkage between the rubber and the alkyd. The alkyd is of much lower molecular weight as compared to the ENR. Formation of an ester linkage would be equivalent to having a small alkyd side-chain grafted onto the rubber. When more than one  $-\text{COOH}$  groups of one alkyd have reacted with more than one epoxide groups in the same ENR molecule, it is not an effective crosslinking. Effective crosslinking is formed only when more than two or more  $-\text{COOH}$  groups of a particular alkyd have reacted with more than one epoxide groups in different ENR molecules. Presumably, the toluene insoluble fraction is due to the ENR molecules that have undergone effective intermolecular crosslinking. This could also explain why the gel fraction has a much higher  $T_g$  than the whole sample.

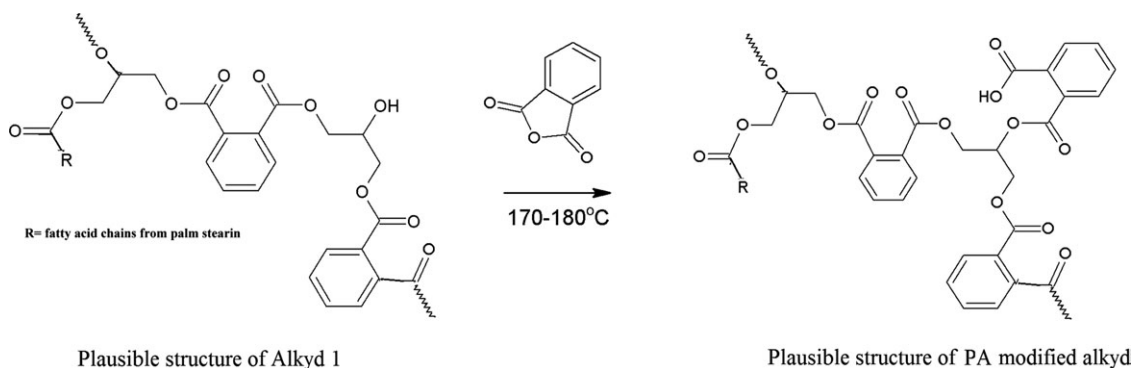
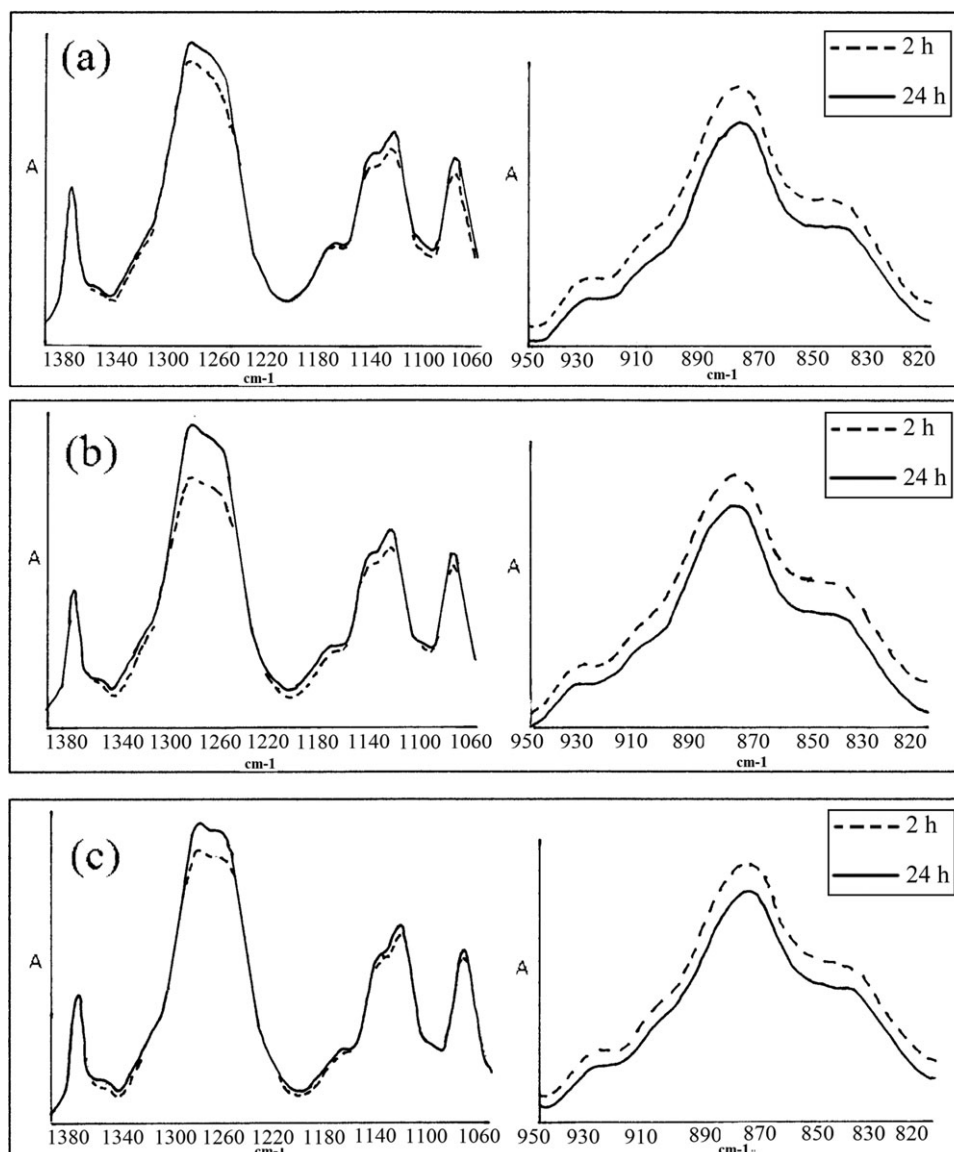
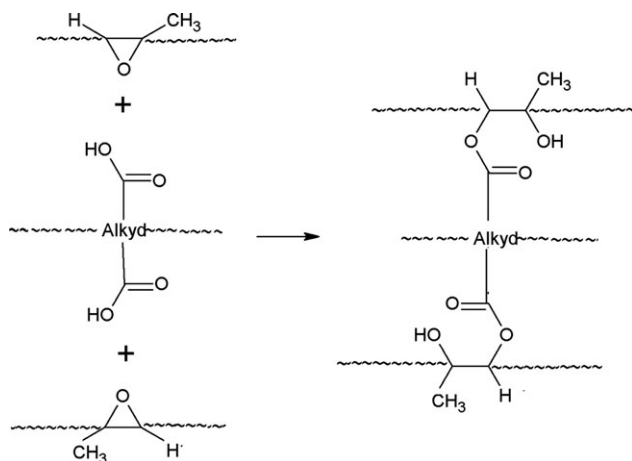


Figure 4. Plausible incorporation of PA into Alkyd 1.



**Figure 5.** Expanded FTIR spectra at 1060–1380  $\text{cm}^{-1}$  and 820–950  $\text{cm}^{-1}$  regions of ENR 50-Alkyd blends, blended for 2 and 24 h: (a) E50-A1, (b) E50-A1A, and (c) E50-A1B.



**Figure 6.** Plausible crosslinking reaction between ENR 50 and the modified alkyd.

**Table IV.** FTIR Peak Absorbance Ratio at 877 to 1380  $\text{cm}^{-1}$  ( $A_{877}/A_{1380}$ ) of ENR 50-Alkyd Blends at 1 : 1 weight ratio

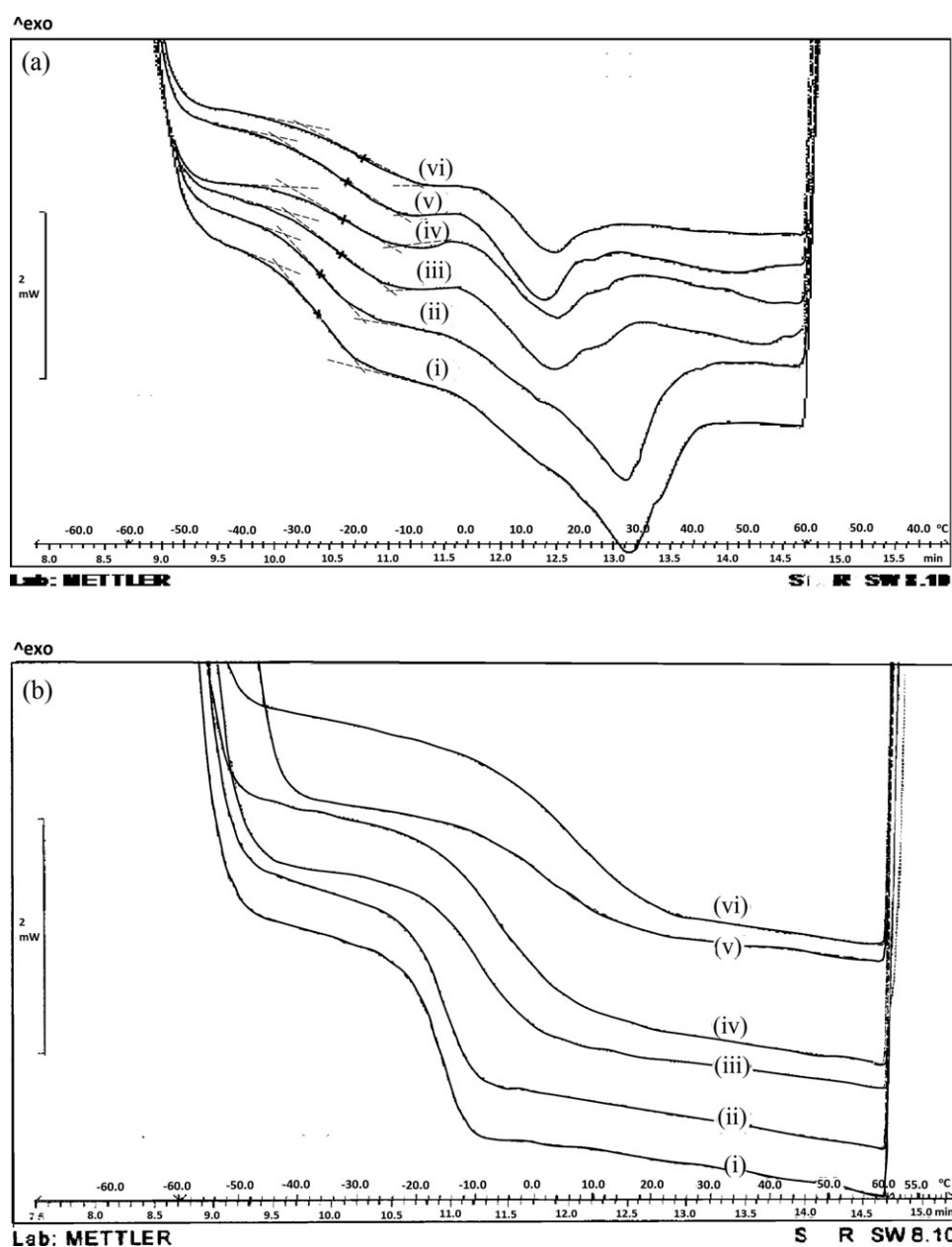
Sample	Reaction time (h)	$A_{877}/A_{1380}$	% Change in $A_{877}/A_{1380}$ from 2 to 24 h
E50-A1	2	0.42	-6.2
	24	0.40	
E50-A1A	2	0.43	-11.1
	24	0.39	
E50-A1B	2	0.42	-12.0
	24	0.38	

**Table V.** Percentage of Toluene Soluble and Insoluble Fraction of ENR 50, Alkyds, and ENR 50-Alkyd Blends at 1 : 1 Weight Ratio at 30°C

Sample	Reaction time (h)	% Soluble	% Insoluble
ENR 50	-	98.0	2.0
Alkyd 1	-	100	0
Alkyd 1A	-	100	0
Alkyd 1B	-	100	0
E50-A1	2	54.2	45.8
E50-A1	24	46.7	53.3
E50-A1A	2	41.4	58.6
E50-A1A	24	34.3	65.7
E50-A1B	2	33.4	66.6
E50-A1B	24	27.9	72.1

**Table VI.**  $T_g$  of Whole Sample and Toluene Insoluble Fraction of ENR 50-Alkyd Blends

Sample	Reaction time (h)	$T_g$ (°C)	
		Whole sample	Toluene Insoluble Fraction
E50-A1	2	-25.9	-15.8
E50-A1	24	-24.4	-15.5
E50-A1A	2	-23.4	-9.6
E50-A1A	24	-21.1	-6.1
E50-A1B	2	-19.6	2.6
E50-A1B	24	-16.1	7.1



**Figure 7.** DSC thermograms of (a) whole sample of ENR 50-Alkyd blends and (b) dried gel of toluene insoluble fraction of ENR 50-Alkyd blends: (i) E50-A1 blended for 2 h, (ii) E50-A1 blended for 24 h, (iii) E50-A1A blended for 2 h, (iv) E50-A1A blended for 24 h, (v) E50-A1B blended for 2 h, and (vi) E50-A1B blended for 24 h.

There is only very small increase in the  $T_g$  of E50-A1 when blending time was increased from 2 to 24 h, whereas E50-A1B experienced more significant increase in its  $T_g$ . This is presumably due to the reduced segmental mobility imposed by the increased effective crosslinking between the blend components. The increase in the  $T_g$  could also be due to other factors such as the presence of polar hydroxyl and ester groups in the ring-opened structure of ENR 50-Alkyd blend, which might be involved in the intermolecular and intramolecular hydrogen bonding.<sup>23</sup>

## CONCLUSIONS

Alkyd 1 with large number of hydroxyl groups was first synthesized. It was reacted with specified amounts of PA to form Alkyd 1A and Alkyd 1B with higher amount of  $-\text{COOH}$  groups, through the formation of phthalate half ester at controlled reaction temperature. Acid number analysis showed that Alkyd 1B has the highest amount of  $-\text{COOH}$  groups, followed by Alkyd 1A and Alkyd 1. The alkyds were blended with ENR 50 at 1 : 1 weight ratio in toluene. The product is not a simple mixture, as there is a random ring-opening reaction of the epoxide groups of the ENR by the  $-\text{COOH}$  of the alkyds, leading to certain amount of crosslinking. Alkyd with higher  $-\text{COOH}$  content was found to crosslink more extensively with ENR 50 and result in higher  $T_g$  and gel content.

## ACKNOWLEDGMENTS

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