

Reactions Between Epoxidized Natural Rubber and Palm Oil-Based Alkyds at Ambient Temperature

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ABSTRACT: The reactions between epoxidized natural rubber (ENR) and a low-molecular weight palm oil-based alkyd (A1) have been investigated. Experimental results (FTIR and toluene swelling tests) showed that the alkyd having both hydroxyl and carboxylic groups could react with the epoxide groups of ENR at ambient temperature to cause crosslinking. To establish the predominant reaction, alkyd A1 was chemically modified to vary the amount of hydroxyl and carboxylic groups. A1 was treated with maleic anhydride under two different temperatures of 130 and 185°C. At 130°C, the anhydride has reacted partially with the hydroxyl groups to produce alkyd A2 with higher carboxylic content and lower

hydroxyl content. 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 content. Subsequent reactions of A2 and A3 with ENR under similar conditions have demonstrated that the predominant reaction with epoxide groups was due to the carboxylic groups from the fact that A2 could form higher amount of crosslinkages than A3, which has lower carboxylic content similar to A1. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1503–1509, 2011

Key words: crosslinking; swelling; esterification; Fourier transform infrared; rubber

INTRODUCTION

The epoxidized natural rubber (ENR) is a derivative from the chemical modification of natural rubber (NR), where a portion of the carbon–carbon double bonds of the NR molecular chains had been converted to epoxide groups, leading to the improvements of NR physical properties such as oil resistance, low-gas permeability, better wet grip, and higher damping characteristics.¹ ENR contains both epoxide and unsaturated sites, which could be used for chemical modifications. Although the double bonds can be involved in addition reactions such as vulcanization by sulfur and peroxide, the epoxide groups provide alternative sites for interaction with compounds having other functional groups^{2–5} such as carboxylic and amino groups.

Alkyd resins are polyfunctional vegetable oil-modified polyesters, synthesized by reacting polybasic acids with polyhydric alcohols together with a vegetable oil or its derivatives, via a step-wise polymerization process.⁶ In the case of using an acid an-

hydride, a half-ester was first formed, which could then condense by further esterification with other similar molecules to give longer chain polyesters.⁷ Recently, there are considerable interests in the studies of polymeric materials from natural and renewable resources, with the objectives to develop more environmental friendly products.

In an attempt to replace some of the toxic petroleum-based additives in rubber compounds, we found that certain alkyd resins can be used as tackifiers in dry rubber compounds. In the tire industry, a tackifier has many applications. During the forming process, parts are attached together by the tackifier. In the construction of high-performance tire, the incorporation of a suitable tackifier could improve the road-gripping properties.

The current commercial tackifiers commonly in use include rosin or terpene resins and the petroleum resin. We were the first to investigate the use of palm oil-based alkyds as tackifiers in tire compounds, with the objective to reduce the petroleum-based constituents and, at the same time, improve tire performance.⁸ These alkyd resins, containing more than 70% by weight of natural materials, could be used to replace petroleum resin in ENR compounds. They can provide better tack strength than petroleum resin, impart better road gripping, and reduce rolling resistance in tread rubber.

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TABLE I
Formulation of Alkyd A1

Material	Weight (g)	Remark
PKO	242	PKO reacts with first portion of glycerol at stage 1
Glycerol	115	Divided into first portion 63 g, second portion 52 g
PA	148	PA and second portion of glycerol were added at stage 2

It is not the aim here to discuss the details of the physical and mechanical properties of the rubber compounds, which have been presented elsewhere.⁸ Instead, we scrutinize the reactions of ENR with palm oil-based alkyds that contained both hydroxyl and carboxylic groups and to establish the predominant reaction between these two functional groups with rubber epoxide groups by varying the proportions of the carboxylic and hydroxyl contents in the alkyds.

In this study, three alkyds with varying proportions of the carboxylic and hydroxyl contents were synthesized. A low-molecular weight alkyd A1 was first synthesized with high hydroxyl number and low-acid value. Alkyd A1 was subsequently treated with maleic anhydride (MA) under two different temperatures of 130 and 185°C. At 130°C, the anhydride has reacted with some of the hydroxyl groups of A1 to a half ester to produce alkyd A2 with higher carboxylic content. On the other hand, at 185°C, the anhydride has reacted completely to produce alkyd A3 with similar carboxylic acid content as A1.

EXPERIMENTAL

Materials

Epoxidised NR, grade "Epoxyrene 50" with 50% epoxidation level was supplied by Malaysian Rubber Board. Palm kernel oil (PKO) was extracted from the nut of the oil palm (*Elaeis guineensis Jacq.*) fruit. The refined, bleached, and deodorized PKO and glycerol (>99.5% pure) used in this research was supplied by Emery Oleochemicals (M) Sdn. Bhd. Phthalic anhydride and from P.T. Petrowidada, Indonesia. MA, lithium hydroxide, toluene, chloroform, and methanol were reagent grade chemicals, purchased from Merck, and they were used as received.

Preparation of ENR solution

ENR was mechanically masticated using laboratory two rolls mill to reduce the molecular weight and increase its solubility in toluene. About 10 g of the sample was milled at nip setting of 4 mm for 46 passes. The rubber was then dissolved in toluene to produce an ENR solution of 12% w/w.

Preparation of PKO alkyd A1

The composition of materials used for making alkyd A1 is given in Table I. The alkyd A1 was synthesized in two stages. In the first stage, PKO and first part of glycerol (in the amount of ~ 55% of total glycerol used) and 0.15% w/w of lithium hydroxide were placed into the reaction flask equipped with a stirrer through the central neck and a Dean and Stark decanter on a side-neck. The mixture was heated to 225–230°C until alcoholysis of PKO to monoglycerides was completed. The mixture was allowed to cool down to 180°C and the remaining glycerol, together with requisite amounts of phthalic anhydride and toluene was added. The mixture was heated to reflux at 210–220°C, and the water generated was collected at the decanter arm. The reflux mixture was sampled periodically to check the acid value, until it fell below 2 mg KOH g⁻¹. The product was a viscous liquid containing 87.9% of alkyd by weight.

Preparation of alkyd A2

Alkyd A2 was prepared by reacting 100 parts of A1 with 2.5 parts of MA at temperature of 120–130°C, until the acid value was around 7 mg KOH g⁻¹.

Preparation of alkyd A3

Alkyd A3 was prepared by reacting 100 parts A1 with 2.5 parts of MA at temperature of 185°C, until water of reaction has stopped evolving. The reaction was also monitored by taking sample periodically to check the acid value, until it fell below 2 mg KOH g⁻¹.

Reaction of ENR and alkyd

The reaction of ENR and alkyd resin was performed at ambient temperature of 27–29°C. 27 mL of ENR solution in toluene were mixed with 3.7 mL of alkyd resin solution (containing about 88% alkyd in toluene) in a conical flask and flushed with nitrogen for 5 min before being closed with stopper. The flask was agitated on an orbital shaker. Visual observation showed that the solution could blend homogeneously, and the viscosity increased with reaction time. At the end of the specified time, the mixture was poured into 500 mL of methanol to precipitate the rubber, which was isolated by filtration. Any excess unreacted alkyd was washed off with methanol, and the reacted rubber was dried in a vacuum oven at 50°C.

Determination of hydroxyl number and acid value

The hydroxyl number was determined according to the standard test method as described under

TABLE II
Characteristics of Palm Kernel Oil⁹

Property		
Saponification value, mg KOH/g	–	246.0
Iodine value, g iodine/100 g	–	18.1
Free fatty acid (% wt)	–	–
C ₆ :0	–	0.3
C ₈ :0	Caprylic acid	4.2
C ₁₀ :0	Capric acid	3.7
C ₁₂ :0	Lauric acid	48.7
C ₁₄ :0	Myristic acid	15.6
C ₁₆ :0	Palmitic acid	7.5
C ₁₈ :0	Stearic acid	1.8
C ₁₈ :1	Oleic acid	14.8
C ₁₈ :2	Linoleic acid	2.6
Others	–	0.1

ASTM D4274-94. The acid value of alkyd resin was determined by dissolving a known weight of the alkyd in a mixture of ethanol and toluene (1 : 2) and titrated with standardized potassium hydroxide solution, a procedure adapted from ASTM D 1980-87.

Swelling in toluene of reacted ENR

Amount of swelling of sample was measured by immersing a known weight of the sample in toluene in the dark at ambient temperature for 20 h. Excess toluene was removed, and the weight of swollen sample was measured. Extend of toluene swelling was expressed as the percentage by weight of toluene that could be held by the swollen gel of the reacted ENR.

Fourier transform spectroscopy

Samples were cast as thin films and dried under vacuum. FTIR spectra were recorded with a PerkinElmer FTIR 1600 spectrometer at ambient temperature, with 16 scans from 4000 to 600 cm⁻¹ and resolution of 2 cm⁻¹.

RESULTS AND DISCUSSION

Alkyd resins

The chemical characteristics⁹ of PKO is given in Table II.

Figure 1 represents a plausible reaction mechanism in the preparation of the alkyd A1. At the first stage of preparation of A1, the triglyceride of PKO was converted to monoglycerides through its reaction with first portion of glycerol at 225–230°C. Excess glycerol was avoided to prevent the occurrence of etherification.⁶ At the second stage, the resulting monoglycerides were converted to alkyd by reaction with phthalic anhydride and the second portion of glycerol.

In the subsequent step, calculated amount of MA was added to A1 to synthesize MA-modified alkyds. MA is a dibasic acid; the anhydride is more reactive than the ring-opened carboxylic acid. Thus, the first reaction of the anhydride with the hydroxyl groups of alkyd A1 was carried out under controlled conditions of moderate temperature of 130°C to produce alkyd A2, which still contained half-ester of the anhydride. A plausible mechanism in the preparation of A2 is shown in Figure 2.

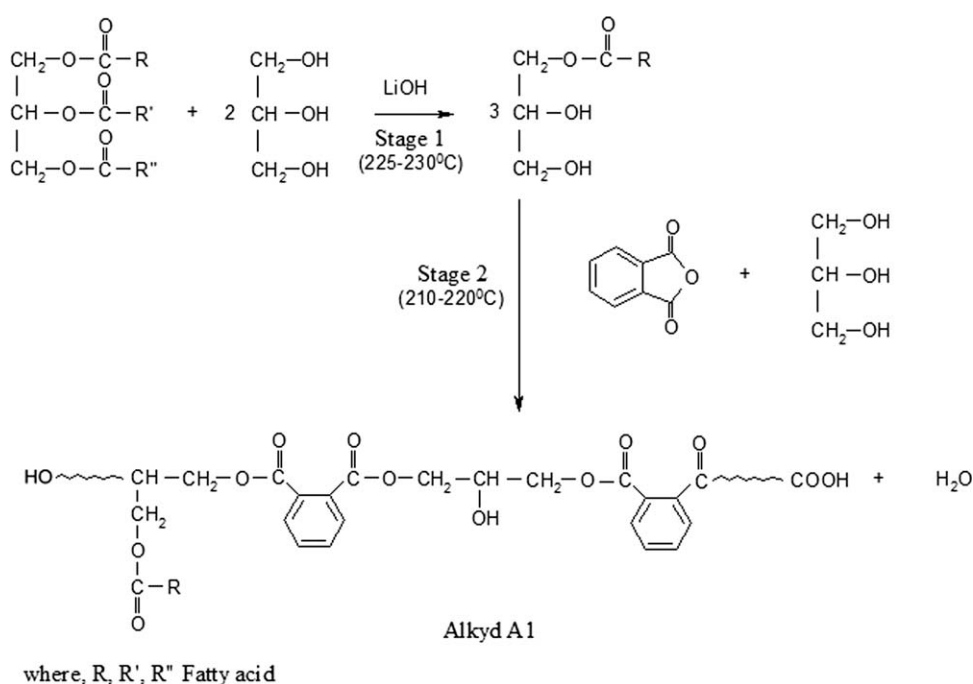


Figure 1 A plausible reaction mechanism in the preparation of the alkyd A1.

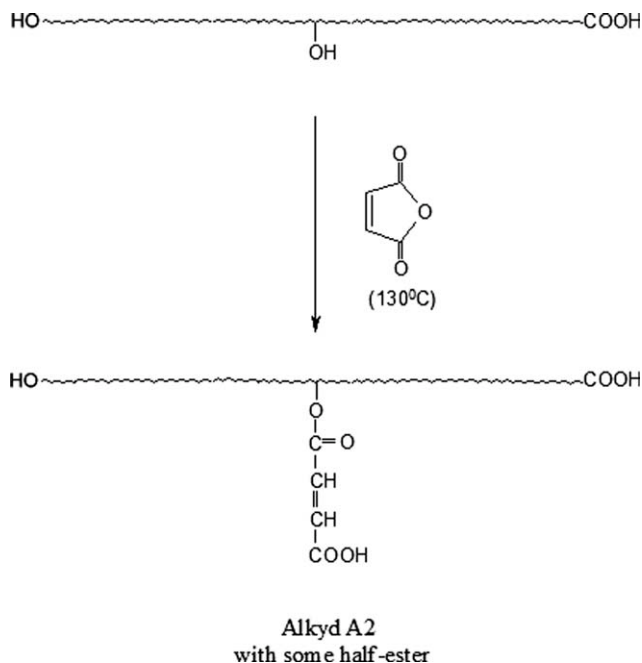


Figure 2 A plausible reaction mechanism in the preparation of the alkyd A2.

On the other hand, the second reaction of the MA with alkyd A1 was carried at much higher temperature of 180°C, where all the anhydride could react

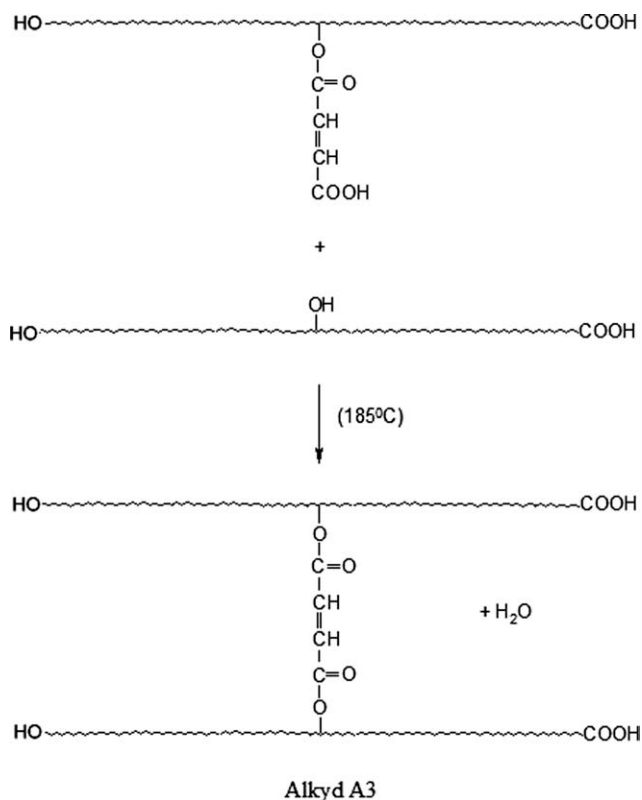


Figure 3 A plausible reaction mechanism in the preparation of the alkyd A3.

TABLE III

Hydroxyl Numbers and Acid Values of Alkyd Resins

Alkyd	Hydroxyl number (mg KOH/g resin)	Acid value (mg KOH/g resin)	Ratio of —OH to —COOH
A1	194.0	1.8	108
A2	166.4	6.8	24
A3	161.3	1.7	95

completely to form alkyd A3. A plausible mechanism in the preparation of A3 is shown in Figure 3.

Table III summarizes the hydroxyl numbers and the acid values of the three alkyds.

Changes in acid values during synthesis of A2 and A3

Figure 4 shows the changes in acid values with reaction time during the synthesis of alkyds A2 and A3. In both cases, the reaction of MA with the hydroxyl groups of A1 had proceeded rapidly to form the half ester within 100 min. At 130°C, the reaction of —COOH of the half ester of the anhydride with —OH had occurred at a slow rate, and the target acid value of around 7 mg KOH g⁻¹ was achieved after 550 min.

On the other hand, at 180°C, the reaction of —COOH with —OH had occurred at a much faster rate, and the acid value has dropped below 2 mg KOH g⁻¹ within 200 min.

Reactions of ENR and alkyd

Although both ENR and alkyd were soluble in toluene, ENR was insoluble in methanol but the low-molecular weight alkyd was miscible with methanol. Initial mixing of the ENR solution (12% w/w in toluene) with the alkyd A1 (87.9% in toluene) has produced a freely flowable solution. The reaction between ENR and the alkyd could be observed visually from the progressive increase in viscosity of the

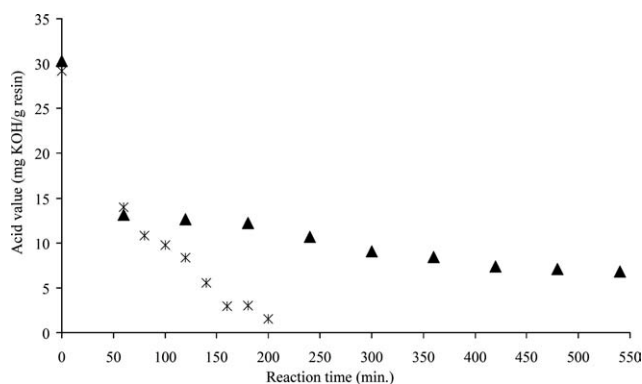


Figure 4 Changes in acid values with reaction time during the synthesis of alkyds: ▲ A2 prepared at 120–130°C; * A3 prepared at 180°C.

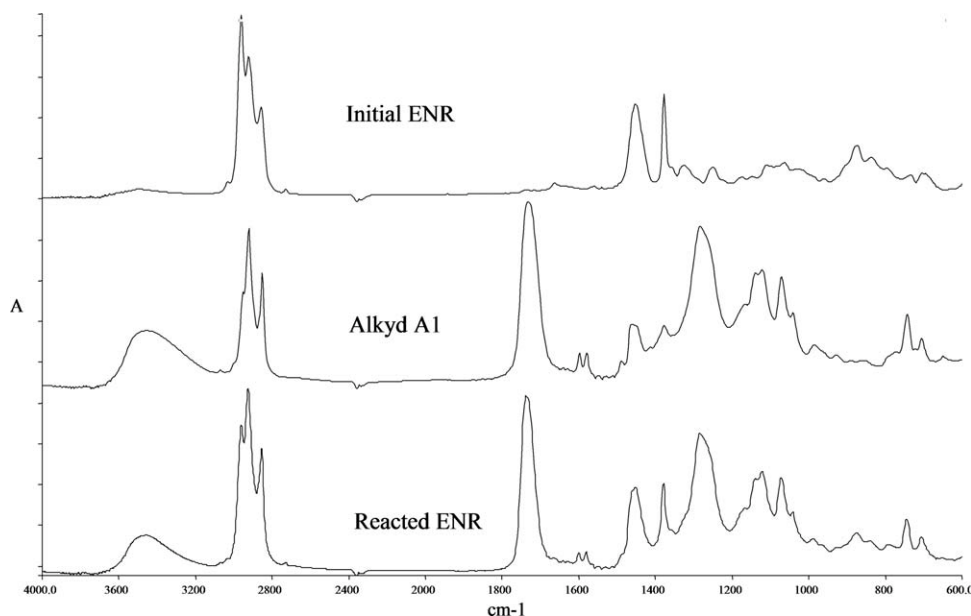


Figure 5 FTIR spectra of the initial ENR, alkyd A1, and the reaction product between ENR and A1.

mixture, and a jellylike material had formed after 7 days at ambient temperature of around 28°C.

At the end of the specified time, methanol was added to precipitate the reacted ENR and remove any unreacted alkyd. Figure 5 shows the overlaid FTIR spectra of the initial ENR, alkyd A1, and the final ENR. Many characteristic peaks of the alkyd were seen in the reacted ENR, providing evidence that the alkyd had been chemically incorporated into the ENR molecules.

Percentage 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 h. The alkyd had presumably crosslinked the ENR. 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 would have a smaller swelling capacity.

The percentage of swelling of the reacted ENR is defined by the following equation.

$$\% \text{ Swell} = \frac{\text{swollen weight} - \text{original weight}}{\text{original weight}} \times 100\%$$

The equilibrium degree of swelling for a swollen rubber network is related to the concentration of physical effective crosslink density.¹⁰ The crosslink density can be approximated from Flory–Rehner equation,¹¹

$$-\ln(1 - V_r) - V_r - \chi V_r^2 = 2\rho V_0 \eta_{\text{phys}} V_r^{1/3} \quad (1)$$

where V_r is the volume fraction of the rubber in the swollen gel, χ is the rubber–solvent interaction con-

stant, ρ is the density of rubber, and V_0 is the molar volume of solvent.

In fact, two opposing forces were being experienced when the rubber was brought into contact with toluene, which caused the segment in between crosslinkages to swell. The driving force for swelling was the decrease in Gibbs energy during the mixing of toluene with the polymer particles, whereas the elastic force in rubber would cause 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.

$$G = \frac{RT\rho}{M_c \times V_r} \quad (2)$$

where R is the gas constant, T is the temperature in kelvin, and M_c is the number-average molecular weight between crosslink. M_c can be expressed as follows:

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

$$\eta_{\text{phys}} = \frac{1}{2M_c} \quad (4)$$

Combining eqs. (1) and (3), we can obtain a relationship between the physical effective crosslink density, η_{phys} , and the average molecular weight between crosslink, M_c , as given in eq. (4).

TABLE IV
Percentage of Swelling in Toluene, Physical Effective Crosslink Density, Average Molecular Weight Between Crosslink, and Modulus of Swollen Crosslinked ENR

Crosslinked ENR	% swelling (10^{-6} mol g $^{-1}$)	$\eta_{\text{phy}}/$ (10^5 g mol $^{-1}$)	$M_c/$ (10^5 g mol $^{-1}$)	G , Modulus of swollen rubber (J mL $^{-1}$)
ENR/A1	2100	1.85	2.70	0.25
ENR/A2	680	14.7	0.34	0.66
ENR/A3	2050	2.15	2.32	0.26

Taking $\chi = 0.42$, by assuming the ENR–toluene interaction, constant was approximately the same as that of NR–toluene interaction constant, the rest of the volume fractions and densities could be measured experimentally.

Table IV summarizes the swelling capacities, and the values of η_{phy} , M_c , and G of the crosslinked ENR from the reaction with A1, A2, and A3, where ENR/A1, ENR/A2, and ENR/A3 denote the reaction product of ENR with A1, A2, and A3, respectively.

Although the alkyd structure of A3 was more complex than A1, the crosslink density in ENR/A3 was similar to that of ENR/A1 (within 3% experimental error) but that of ENR/A2 was significantly higher. This could be attributed to the fact that A3 and A1 had similar amount of carboxylic groups, while the amount of carboxylic groups in A2 was 3.8 times that of A1. The average molecular weight between crosslink was inversely proportional to the crosslink density; thus, M_c for ENR/A2 was very much smaller. G values of all the three samples were very low, several orders of magnitude smaller than the typical G value for vulcanized rubbers. The physical effective crosslink density of ENR/A3 was slightly higher than that of ENR/A1; this could be attributed to the alkyd structure of A3 being more complex than A1, presumably causing slightly more chain entanglements in ENR/A3.

CONCLUSIONS

The three alkyds contained overwhelmingly more hydroxyl than carboxylic groups. They could react with ENR at ambient temperature to cause crosslinking of ENR. FTIR provided evidence of the chemical incorporation of the alkyd into ENR. From the extent of crosslink through determining the % swelling of the rubber in toluene, results showed that A2 was very much more reactive than A1 or A3 toward rubber epoxide due to its higher carboxylic content. Hydroxyl group did not appear to react significantly with ENR at ambient temperature, as A1 had 15% more $-\text{OH}$ group than A3, and yet they showed similar reactivity,

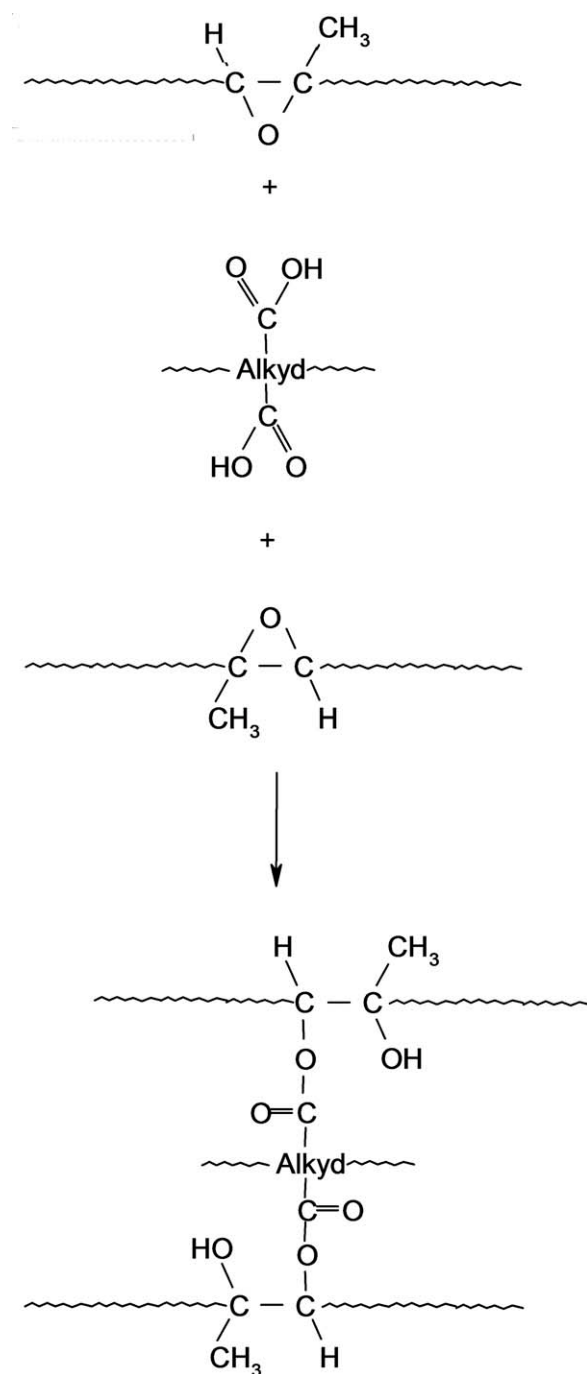


Figure 6 The predominant crosslinking reaction between ENR and alkyd.

due to their similar carboxylic content. Thus, it could be concluded that the predominant crosslinking reaction could be represented in Figure 6.

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