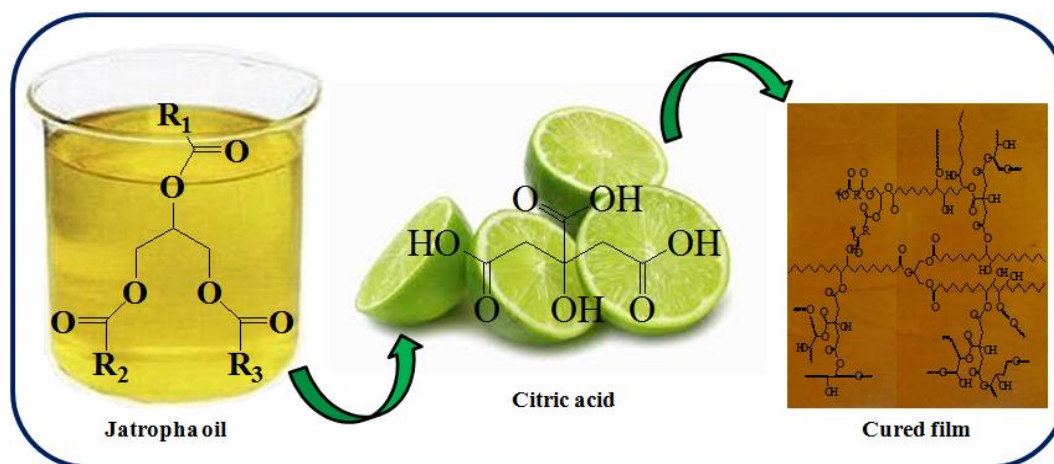


Chapter 3

Blends of epoxidized alkyd resins based on jatropha oil and the epoxidized oil cured with aqueous citric acid solution: A green technology approach

GRAPHICAL ABSTRACT



3.1 Introduction

Recently, the use of renewable raw materials in the synthesis of polymer has received worldwide attention because of the environmentally aware consumer society and high rate of depletion of petroleum resources. Among the different kinds of renewable raw materials, vegetable oils have attracted much more attention due to their economic, environmental, and social advantages.¹⁻⁴ Moreover, various chemical modifications can be performed on vegetable oils, yielding functionalized vegetable oils (FVOs) that can be used to obtain diverse products.⁵

A large number of vegetable oils have been utilized in the synthesis of various polymeric resins, for example, polyester,⁶ epoxy,⁷ poly(urethane),⁸ poly(esteramide),⁹ etc. Amongst the various products of vegetable oils, alkyd resins are one of the most popular in the paint industries. Moreover, alkyd resins have extensive applications in surface-coating, adhesives, composite materials,¹⁰ etc. However, these resins suffer some major drawbacks such as low mechanical strength, low hardness, low thermal stability, long curing time, etc. To overcome these drawbacks of the vegetable oil based alkyd resins, blending with other suitable resins, such as epoxy resin, amino resin, silicone resin, and ketonic resin, can be carried out.¹¹

In general, all the vegetable oils have esters and C=C double bonds, which can be functionalized to give a variety of monomers. Epoxidized vegetable oils (EVO), such as epoxidized soybean oil (ESO), are industrially produced and commercially available, and

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being used mostly as a plasticizer in the plastics industry. EVO finds interesting applications in the synthesis of polymer networks, giving a higher value added biomass derived material.^{12,13} Polymer networks can be obtained by cross-linking of EVO or mixtures of EVO with a synthetic epoxy resin with some of the petroleum derived curing agents, such as amines¹⁴ and anhydrides.¹⁵ It is obvious that epoxy groups react with carboxylic acids to yield β -hydroxyester linkages. There are numerous poly(carboxylic acid)s produced by sustainable biological processes that can be used as curing agents for EVO.¹⁶ However, the mutual insolubility of the components has limited the interest in developing polymer networks based on EVO and poly(carboxylic acid)s. Altuna et al.⁷ has reported the cross-linking of ESO by an aqueous citric acid (CA) solution. The resulting polymer networks have remarkable thermal and mechanical properties with self-healing ability. Roudsari et al.¹⁷ has reported the study of the curing kinetics of epoxy resins with sebacic acid and ESO. Shogren et al.¹⁸ reported the synthesis of thermosets from ESO using several curing agents, including citric acid with aluminum acetyl acetonate or tetrabutyl ammonium bromide as a catalyst.

Epoxidized jatropha oil (EJO) produced from jatropha oil provides advantages as a potential renewable raw material for industrial applications due to its worldwide availability and nonedible nature. Jatropha is a drought-resistant perennial plant (produces seeds up to 50 years) and grows well in waste land. Moreover, the overall cost of jatropha oil is comparatively lower than that of other oils, such as soybean and rapeseed oil.¹⁹ Jatropha oil contains a significant amount of oleic acid (34.3–45.8%) and linoleic acid (29.0–44.2%) and a traceable amount of palmitoleic acid (0–1.3%) and linolenic acid (0–0.3%). The typical iodine value of jatropha oil, which indicates unsaturation or double bonds content, is about 105 g I₂/100 g. The average number of double bonds in a fatty acid chain of jatropha oil is about 1.08–1.13, fraction of unsaturated fatty acid is 0.78–0.79, and the average number of carbon length of fatty acid chain is 17.3–17.8.²⁰

Recently, Aung et al.¹⁹ reported the preparation of polyurethane wood adhesive based on EJO and found that the overall chemical resistance of the jatropha oil based polyurethane adhesives was superior compared to palm oil based adhesives. Daniel et al.²⁰

has reported the synthesis of highly branched jatropha oil via epoxidation and by ring opening reactions. Hazmi et al.²¹ reported the utilization of EJO for the production of polyol via ring opening reaction. The polyol were further used for the preparation of polyurethanes.

In the present chapter, effort has been devoted to cure alkyd resins via epoxidation followed by epoxy ring opening polymerization with a bio-based hardener. *In situ* blending of the resulting polymer network was done with different wt % of EJO and cured by an aqueous citric acid solution. The method avoids the use of conventional epoxy hardener, resins, and any other solvent or catalyst and introduces a green technology approach. The properties like scratch hardness, thermal stability, tensile strength, and chemical resistance of the blends were investigated with different wt % of EJO and CA.

3.2 Experimental

3.2.1 Materials

Jatropha seed was collected from local areas of Tezpur, Assam, India, and the oil was extracted with petroleum ether in a Soxhlet extractor. Crude oil was purified by column chromatography over silica gel using a mixture of 98% petroleum ether and 2% ethyl acetate as the eluent. The average molecular weight of the oil was found to be 883 g/mol with PDI 1.05. EJO (iodine value = 21; epoxy equivalent weight = 397 g/eq; average molecular weight = 918 g/mol; average functionality = 2.40 epoxides per triglyceride) was prepared from jatropha oil. Citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$; $\geq 99.5\%$; molecular weight = 210 g/mol), hydrogen peroxide (H_2O_2 ; 50%), and formic acid ($HCOOH$; 85%) was purchased from Merck. All the materials were used as received without any further purification.

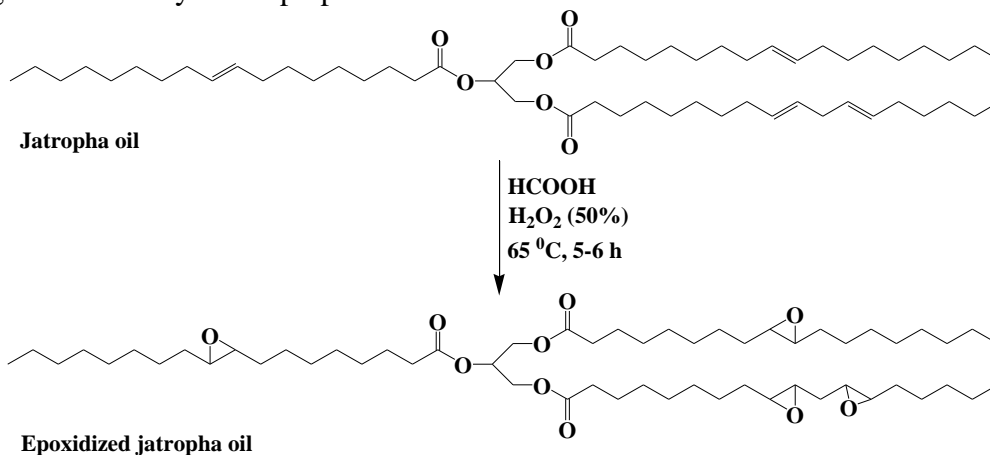
3.2.2 Preparation of jatropha oil modified alkyd resins

Jatropha oil based alkyd resins were synthesized by a two-step method. The first step was the alcoholysis process in which monoglyceride of jatropha oil was prepared by reaction of jatropha oil with glycerol in a 1:2 mol ratio at 220 °C using CaO as the catalyst

(0.05 wt % with respect to oil). The reaction was continued for 1.5 h, and the formation of the product was confirmed by checking the solubility in methanol at a regular interval of time. The reaction was stopped when the reaction product was completely soluble in methanol at room temperature. In the second step, the esterification reaction was carried out between monoglyceride and phthalic anhydride (0.12 mol) at 225 °C and the reaction was continued until it reached acid value in the range of 10–20.⁶

3.2.3 Preparation of epoxidized jatropha oil (EJO)

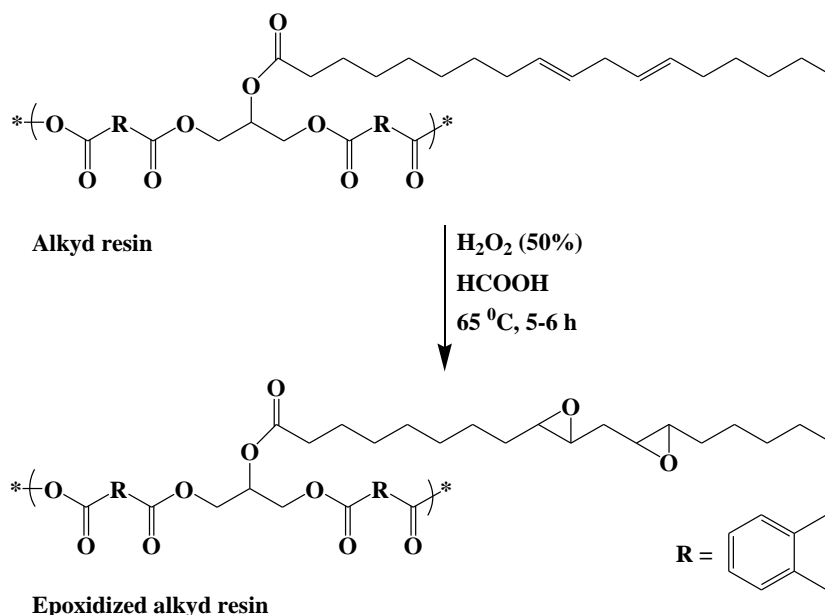
Epoxidation of jatropha oil was carried out in the presence of a mixture of formic acid and hydrogen peroxide (Scheme 3.1). The molar ratio of formic acid:double bond:hydrogen peroxide was taken as 0.4:0.8:1.7. Briefly, 4.6 g (0.10 mol) of formic acid was added to 100 g (0.113 mol) of jatropha oil in a three necked round-bottom flask and the reaction temperature was raised to 65 °C with continuous stirring. Then 115.6 g (1.70 mol) of hydrogen peroxide (50%, w/v) was added dropwise to the reaction mixture and the reaction continued for 5 h. Since the epoxidation process is exothermic, proper precaution was taken to avoid overheating the reaction mixture. The resulting mixture was cooled to room temperature and washed with distilled water followed by sodium bicarbonate solution repeatedly until neutral pH was attained. The oily phase was collected and dried over anhydrous sodium sulfate.²¹ The yield was about 91–93%. The properties such as acid value, iodine value, epoxy equivalent weight, viscosity, and average functionality of the prepared EJO are summarized in Table 3.1.



Scheme 3.1: Schematic of epoxidation of jatropha oil.

3.2.4 Epoxidation of alkyd resin

Epoxidation of alkyd resin was carried out by following the same procedure as that of jatropha oil. The properties like acid value, iodine value, epoxy equivalent weight, and viscosity of the epoxidized alkyd resin (EAR) were investigated, and the results are summarized in Table 3.1. The schematic of preparation of EAR is presented in Scheme 3.2.



Scheme 3.2: Schematic of epoxidation of alkyd resin.

Table 3.1: Properties of the EJO and EAR.

entry	acid value (mg of KOH/g)	hydroxyl value (mg of KOH/g)	iodine value (g I ₂ /100g)	epoxy equivalent weight (g/eq)	viscosity at 25 °C (Pa.s)	average functionality
JO ^a	2.50	4	105	---	0.518	---
EJO	3.80	37 ± 5	21 ± 2	397 ± 5	0.623	2.40
AR ^b	18.30	18 ± 3	37 ± 2	---	23.14	---
EAR	21.15	26 ± 3	9 ± 2	724 ± 7	23.47	---

^aJO = jatropha oil; ^bAR = alkyd resin.

3.2.5 Preparation of the blends

A concentrated aqueous solution of citric acid was prepared by mixing 3 parts by weight of citric acid with one part of distilled water, and heated the mixture to 90 °C. After the citric acid completely dissolved, the solution was poured in a 50 mL round bottom flask containing the different amounts of EAR and EJO with continuous stirring to generate an emulsion of the said components. In all the cases stoichiometric ratio of carboxylic acid equivalents and epoxy equivalents was taken as 1:1 for the completion of the reaction. Table 3.2 summarizes the compositions of the different formulations. The effect of different wt % of EJO on the performance characteristics of the blends was evaluated.

Table 3.2: Composition (g) of blends of EAR and ESO.

sample particulars ^a	EAR	EJO	citric acid ^b	water
AJO20	4	0.8	0.796	0.264
AJO30	4	1.2	1.002	0.333
AJO40	4	1.6	1.207	0.401
AJO50	4	2.0	1.412	0.470

^athe number denotes wt % of EJO with respect to EAR. ^b(epoxy equivalents)/(carboxylic acid equivalents) = 1.

The reaction was continued for a period of 0.5–0.75 h at 90 °C and as the epoxy-acid reaction took place the emulsion was converted into a homogeneous mixture. The resulting mixture was placed overnight in a vacuum oven at 45 °C to remove the moisture and trapped air. After that, the mixture was poured on a Teflon sheet by an applicator maintaining the thickness of 0.5 mm and allowed to cure at 120 °C in an oven. The influence of postcure of the films at 160 °C for a defined period of time (10 h) on thermal and mechanical properties was evaluated.

3.3 Instruments and methods

3.3.1 Fourier transform infrared spectrometer (FT-IR)

FT-IR spectra were recorded with a Nicolet Impact-410 IR spectrometer (USA). Spectra were recorded using a spectral width ranging from 4000 to 450 cm^{-1} in KBr medium at room temperature.

3.3.2 Nuclear magnetic resonance spectrometer (^1H and ^{13}C NMR)

A Jeol FT-NMR spectrometer (400 MHz) was used to record the ^1H and ^{13}C NMR spectra by using TMS as the internal standard and CDCl_3 as the solvent as soon as the reaction was over at 90 $^\circ\text{C}$.

3.3.3 Mechanical properties

The tensile strength, elongation, and elastic modulus of the cured films were measured on a universal tensile testing machine (Zwick Z010, Germany) at room temperature. The extension rate was 5 mm/min and the load cell was 10-kN, with a gauge length of 40 mm. The specimen dimension was 60 mm in length, 10 mm in width, and 0.4 mm in thickness. Scratch hardness test on the cured films was carried out by a scratch hardness tester (Sheen instrument Ltd., UK).

3.3.4 Scanning electron microscope (SEM)

The surface morphology of the composites was observed using a scanning electron microscope (SEM) (Model- JSM-6390LV, JEOL, Japan). The surface of the sample was platinum coated before SEM analysis.

3.3.5 Thermogravimetric analysis (TGA)

To study the thermal stability of the blends, thermogravimetric analysis (TGA) was carried out on a Shimadzu TGA 50, thermal analyzer in nitrogen atmosphere at a heating rate of 10 $^\circ\text{C min}^{-1}$ in the temperature range 25-600 $^\circ\text{C}$.

3.3.6 Viscosity

The viscosity of the specimens was measured with shear rate of 10 s^{-1} by a modular compact rheometer (MCR 500, Physica, Anton Paar) at 25 $^\circ\text{C}$.

3.3.7 Chemical resistance

The chemical resistance test was carried out to study the effect of chemicals, such as water, ethanol (20%, aq.), NaOH (2%, aq.), and HCl (10%, aq.) on the thermosets. Small pieces of the cured films were kept in the aforesaid medium in 100 mL amber glass bottles at 30 °C. The percent weight loss of the films was measured by following equation:

$$\% \text{ weight loss} = \left(\frac{W_o - W_t}{W_o} \right) \times 100 \quad (\text{Eqn. 3.1})$$

where, W_o and W_t are weight of the specimen at time, $t = 0$ and $t = 20$ days of the test respectively.

3.3.8 Gloss

The gloss of the cured films was measured at an incident angle of 60° as the method referred in Chapter 2.

3.3.9. Evaluation of physical properties

The physical properties like acid value, iodine value, hydroxyl value, and epoxy equivalent weight of the resins were determined following standard methods.^{10,21} Acid value and iodine value of the resins were determined as the methods described in Chapter 2.

Hydroxyl value (HV) is a measure of the content of free hydroxyl groups in a chemical entity, usually expressed in units of the mass of KOH in milligrams equivalent to the hydroxyl content of one gram of the substance. In a typical method hydroxyl value was determined by treating the resins with 5 ml of acetylating reagent (acetic acid and pyridine, 1:3 v/v) under reflux condition. Finally, the mixture was titrated with 0.1 M KOH (ethanolic) and the volume required for neutralization was recorded (T mL). A blank treatment was also run without sample and the volume of KOH required for neutralization is noted (B mL). Hydroxyl value was calculated by the following equation:

$$HV = \frac{[(B-T) \times \text{Normality of KOH} \times 56.1]}{\text{Weight of the sample}} + \text{Acid value} \quad (\text{Eqn. 3.2})$$

Epoxy equivalent weight (EQV) is the weight in grams of resin containing 1 mol equivalent of epoxide (g/mol). It was determined by refluxing the resins with 10 mL, 2 N HCl in 20 mL of ethanol for 90 min. After titrating the mixture with 0.5 N NaOH, the epoxy equivalent was calculated by the following Eqn. 3.3. The volume of NaOH required for neutralization (T mL) and for blank treatment was determined (B mL).

$$EQV = \frac{[(\text{Weight of sample} \times 1000) \times \text{Normality of KOH}]}{B - T} \quad (\text{Eqn. 3.3})$$

3.4 Results and discussion

Jatropha oil based alkyd resins were synthesized by a two-step alcoholysis followed by polyesterification reaction, and subsequent epoxidation was carried out in the presence of a mixture of formic acid and hydrogen peroxide. EJO was prepared by the reaction of jatropha oil with formic acid and hydrogen peroxide at 65 °C for 5 h. A slight increase in acid value and hydroxyl value was observed during the course of the epoxidation reaction (Table 3.1). The increase in acid value and hydroxyl value may be due to the hydrolysis of triglyceride moiety and epoxy group, respectively, in the presence of formic acid. The product was of low-viscosity, and the structure was confirmed by FT-IR, ¹H NMR, and ¹³C NMR study. The alkyd and EJO blends were prepared by mixing the components in different proportions and cured by aqueous citric acid solution at 120 °C. The curing time of the blends are recorded.

3.4.1 Spectroscopic (FT-IR and NMR) study

The plausible reaction mechanism of epoxy ring opening polymerization of EJO and EAR by an aqueous citric acid solution is presented in Scheme 3.3. The epoxidation and epoxy ring opening polymerization reaction was monitored by FT-IR and NMR (¹H and ¹³C) analysis. Fig. 3.1 presents the FT-IR spectra of jatropha oil, EJO, EAR, and AJO30. In the FT-IR spectrum of jatropha oil (Fig. 3.1a), absorption bands near at 2925 and 2854 cm⁻¹ are assigned to the -CH symmetric and asymmetric stretching vibrations of -CH₂

groups, respectively. An intense peak at 1740 cm^{-1} is due to the C=O stretching vibration. The peaks at 1455 , 1278 , and 721 cm^{-1} are attributed to $-\text{CH}_2$ bending, wagging, and rocking vibrations, respectively. The peak associated with C–O–C stretching vibration of ester group is observed at 1160 cm^{-1} . The peak at 1650 cm^{-1} is assigned to the alkene double bond, which disappeared upon epoxidation. It indicates that the C=C double bonds are expended in the formation of the epoxy groups in the presence of H_2O_2 and formic acid. At the same time formation of epoxy group in EJO is indicated by the appearance of a new peak at 825 cm^{-1} (Fig. 3.1b). The oxirane ring was introduced at the double bond positions, probably between carbons 8 and 9 or/and carbons 11 and 12 (Scheme 3.1). During the epoxidation process, a side reaction such as oxirane ring opening may occur with water and/or acid. The peak at 3460 cm^{-1} is evidence for the formation of by-product hydroxyl group in EJO.²²

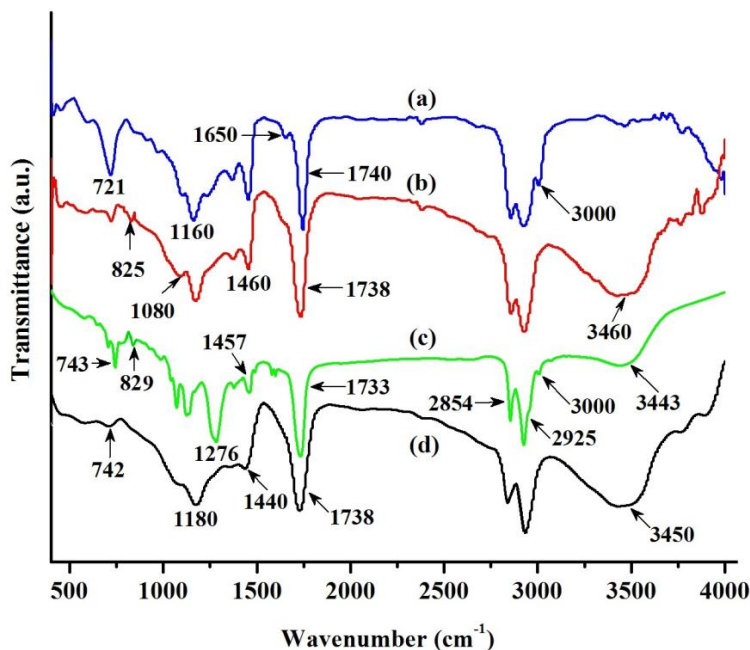


Fig. 3.1: FT-IR spectra of (a) jatropha oil, (b) EJO, (c) EAR, and (d) AJO30.

In the FT-IR spectrum of the EAR (Fig. 3.1c), the appearance of the peak at 829 cm^{-1} confirms the successful epoxidation of double bonds of alkyd resins. The absorption band for C=O stretching vibration appears at 1733 cm^{-1} , whereas in the case of oil, the peak for C=O vibration is observed at 1740 cm^{-1} . However, the same for the blend is

observed at 1738 cm^{-1} . It can be said that some sort of structural modifications around the carbonyl groups are taking place. The FT-IR spectrum for the blend is presented in Fig. 3.1d. The peak at 1180 cm^{-1} is assigned to C–O–C symmetric bending vibration. The spectrum of the blend shows that the absence of absorption band at 825 and 829 cm^{-1} , which was assigned to epoxy group disappeared while the absorbance of the C–O–C (β -hydroxyester) vibration appeared at 1180 cm^{-1} .²³ This implies that complete reaction of citric acid with EAR and EJO has taken place.⁷ Moreover, the broadening of the peak at 3450 cm^{-1} can be assigned to hydroxyl groups generated in the ring opening polymerization reaction (Scheme 3.3).

^1H NMR spectra of jatropha oil, EJO, alkyd resin, and AJO30 are presented in Fig. 3.2. In the ^1H NMR spectrum of jatropha oil (Fig. 3.2a), the triplet at δ 0.88–0.89 ppm is assigned to the protons of the terminal methyl group. The protons of all the internal $-\text{CH}_2$ groups present in the fatty acid chains appeared at δ 1.25–1.60 ppm. Characteristic peaks for allylic and double allylic protons of $-\text{CH}_2$ group are observed at δ 1.72–1.74 and δ 2.29–2.31 ppm, respectively. The peak at δ 2.89 ppm is due to the protons adjacent to the C=O group. The protons of glyceride and C=C moiety appeared at δ 4.15–4.28 ppm and δ 5.26 ppm, respectively. However, in the ^1H NMR spectrum of EJO (Fig. 3.2b), the peak at δ 5.26 ppm associated with C=C disappeared with the formation of new peaks at δ 3.11–3.12 ppm corresponding to the protons on the epoxy groups. It implies that C=C double bonds have been converted into epoxy groups in the presence of H_2O_2 and formic acid. The peak at δ 2.0 ppm corresponds to $-\text{OH}$ protons generated in the ring opening polymerization reaction.

In ^1H NMR spectrum of EAR (Fig. 3.2c) all the characteristics protons as that of jatropha oil is observed. Peaks at δ 3.11–3.12 ppm are due to the protons on the epoxy groups of EAR. The peaks correspond to aromatic protons appeared at δ 7.35–7.58 ppm. However, the peaks correspond to protons on epoxy groups (EJO and EAR) at δ 3.11–3.12 ppm disappeared in ^1H NMR spectrum of blend (Fig. 3.2d). It is evident from FT-IR and ^1H NMR study that the complete reaction of epoxy groups with aqueous citric acid solution (Scheme 3.3) has been occurred.

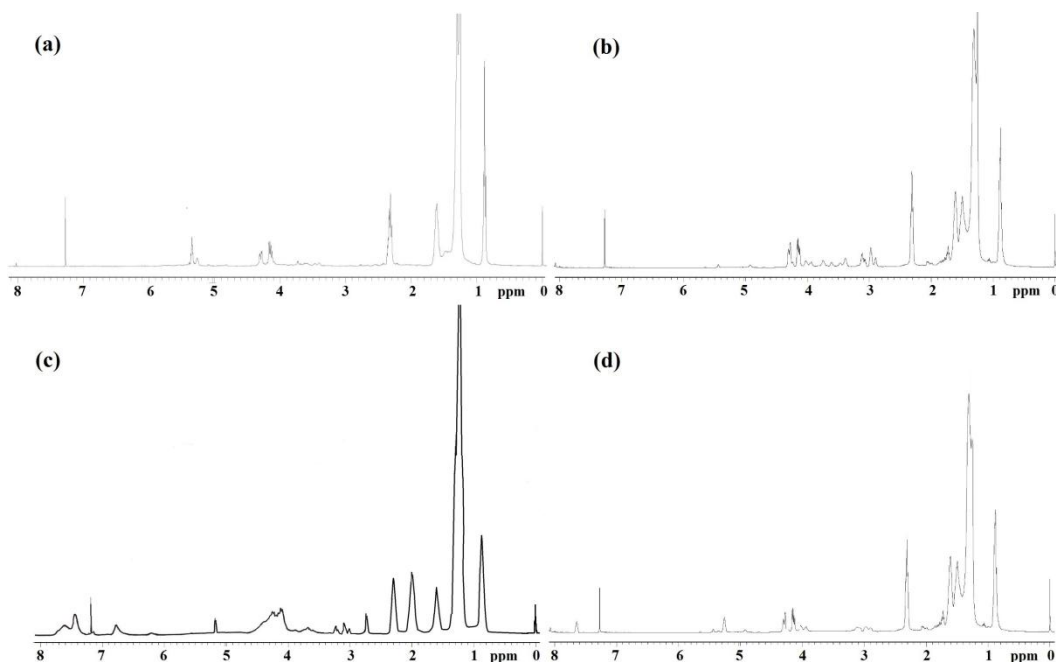


Fig. 3.2: ^1H NMR spectra of (a) jatropha oil, (b) EJO, (c) EAR, and (d) AJO30.

Furthermore, successful formation of polymer networks by ring opening polymerization of EJO by citric acid solution is evident from ^{13}C NMR study. Fig. 3.3 presents the ^{13}C NMR spectra of jatropha oil, EJO, alkyd resin, and AJO30. The peak at δ

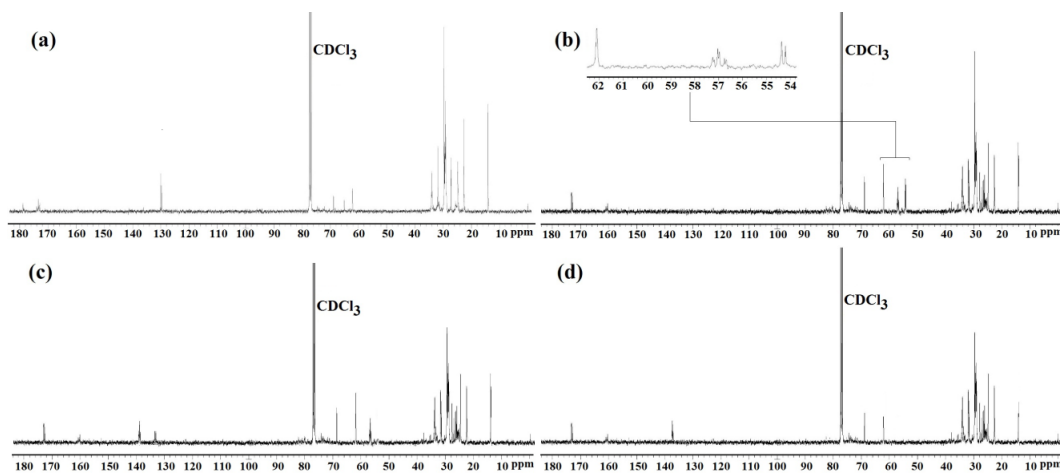


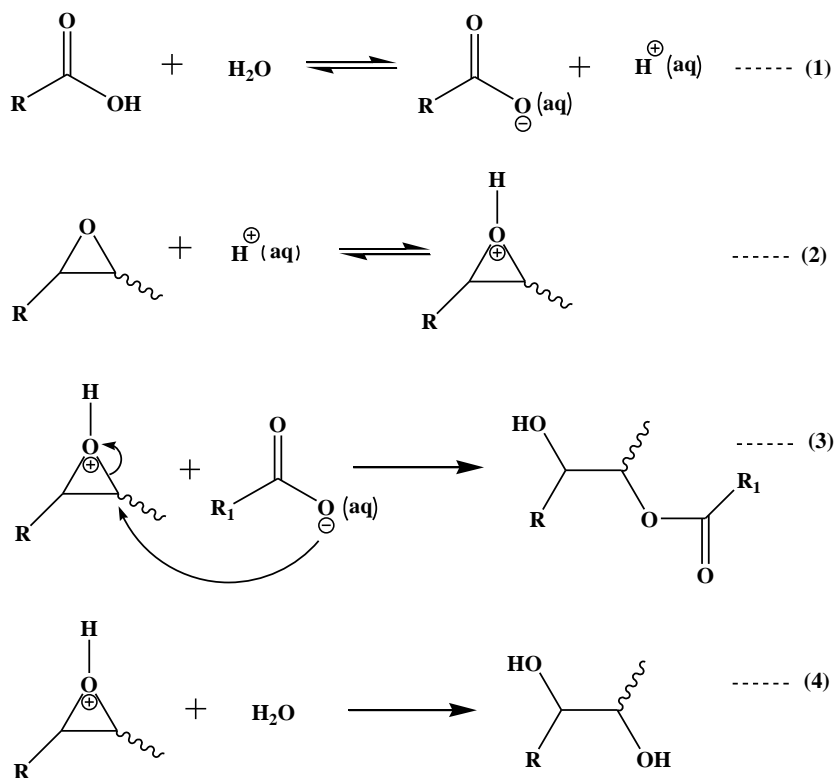
Fig. 3.3: ^{13}C NMR spectra of (a) jatropha oil, (b) EJO, (c) EAR, and (d) AJO30.

130 ppm (Fig. 3.3a) corresponding to unsaturated carbon atoms is replaced by two resonances at δ 54.2–54.4 ppm (Fig. 3.3b) corresponding to the carbon atoms on epoxy

groups. However, the peak at δ 54.2–54.4 ppm disappeared on polymerization by citric acid solution (Fig. 3.3d). The peak at δ 138 ppm is assigned to the carbon atoms of the aromatic moiety of phthalic anhydride in alkyd resin.^{22,24}

3.4.2 Curing study of the blends

The curing times of the blends are noted and summarized in Table 3.3. It is observed that the curing time decreases gradually with increase in EJO content in the blends. It can be attributed to the high concentration of reactive epoxy and COOH groups. Scheme 3.3 presents the plausible reaction mechanism of cross-linking of EJO by aqueous citric acid



Scheme 3.3: Plausible reaction mechanism accounting for the ring opening polymerization reaction.

solution. The ring opening polymerization of EJO by citric acid is catalyzed by protons produced by the dissociation of citric acid in the aqueous medium (Step 1). The next step of the mechanism is the protonation of the epoxy group (Step 2), followed by the attack of the carboxylate anion (Step 3). Although the reaction of epoxy group with carboxylate

anion leading to a β -hydroxyester is favored, the hydrolysis of epoxy groups also takes place (Step 4). In all the cases, water was added with citric acid and the initial molar ratio $H_2O/COOH$ is approximately 1.6. Moreover, the central $-COOH$ group of citric acid is comparatively less reactive.⁷ Though the ratio of (epoxy equivalents/carboxylic acid equivalents) was equal to one, due to the occurrence of hydrolysis of the epoxy groups some of the $-COOH$ groups remain unreacted. Thus, it can take part in thermally activated transesterification reactions during postcure at 160 °C with the $-OH$ groups produced by Steps 3 and 4. The most apparent cross-linked structure of EJO and citric acid polymer networks is presented in Fig. 3.4.

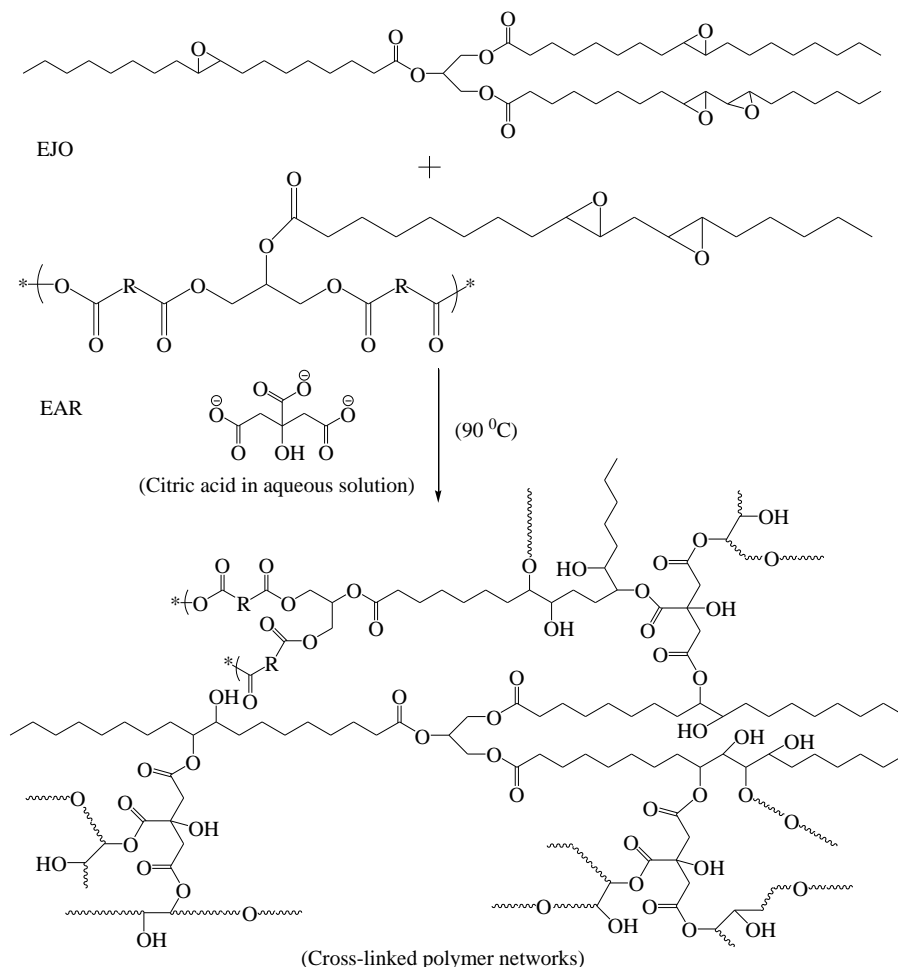


Fig. 3.4: Cross-linked polymer networks of EAR and EJO with citric acid.

3.4.3 Morphology

To produce blends with an improved combination of properties depends on the degree of compatibility of the components in the blends. Alkyd resin has good compatibility with EJO and citric acid. Strong electrostatic and H-bonding interactions of the polar functional groups (like hydroxyl, epoxy, carbonyl, ether, etc.) of the polymer networks facilitate miscibility of the components in the blends. The SEM micrographs of the blends are presented in Fig. 3.5. In all the cases, a uniform surface morphology of the blends is observed. Thus, the formation of homogeneous blends is evident from the SEM study. Moreover, there is no distinct difference in the surface morphology of the blends that is visible as the amount of EJO and citric acid is increased.

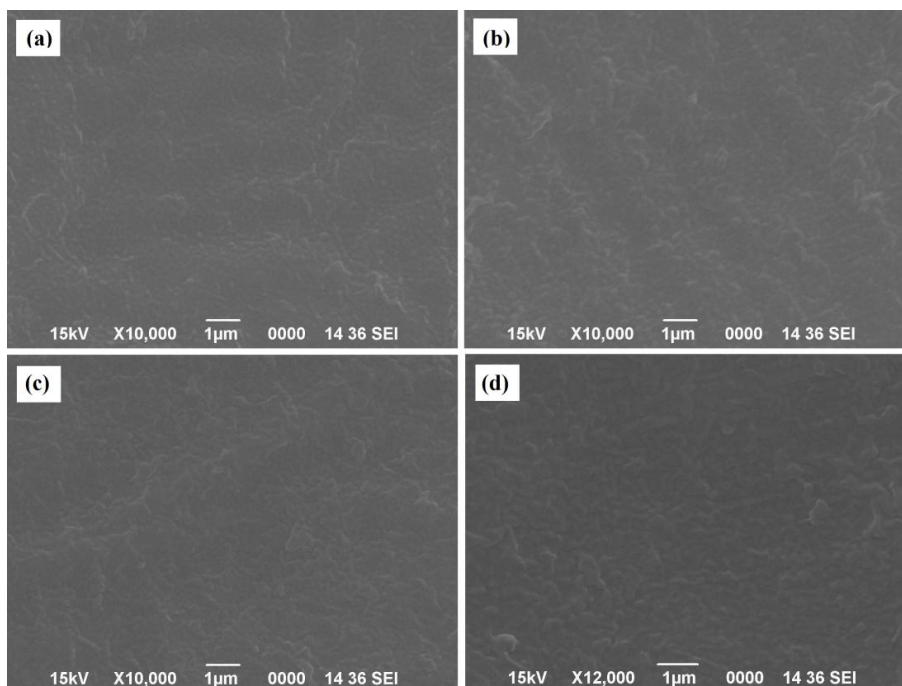


Fig. 3.5: SEM micrographs of (a) AJO20, (b) AJO30, (c) AJO40, and (d) AJO50.

3.4.4 Thermogravimetric analysis

Fig. 3.6 shows the TGA curves for alkyd resin and the blends in nitrogen atmosphere. TGA data such as initial degradation temperature (T_i), decomposition temperature at different weight losses (T_d), and residual weight (%) are summarized in

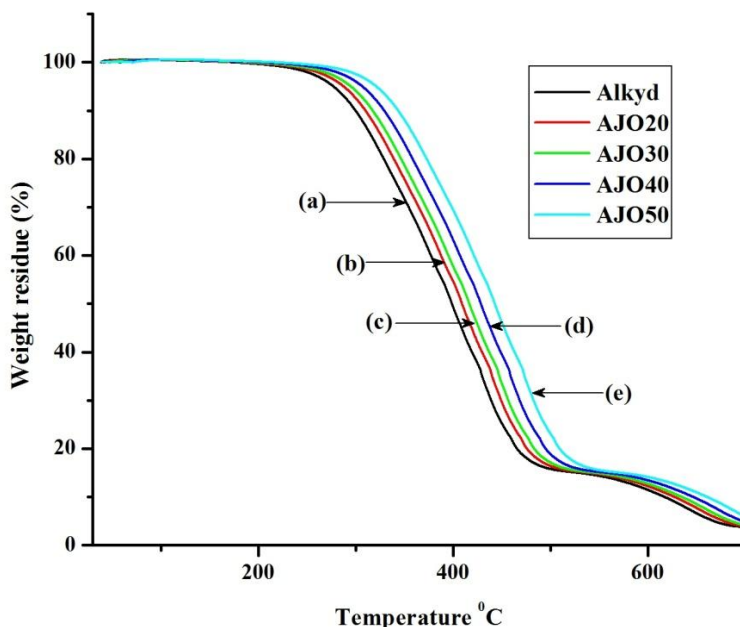


Fig. 3.6: TGA curves of (a) alkyd resin, (b) AJO20, (c) AJO30, (d) AJO40, and (e) AJO50.

Table 3.3. Thermal stability of the alkyd resins significantly improved upon blending with EJO. Moreover, thermal stability increases gradually with EJO and citric acid content. For example, the initial degradation temperature of the blend is increased by 42 °C with 50 wt % EJO content. The 5% weight losses for the alkyd resin is taking place at 278 °C whereas the same weight loss for AJO50 occurs at 321 °C. However, all the blends

Table 3.3: Thermal degradation data of the alkyd resin and the blends.

entry	sample	T _i (°C)*	decomposition temperature (T _d) at different wt losses (°C)			residue (%) at 700 °C
			5%	25%	50%	
1	alkyd resin	280	278	341	398	3.88
2	AJO20	291	287	352	409	3.91
3	AJO30	299	295	359	416	4.15
4	AJO40	310	307	371	428	4.83
5	AJO50	322	321	385	442	5.04

*T_i = initial degradation temperature.

followed a single-step degradation pattern. This is due to the good combination and compatibility of the components in the blends. The improvement in thermal stability of the blends can be attributed to the increasing cross-linking density of the polymer networks by EJO and citric acid. Moreover, strong electrostatic and H-bonding interactions of the polar functional groups (like hydroxyl, epoxy, carbonyl, ether, etc.) of the polymer networks contribute to improve the thermal stability of the blends. The degradation observed in the temperature range 470–580 °C can be assigned to the chain scission in the jatropha oil.¹³

3.4.5 Performance of the blends

The performance of the alkyd/EJO blends effectively changed with the EJO and citric acid content. Mechanical properties like tensile strength, elongation at break (%), scratch hardness, gloss, and adhesion of the cured films are summarized in Table 3.4. It is observed that the tensile strength of the blends increases gradually with EJO content and finally found to be 3.13 MPa for 50 phr EJO. Noticeably, elongation at break of the blends also observed to be increased with EJO content. The increment in tensile strength of the blends with the EJO content can be attributed to the increased cross-linking density of the polymer networks. Moreover, strong electrostatic and H-bonding interactions of the polar functional groups (like hydroxyl, epoxy, carbonyl, ether, etc.) of the polymer networks help to enhance the rigidity, as reflected by the enhancement of strength. As a result the overall performance, including the tensile strength, elongation at break, and hardness of the blend is enhanced. However, the long hydrocarbon chains of the fatty acid part of the oils act as a plasticizer, which impart flexibility to the final material. The increase in elongation at the break with EJO content is a consequence of this phenomenon. The increment in the gloss with the EJO content in the blends indicated that the cured films possess good dimensional stability and smooth surface morphology (as evident from SEM study, Fig.3.5). The increment in scratch hardness of the blends with the EJO content can be attributed to the enhanced strength of the highly cross-linked polymer networks and flexibility of the fatty acid chains.²⁵ The excellent adhesion of all the blends results from the large number of polar functionalities of the polymer networks.¹⁰

Table 3.4: Performance of the blends.

properties	alkyd	AJO20	AJO30	AJO40	AJO50
curing time (h, at 120 °C)	9.0	8.5	8.0	7.25	6.45
scratch hardness (kg) ^a	-	2.5	2.7	2.9	3.2
tensile strength (MPa)	0.72	1.63	2.13	2.58	3.18
elongation at break (%)	67	90	102	116	129
gloss (60°)	80	82	83	84	85
adhesion (%)	100	100	100	100	100

^aLimit of the instrument for scratch hardness was 10.0 kg (highest).

3.4.6 Chemical resistance test

The chemical resistance test of the thermosets is carried out in water, NaOH (2%, aq), HCl (10%, aq), ethanol (20%, aq), and NaCl (10%, aq), and the results are summarized in Table 3.5. The cured films exhibited excellent solvent (water and ethanol) and salt solution resistance and good acid and alkali resistance. This is due to the compact and highly cross-linked structure of the polymer networks of EJO and citric acid. Moreover, strong H-bonding interactions of the polar functional groups of the polymer networks induce rigidity and strength of the material. Further, the weight loss (%) decreases with increasing EJO and citric acid content in the blends. As the alkyd resins and EJO contains hydrolyzable ester linkages in the structure, the alkali resistance of the blends is relatively poor. But due to the presence of rigid aromatic moieties in the alkyd resins, the alkali resistance of the blends is yet satisfactory.

Table 3.5: Chemical resistance (wt loss %) of the blends in different chemical environments.

chemical environment	alkyd	AJO20	AJO30	AJO40	AJO50
water	0.018	0	0	0	0
ethanol (25%, aq.)	0.043	0	0	0	0
NaCl (10%, aq.)	0.074	0	0	0	0
NaOH (2%, aq.)	1.86	3.43	2.74	2.18	1.53
HCl (10%, aq.)	4.27	3.82	3.27	2.65	2.09

3.4.7 Effect of postcure on the thermal and mechanical properties

The influence of postcure of the films at 160 °C on thermal and mechanical properties was investigated. From Table 3.6, it is observed that thermal stability of the blend (AJO20) is improved by 18 °C (Fig. 3.7). Moreover, the tensile strength increased

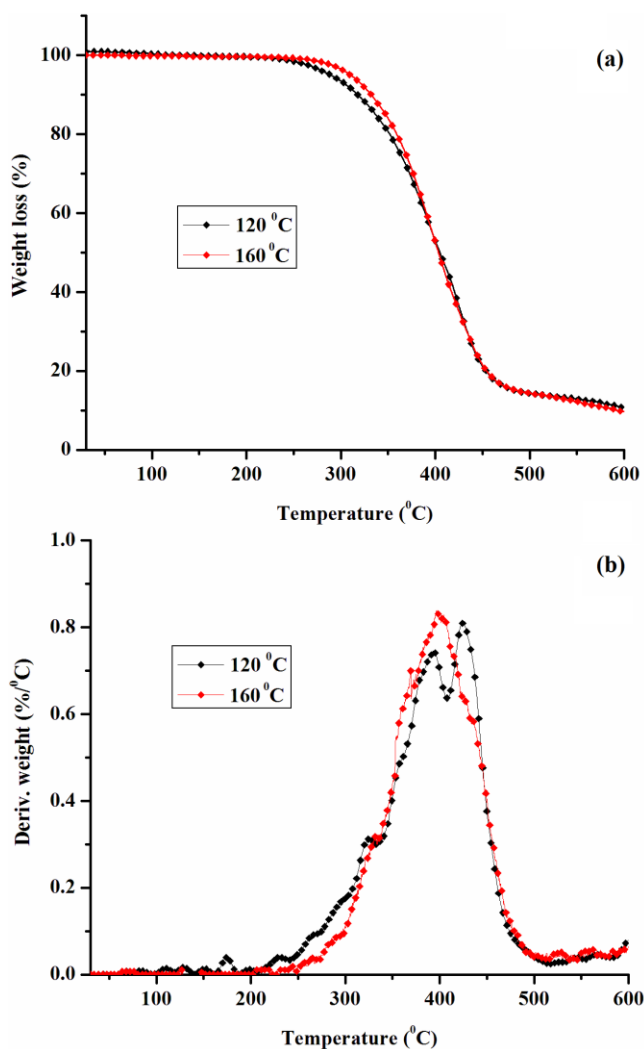


Fig. 3.7: TGA (a) and DTG (b) curves of AJO20 cured at 120 °C and 160 °C.

by 0.35 MPa (21.47%) with decreased elongation at the break. The improvement in thermal and mechanical properties of the films on postcure at 160 °C can be attributed to the increased cross-linking density of the polymer networks. The molecular rearrangements produced by thermally activated transesterification reactions of –OH

groups generated in the ring opening polymerization reaction (Scheme 3.3, Steps 3 and 4) with residual –COOH groups resulted increased in crosslinking density of the polymer networks.⁷ Most of the citric acid units were converted into cross-linkers producing the observed increase of the thermal and mechanical properties.

Table 3.6: Performance of the postcured AJO20.

curing conditions	tensile strength (MPa)	elongation at break (%)	scratch hardness (kg)	T _i (°C)
120 °C	1.63	90	2.5	291
*160 °C	1.98	69	3.1	309

*postcured at 160 °C for 10 h.

3.5 Conclusion

- Jatropha oil based alkyd resins were cured by bio-based polymer networks of EJO and aqueous citric acid solution.
- Epoxidation of the alkyd resins facilitated the cross-linking reactions with EJO in the presence of citric acid.
- The curing time, thermal stability, and mechanical properties of the alkyd resins were improved significantly upon blending with EJO. The curing time of the alkyd resins was reduced to 6.45 h, and the thermal stability and tensile strength were increased by 42 °C and 3.18 MPa, respectively.
- The technique used here offers a number of advantages, including environmentally friendly, low cost, easy performance, solvent-free/catalyst-free, and bio-based content, opening a number of opportunities in the paint industries.
- In addition, the thermal and mechanical properties of the films were observed to be improved further on postcuring at 160 °C.
- The molecular rearrangements produced by thermally activated transesterification reactions of –OH groups generated in the ring opening polymerization reaction

with residual –COOH groups resulted in increased cross-linking density of the polymer networks during postcuring.

- Overall, the results of the study suggest a high potential for these blends to be used for surface coatings.

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