

# Synthesis and Characterization of *Jatropha Curcas* Oil-Based Alkyd Resins and Their Blends with Epoxy Resin

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**ABSTRACT:** Alkyd resins based on *Jatropha curcas* oil with different molar ratios of phthalic anhydride (PA) and maleic anhydride (MA) were prepared by alcoholysis followed by polyesterification reaction. The progress of the reaction was traced by the determination of acid value at regular time intervals. From the kinetic study the extent of the reaction was found in the range of 52.4–61.2%. The prepared resins were blended with a commercially available fast-curing epoxy resin in order to improve the properties like curing time, chemical resistance, tensile strength, and thermal stability. The morphology study of the blends showed good compatibility of alkyd and epoxy resins. On blending with epoxy the tensile strength of the alkyd resins improved significantly and the thermal stability increased by 20°C. From the various properties of the blends it was observed that the blend with 100% phthalic anhydride has the best performance characteristics and is the most efficient. The blends possess properties that are much more superior in many aspects than the individual components and have potential for application as coatings.

**KEYWORDS:** *Jatropha curcas* oil, alkyd resin, epoxy, blend, coating, tensile strength

## 1 INTRODUCTION

Growing public concern about environmental pollution caused by accumulation of nondestructible solid waste, environmental issues and declining petroleum-based products, have stimulated the development and design of renewable biodegradable polymers as well as composite materials from renewable resources [1]. Polymers from renewable resources can form a basis for the replacement or substitution of petroleum-based polymers through the inventive design of new biodegradable polymers [2]. Vegetable oil-based alkyd resins have a wide range of industrial applications such as in industrial finishes and maintenance, architectural uses and surface coatings, etc. [3]. Alkyd resins based on vegetable oil have a number of advantages, including versatility in structure and properties, overall low cost and ease of application [4]. Moreover, alkyd resins are advantageous over acrylic resins in high solids coatings. In contrast, it is difficult to prepare low molecular weight acrylic resins with at least two hydroxyl groups on essentially all molecules. But the synthesis

of alkyd resins with two or more hydroxyl groups on essentially all of the molecules is relatively easy [5]. However, due to some major drawbacks like the low alkali resistance, low mechanical strength, low hardness and low thermostability of alkyd resins, their use is limited in practical applications. To improve these drawbacks of alkyd resins, blending with other suitable resins such as epoxy resin, amino resin, silicone resin and ketonic resin can be performed [6]. The better compatibility comes from the relatively low viscosity of the resin and from its structure, which contains a relatively polar and aromatic backbone and aliphatic side chains with low polarity [7].

Dutta *et al.* synthesized and characterized polyester resins based on nahar seed oil as binder material for industrial stoving paint. The performance characteristics like hardness, thermal stability and chemical resistance of the synthesized resins were improved by blending with epoxy resin [8]. Aigbodien *et al.* studied the utilization of maleinized rubber seed oil and its alkyd resin as binders in waterborne coatings. The rubber seed oil was treated with different amounts of maleic anhydride and evaluated as binder in nonpolluting coating, and also for use in preparing alkyd resin. The alkyd films were highly resistant to acid, brine and water but fairly resistant to alkali, while maleinized rubber seed oil films exhibited poor

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chemical resistance [9]. Guner *et al.* reported the preparation of various polymers from triglyceride oils. The presence of fatty acid chain in the polymer structure improves some physical properties of polymer in terms of flexibility, adhesion, resistance to water and chemicals. These polymers were reported to be biodegradable and biocompatible [10]. Kumar *et al.* made an evaluation of *Jatropha curcas* as multipurpose oil seed crop for industrial uses. *Jatropha Curcas* is a drought resistant shrub or tree which is widely distributed in the wild or semicultivated areas of Central and South America, Africa and Southeast Asia. The first commercial applications of *Jatropha curcas* were reported from Lisbon, where the oil imported from Cape Verde was used for soap production and for lamps. The *Jatropha curcas* oil was blended with Palm biodiesel to improve oxidation stability needed for South and Southeast Asian countries [11–13]. Akintayo *et al.* studied the characteristics and composition of *Jatropha curcas* oil and cakes. From their study, the fatty acid composition of *Jatropha curcas* oil was found as: palmitic acid (19.9%), stearic acid (6.8%), oleic acid (41.3%), linoleic acid (31.4%), and linolenic acid (3.0%), etc., which corresponds to saturated acids (26.3%) and unsaturated acids (72.7%) [14].

Epoxy resins have been commercially available for more than 60 years and find uses in a wide range of applications, especially in the adhesive and surface coating industry. Epoxy resins possess better adhesion, thermal stability, mechanical properties, curing time, alkali and water resistance than the alkyd resins. However, the epoxy resins suffer from inferior properties like acid resistance, toughness, and gloss [15].

*Jatropha curcas* is a versatile plant with several potential uses such as for biodiesel, medicine, cosmetics, etc. This oil has also been used for making soap commercially in many countries. In addition, several parts of the *Jatropha* plant have medical and cosmetic uses [16]. *Jatropha* oil is becoming the future source of biodiesel for India and for other countries also. Among the various oil seeds, *jatropha* oil has been found more suitable for biodiesel production on the basis of various characteristics. The cultivation of *Jatropha curcas* is possible under stress conditions and the oil of these species has various characteristics which are more suitable for biodiesel production [17].

Although *jatropha* oil is exploited for different potential applications, it has not been getting very much interest from the surface coating industry. In our earlier work we have reported the synthesis and characterization of *Jatropha curcas* oil-based alkyd resins [18]. We have found that the alkyd resins have long curing time, low alkali resistance and relatively low hardness, which will limit their use in various

coating applications. So, in this work our main objective is to improve these drawbacks of the *Jatropha curcas* oil-based alkyd resins by blending with a commercially available epoxy resin. This article reports the kinetic study of the polyesterification reaction in the alkyd resin preparation from *jatropha* oil. The coating performance of the alkyd and epoxy blends makes them appealing as low-cost and multipurpose coatings.

## 2 EXPERIMENTAL

### 2.1 Materials and Methods

*Jatropha curcas* seeds were collected from the rural area of Tezpur (Sonipur district, Assam, India). The oil was extracted from the seeds by solvent extraction and the extracted oil was purified by heating and alkali refining (specific gravity 0.9032 g/cm<sup>3</sup>, saponification value 194 mg KOH/g, iodine value 103 g I<sub>2</sub>/100 g, and acid value 1.03 mg KOH/g). Epoxy resin (epoxy equivalent: 170–180 g/eq), epoxy hardener (polyamidoamine, amine value 320–350 mg KOH/g), methyl-ethyl ketone peroxide (MEKP) and Cobalt-octoate of commercial grade were used as received (Kumud Enterprise, Kharagpur, India). Glycerol, phthalic anhydride (PA), maleic anhydride (MA) and LiOH were purchased from Merck and used without further purification.

### 2.2 Preparation of Alkyd Resins

A three-necked round bottom flask equipped with a mechanical stirrer, a thermometer and a nitrogen gas inlet was charged with 32.68 g (0.04 mol) of *Jatropha curcas* oil, 7.36 g (0.08 mol) of glycerol and 0.05 weight percent (with respect to the oil) of LiOH with continuous stirring. The mixture was heated continuously at 225–230°C for 45–60 minutes until it formed monoglyceride, confirmed by solubility in methanol (resin:methanol=1:3 v/v) at ambient temperature (30°C). Then the reaction mixture was cooled to 125°C and 0.12 mol of acid anhydride (PA and MA) in the form of fine powder was added to it. Next, the reaction temperature was raised to 220°C until it reached acid value in the range of 20–30 mg KOH/g. The acid value of the alkyd resins was determined in ethanol by titration with 0.1 N ethanolic KOH solution at a regular time interval of 10 min. The prepared resins were characterized fully according to our previous work [18]. The byproduct water formed in the polyesterification reaction was removed by azeotropic distillation using ethanol. The compositions of the prepared resins are shown in Table 1.

**Table 1** Mass (g) of each reagent used in resin formulations.

| Resins | Compositions (%) | Oil   | MA    | PA    | Glycerol |
|--------|------------------|-------|-------|-------|----------|
| Resin1 | 100% PA          | 32.68 | 0     | 17.77 | 9.34     |
| Resin2 | 50% PA & 50%MA   | 32.68 | 5.883 | 8.88  | 9.34     |
| Resin3 | 75% MA & 25% PA  | 32.68 | 8.825 | 4.44  | 9.34     |

### 2.3 Determination of Extent of Reaction and Average Degree of Polymerization

From the acid value of the reaction at regular time intervals, the extent of the reaction  $P$  is calculated using the equation [19],

$$P = (C_0 - C_t) / C_0 \quad (1)$$

where  $C_0$  and  $C_t$  are the acid value at zero and  $t$  the reaction time respectively. Using the value of  $P$ , the average degree of polymerization (DP) is calculated using the equation,

$$DP = 1 / (1 - P) \quad (2)$$

### 2.4 Preparation of Alkyd/Epoxy Blends

The blends of alkyd and epoxy resin were prepared by mechanical mixing of the components. Before the curing of blends, the mixture was placed in a vacuum oven at 45°C to remove the moisture, trapped air and volatiles to get void-free film. The different alkyd resins and epoxy were mixed at predetermined ratios of 50:50 (w/w) to obtain the Blend A, Blend B and Blend C. along with the required amount of poly(amido amine) hardener. The recipes of the three different blends are shown in Table 2. In each case the hardener was added and the ratio of epoxy to hardener was maintained at 2:1 (w/w). MEKP and Cobalt-octoate, which act as hardener and accelerator respectively, were added in 4% and 2% weight respectively with respect to the alkyd resin. The mixture was then placed on a Teflon sheet by an applicator maintaining the thickness uniformly (0.4 mm) and allowed to cure at 90°C.

### 2.5 Chemical Resistance

A fixed amount of the samples (0.5 g) were coated on glass plate and kept in a 250 mL beaker containing 200 mL of different chemicals, viz. 20% aqueous hydrochloric acid (v/v) solution, 5% aqueous sodium hydroxide (w/v) solution, 25% aqueous sodium chloride solution and distilled water, at room temperature for a week. After that, the samples were taken out of

**Table 2** Mass (g) of each reagent used in blend formulations.

| Sample  | Alkyd resin | Epoxy resin | Epoxy hardener |
|---------|-------------|-------------|----------------|
| Blend A | 5 (Resin1)  | 5           | 2.5            |
| Blend B | 5 (Resin2)  | 5           | 2.5            |
| Blend C | 5 (Resin3)  | 5           | 2.5            |
| Blend D | —           | 5           | 2.5            |

the solutions and dried in a vacuum oven until constant weight was achieved. The physical appearance of the samples were noted.

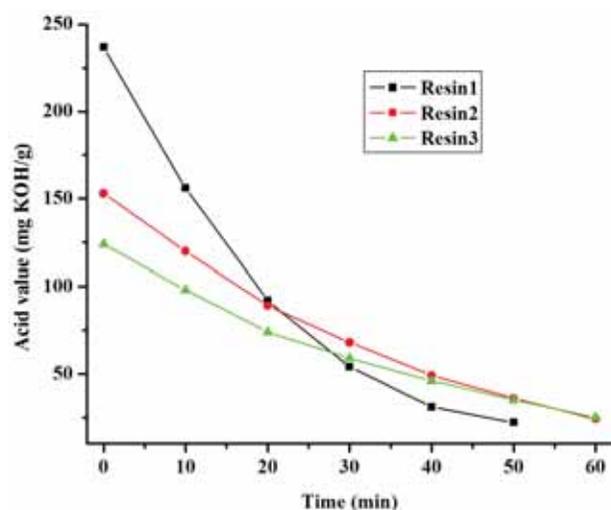
### 2.6 Characterization

The FTIR spectra of the blends were recorded by FTIR Nicolet 410 using KBr pellet. The thermogravimetric analysis was done with a thermogravimetric analyzer (Shimadzu TGA-50) at the heating rate of 10°C/min under  $N_2$  atmosphere. The surface morphology of the blends was studied by scanning electron microscopy (SEM) (model: Jeol-JSM 6390 LV, Japan). The surface of the sample was platinum-coated before SEM analysis. The blends were casted on a teflon-coated plate and allowed to dry at 90°C, and curing time was recorded. The gloss of the different blends was determined by a digital mini gloss meter at an angle of incidence of 60°. The blends were uniformly coated on the mild steel panel and kept for 7 days for maturation after curing, and then a hardness test was performed with lead pencils graded from 6B to 6H with the standard test method [20]. The flexibility was tested with a mandrel tester. A resin-coated tin panel (100 mm x 50 mm x 0.315 mm) was bent over a 6.25 mm-diameter mandrel through 180° and examined for any damage, detachment, or cracking of the film according to the standard procedure [21]. The adhesion performance of the blends and the individual resin was tested with commercial cello tape according to the cross-cut adhesion test method (ASTM D 3359). The chemical resistance of the cured resin blends coated on glass plates was tested according to ASTM D 593-67 [22]. For the determination of the tensile strength, the cured films were cut to a width of 10 mm and 60 mm length. The tensile strength of the blend films was measured with a universal testing machine (UTM) (model: Z010, Zwick) with a 10-kN load cell, at jaw separation speed of 50 mm/min.

## 3 RESULTS AND DISCUSSIONS

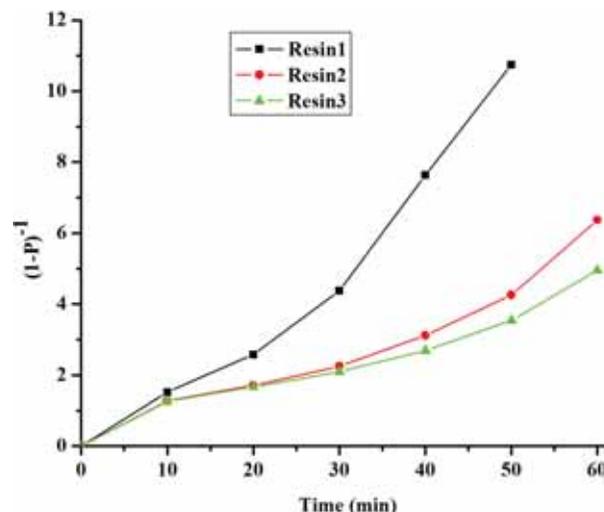
### 3.1 Kinetics of Polyesterification Reaction

During the course of the alkyd resin preparation the polyesterification reaction was monitored by measuring



**Figure 1** Plots of changes in acid value against reaction time during polyesterification.

the acid value at regular time intervals. The plots of acid value as a function of polyesterification reaction time for the alkyd resins having different molar ratios of PA and MA are shown in Figure 1. As the reaction progressed, the acid value was found to be decreased and the decrease was rapid during the initial stages as compared to the later stages of the reaction. This trend of changes in acid value during polyesterification reaction can be explained by the different reactivities of the primary and secondary hydroxyl groups of the mono-glyceride. As primary hydroxyl groups react faster than the secondary hydroxyl groups, the decrease in acid value at the early stages of the reaction is due to the reaction of primary hydroxyl groups, while the later stages correspond to the period when secondary hydroxyl groups react. Moreover, the decrease of the number of hydroxyl groups and increasing viscosity of the reaction mixture leads to relatively slow reduction in acid value at the later stages of the reaction [23]. The decrease in acid value is most rapid for Resin1 (100% PA) and least rapid for Resin3 (25% PA and 75% MA). This can be attributed to the presence of PA in Resin1 which undergoes rapid esterification, rather than the MA present in Resin3, and follows the trend. Thus, it can be inferred that the rate of decrease in acid value could be said to depend on the nature of anhydride used. A similar result was found for alkyds modified with yellow oleander seed oil [24]. Moreover, the decreasing concentration of the acids also decreases the rate of polyesterification towards the end of the reaction [3]. The formation of crosslinked network structure of the alkyd chains can be expected when the reduction in acid value is less rapid at the later stages of the polyesterification reaction. As a consequence of the formation of three-dimensional crosslinked networks,



**Figure 2** Plots of degree of polymerization as a function of reaction time for the alkyd resins.

the viscosity of the alkyd resins was observed to be increased with increasing the reaction time.

The monofunctional and polyfunctional condensation reactions are considered to follow a second-order rate law, as these condensation reactions essentially take place between the functional groups [25].

$$(1-P)^{-1} = C_0 kt + 1 \quad (3)$$

where  $P$  is the extent of reaction,  $C_0$  is the initial concentration of the reactants,  $k$  is the rate constant and  $t$  is the time of the reaction. In our study, concentration is substituted by acid value. As per the Equation (3), the plots of  $(1-P)^{-1}$  against  $t$  should be linear if  $k$  is constant throughout the reaction. However, from Figure 2 it is observed that the plots of  $(1-P)^{-1}$  versus  $t$  for the alkyd resins are not linear throughout the reaction. Up to a certain point (20 to 25 min) it is linear, and thereafter deviates from linearity. The initial linear portion represents the period of formation of linear molecules, and after the point of deviation from linearity the crosslinking of the alkyd chains can be expected. Similar results were observed in the polyesterification of African locust bean and jatropha seed oil. [19, 23].

The extent of the reaction, the average degree of polymerization and the second-order rate constant ( $k$ ) for the alkyd resins as calculated at the point of deviation from linearity are summarized in Table 3. From the table, it is observed that the extent of the reaction varies from 52.4 to 61.2 for the alkyd resins having different molar ratios of PA and MA. The alkyd Resin1 formulation having 100% PA showed the highest degree of polymerization (2.58), followed by Resin2 (2.25) having 50% PA and 50% MA, and was least for Resin3 (2.10) having 25% PA and 75% MA. This can

**Table 3** The extent of reaction, average degree of polymerization, and second-order rate constant ( $k$ ) for the alkyd resins as calculated at the point of deviation from the linearity.

| Parameters   | Alkyd resins |        |        |
|--|--------------|--------|--------|
|  | Resin1       | Resin2 | Resin3 |
| Time (min)   | 20           | 30     | 30     |
| Extent of reaction (%)                                     | 61.2         | 55.5   | 52.4   |
| Average degree of polymerization                           | 2.58         | 2.25   | 2.10   |
| $k \times 10^4$ g (mg KOH) <sup>-1</sup> min <sup>-1</sup> | 4.47         | 2.87   | 2.58   |

**Table 4** Molecular weight and molecular weight distribution of the alkyd resins.

| Sample | Mw   | Mn   | MWD  |
|--------|------|------|------|
| Resin1 | 1833 | 1625 | 1.13 |
| Resin2 | 2158 | 1847 | 1.16 |
| Resin3 | 2718 | 2132 | 1.27 |

$M_w$  = weight average molecular weight.  $M_n$  = Number average molecular weight.

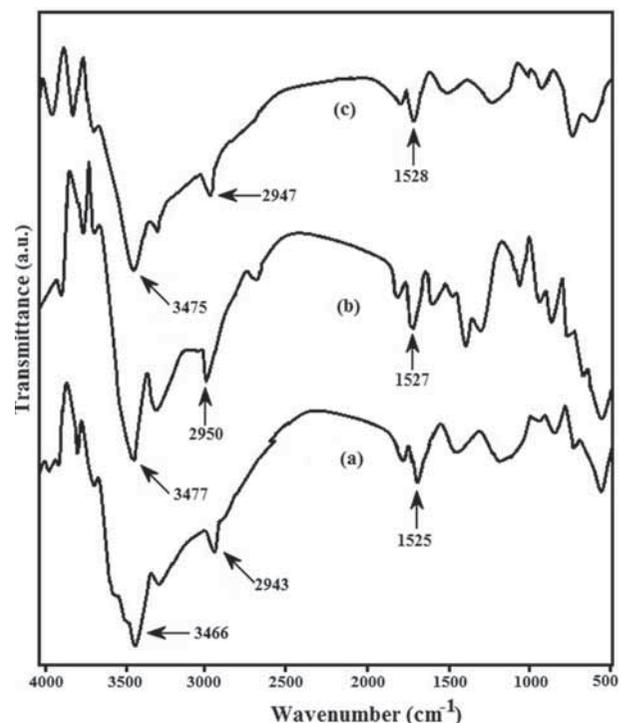
MWD = molecular weight distribution ( $M_w/M_n$ ).

be attributed to the presence of PA in Resin1, which undergoes rapid esterification as opposed to MA. The relatively low degree of polymerization as compared to the typical polyesterification reaction between PA and glycerol [26] may be due to the formation of low molecular weight species at the point of deviation from linearity. The second-order rate constant was found to be highest for Resin1 ( $4.47 \times 10^{-4}$  g (mg KOH)<sup>-1</sup> min<sup>-1</sup>), followed by Resin2 ( $2.87 \times 10^{-4}$  g (mg KOH)<sup>-1</sup> min<sup>-1</sup>), and was least for Resin3 ( $2.58 \times 10^{-4}$  g (mg KOH)<sup>-1</sup> min<sup>-1</sup>). It indicates that the rate of alkyd production depends on the nature of the anhydride used in the formulations. On the basis of these results, Resin1 having 100% PA would be best when prepared with *Jatropha curcas* oil.

In the second step of alkyd resin preparation, i.e., polyesterification reaction of monoglyceride and maleic anhydride, there is always the possibility of some side reaction occurring between maleate double bond and -OH group. This Michael addition reaction leads to an increase in molecular weight of the alkyd resins (Table 4) with MA content.

### 3.2 FTIR Study

The FTIR spectra (Figure 3) of the blends indicate the presence of important linkages, viz. ester group, epoxy, olefinic double bonds and other characteristic

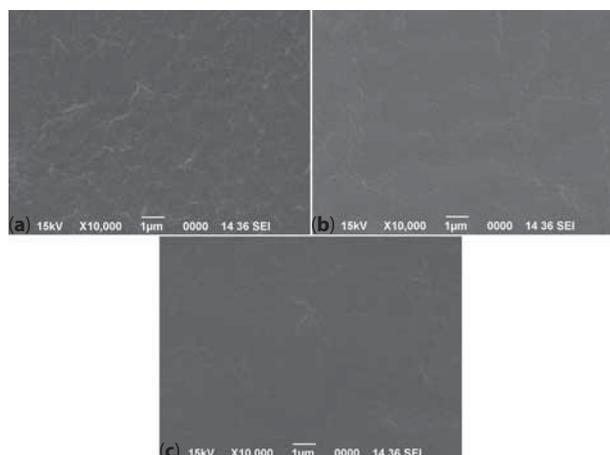


**Figure 3** FTIR spectra of the blends: (a) Blend A, (b) Blend B, and (c) Blend C.

peaks. In FTIR spectrum of the *Jatropha curcas* oil, the peak for  $>C=O$  band appears at  $1744 \text{ cm}^{-1}$ , whereas in the case of synthesized resins, peaks for  $>C=O$  band appear at  $1731\text{--}1733 \text{ cm}^{-1}$ , indicating some modification around the carbonyl group [18], and we observed further shifting of  $>C=O$  stretching frequency, which appears at  $1725\text{--}1728 \text{ cm}^{-1}$  in the blends. This is due to the interaction of the alkyd resin with the epoxy resin and the hardener. The IR absorption peaks for -OH groups appear at  $3466\text{--}3477 \text{ cm}^{-1}$  in the alkyd resins, whereas in the blends the stretching frequency shifted to lower wavenumber  $3410\text{--}3455 \text{ cm}^{-1}$ , indicating the interaction of the -OH group of alkyd resin with the epoxy group in the blends [24].

### 3.3 Blend Morphology

The surface characteristics of the cured blends were investigated by SEM study. The production of blends with an improved combination of properties of the individual components depends on the degree of compatibility of the resins. The SEM micrographs of the blends are presented in Figure 4. The SEM micrographs showed a smooth surface morphology in all the cases. Good compatibility of *Jatropha curcas* oil-based alkyd resins with epoxy resins can be confirmed from SEM micrographs, as there is no observable phase separation.



**Figure 4** SEM micrographs for the blends: (a) Blend A, (b) Blend B, and (c) Blend C.

### 3.4 Curing Study of the Blends

Alkyd resin was cured with MEKP along with Co-octoate at 120°C and takes a long curing time. This is due to the semi-drying nature of the *Jatropha curcas* oil. The curing time of all the alkyd resins was improved significantly, from several hours to several minutes (Table 5), by blending with epoxy resin. This is due to the high reactivity of the epoxide groups towards the amine hardener. There is the possibility of an interaction of hydroxyl and/or epoxide group of epoxy resin with hydroxyl group of the alkyd resin. Moreover, the amine groups in the epoxy hardener can react with the ester groups in the alkyd resin [27]. Further, the hydroxyl groups in both the resins can undergo self-condensation reaction to form ether linkages, as can be seen from the FTIR study (Figure 3).

## 3.5 Coating Performance of the Blends

### 3.5.1 Hardness

The hardness of the alkyd resin improved significantly on blending with the epoxy resin. This can be attributed to high crosslinking of alkyd resin with epoxy resin (Table 6). Blend A shows the highest hardness (3H), because of better compatibility of the aromatic

moiety present in the alkyd resin, as well as the electrostatic interaction between both the components, as supported by SEM study [27]. Moreover, the presence of a rigid aromatic moiety in the matrix reduces the polymer chains mobility and facilitates electrostatic interactions with the polar functionalities within the matrix.

### 3.5.2 Gloss

Most of the light reflected from a coated surface is diffused. Gloss refers to specular reflection or the light reflected at the same angle as the angle of incidence. The gloss of a coated surface depends on the amount of light absorbed or transmitted by the coating material, which is influenced by the smoothness or texture of the surface. In general, alkyds with long chains show semigloss, and this was also observed in our case (Table 6). The gloss of the alkyd resin was much higher than that of the epoxy resin. The gloss of the epoxy was improved via blending with the alkyd resins. This improvement of gloss of the epoxy is due to the better compatibility of these blends and good light stability of the alkyd resins [27]. The gratifying gloss of the blends indicated that the cured films possess good dimensional stability and smooth surface morphology.

### 3.5.3 Flexibility

All the blends were tested for flexibility via the bending of a tin-coated panel at 180°, but no cracking, damage, or peeling was observed (Table 6). This indicated the excellent flexibility of the blends as well as the individual resins. This is mainly due to two factors: first, the nondrying oil acted as a permanent plasticizer, and second, polyamidoamine imparted good flexibility [28].

### 3.5.4 Adhesion

In general, alkyd resins show moderate adhesion, but the epoxy resins show higher adhesion characteristics, as the resins have polar functional groups. However, epoxy resin is rich in polar groups. The prepared blend showed good adhesion as well as individual components (Table 6).

**Table 5** Curing characteristics of the alkyd resins and the blends.

| Sample   | Curing time | Sample  | Curing time | Sample  | Curing time | Sample | Curing time |
|----------|-------------|---------|-------------|---------|-------------|--------|-------------|
| *Resin 1 | 9 hours     | Resin 2 | 6 hours     | Resin 3 | 4 hours     | –      | –           |
| #Blend A | 60 min      | Blend B | 75 min      | Blend C | 70 min      | D      | 38 min      |

\*alkyd resins were cured at 120°C. #blends were cured at 90°C.

**Table 6** The gloss, flexibility, adhesion, and pencil hardness of the cured resins and blends.

| Sample  | Gloss (600) | Flexibility* | Adhesion (100%) | Pencil hardness |
|---------|-------------|--------------|-----------------|-----------------|
| Resin1  | 85          | P            | 100             | H               |
| Resin2  | 80          | P            | 100             | 2B              |
| Resin3  | 77          | P            | 100             | HB              |
| Blend A | 76          | P            | 100             | 3H              |
| Blend B | 64          | P            | 100             | 2H              |
| Blend C | 57          | P            | 100             | 2H              |
| Blend D | 49          | P            | 100             | 4H              |

\*P = Pass

**Table 7** Chemical resistance of the alkyd resins and the blends.

| Sample  | Chemical environment |           |                |           |
|---------|----------------------|-----------|----------------|-----------|
|         | NaOH (5%)            | HCl (10%) | NaCl aq. (25%) | Water     |
| Resin1  | Fair                 | Excellent | Excellent      | Excellent |
| Resin2  | Poor                 | Excellent | Excellent      | Excellent |
| Resin3  | Poor                 | Excellent | Excellent      | Excellent |
| Blend A | Good                 | Excellent | Excellent      | Excellent |
| Blend B | Peel off             | Excellent | Excellent      | Excellent |
| Blend C | Peel off             | Excellent | Excellent      | Excellent |
| Blend D | Excellent            | Good      | Excellent      | Excellent |

### 3.5.5 Chemical Resistance

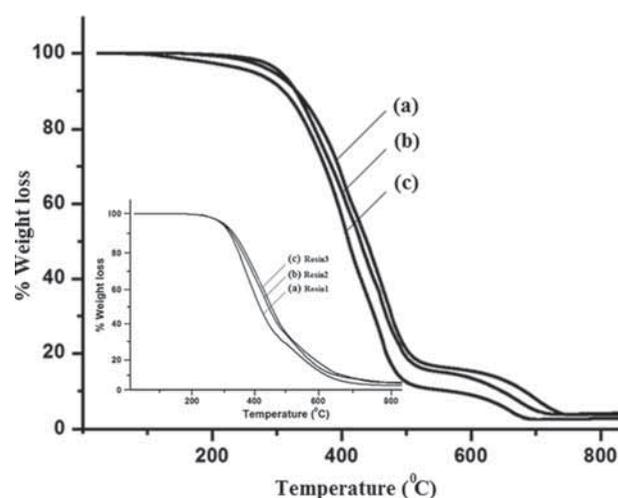
The results of the chemical resistance of the alkyd resins and the blends are shown in Table 7. It has been found that all the blends are unaffected in water and in aqueous salt solution, and are slightly affected in aqueous HCl and aqueous NaOH solutions. The Blend A and Blend B show excellent chemical resistance. Blend A (based on alkyd resin with 100% PA) is fairly resistant to alkali, which can be attributed to the presence of rigid aromatic moiety, and the alkali resistance decreases by increasing the MA content in the alkyd resins.

Both the alkyd and epoxy resins showed good water and salt solution (aqueous NaCl solution) resistance, and so did the blends. The acid resistance of the individual alkyd resins and the blends was quite satisfactory, but the epoxy resin showed poor resistance to an acid solution (20% HCl). It is due to the fact that the free epoxy groups in the epoxy resin were much more attracted toward the H<sup>+</sup> ion of the acid, and so the acid molecules penetrated the side of the coated sample [27]. However, the alkali resistance of the blends improved to a significant extent because

of the better alkali resistance of the epoxy resin. The individual alkyd resins were easily affected by a 2% NaOH solution, whereas the blends showed relatively good resistance up to a 4% aqueous NaOH solution. The poor alkali resistance of the alkyd resins was due to the presence of alkali hydrolyzable ester linkages. However, in the blend, the epoxy component had good resistance to alkali because of the absence of any alkali hydrolyzable groups, and this can be attributed to the formation of some more alkali-resistant amide bonds through the carboxylic groups of alkyd with the amine groups of the hardener. Among the blends, Blend A showed relatively better alkali resistance, which results from the presence of rigid aromatic moieties in the alkyd resin (100% PA) [9].

### 3.6 Thermal Study

The thermostability of the cured resins has been studied by thermogravimetric analysis (TGA) under N<sub>2</sub> atmosphere. The TGA traces for the cured blends are given in Figure 5 (inset TGA traces for the alkyd resins). The initial 1–2% weight loss is attributed to the loss of moisture. It is observed that the blends have good thermostability under nitrogen atmosphere and they started to degrade above 345°C, whereas the initial decomposition of all the resins approximately starts at 320°C. The overall thermal stability of the resins are in the order Resin3 > Resin2 > Resin1. This order of thermostability can be explained by the fact that the increase of MA content in alkyd resins causes an increase in crosslinking density, thereby improving the thermostability of the cured resins [18]. However, the thermostability of the blends do not follow the

**Figure 5** TGA thermograms for the blends: (a) Blend A, (b) Blend B, and (c) Blend C. Inset TGA curves for the alkyd resins.

same order (Figure 5). Blend A shows a higher thermostability (up to 345°C) than Blend B, followed by Blend C (335°C). The relatively higher thermostability of Blend A can be explained by the strong interaction as well as better compatibility of 100% PA-based alkyd and epoxy resin. The better compatibility comes from the aromatic moiety present in alkyd resin as well as the polar functionalities that can facilitate electrostatic interactions between the components in the blend [24]. Thus, *Jatropha curcas* oil modified alkyd and epoxy resin blends bear very good thermostability under nitrogen atmosphere. It is observed that the amount of residue at 700°C is very low (5–7%) and almost equal for all the cases.

### 3.7 Mechanical Properties

The mechanical properties, like tensile strength and elongation at break (%), of the cured films are shown in Table 8. The tensile strength of the alkyd-epoxy blends are lower than the epoxy resin (26.66 MPa) but much higher than the alkyd resins. Blend A showed the highest tensile strength (22.71 MPa) with 62% elongation at break, followed by Blend B (18.54 MPa) with 42% elongation at break and 16.83 MPa for Blend C with 35% elongation at break. This can be explained by the relatively good interaction of 100% PA-based alkyd and epoxy resin blends (Fig. 4i), resulting from the better compatibility of the aromatic moiety as well as electrostatic interaction between both components. However, the increase in tensile strength of the higher MA-based alkyd is not significant. This is due to the fact that the increasing MA content in the alkyd resin increases the unsaturation of the alkyd resins and results in intramolecular crosslinking reactions, thereby leaving less functionality to react with the epoxy resin [27]. This results in the lower compatibility of the higher MA containing alkyd resins as compared to the 100% PA-based alkyd. This also is reflected in the thermal stability of the blend. In the case of epoxy resin there are much better interactions in between the polymer chains and hardener, resulting in higher tensile strength than the blends.

## 4 Conclusions

*Jatropha curcas* oil-based alkyd resins with different molar ratios of PA and MA were prepared successfully. Michael addition reaction between maleate double bond and –OH group leads to increased molecular weight of the alkyd resins with MA content. Kinetic study showed that the extent of polyesterification reaction reached an appreciable level (52.4–61.2%). The second-order rate constant in the initial stage of

**Table 8** Mechanical properties of the cured films.

| Blends  | Tensile Stress (MPa) | Elongation % |
|---------|----------------------|--------------|
| Blend A | 22.71                | 62           |
| Blend B | 18.54                | 47           |
| Blend C | 16.83                | 35           |
| Blend D | 26.66                | 23           |

polyesterification was found in the order of  $10^{-4}$  g (mg KOH) $^{-1}$  min $^{-1}$ . However, it was found to be dependent on the nature of the anhydride used. The ratio of PA and MA in the prepared resin plays an important role in altering the properties of these resins. Due to their low alkali resistance, low mechanical strength, low hardness, low thermostability and long curing time, the use of alkyd resins are limited in practical applications. Blending of the alkyd resins with epoxy resins facilitated overcoming the drawbacks of the resins. The blends exhibited superior performances in terms of curing time, chemical resistance, gloss, hardness, and mechanical strength. The thermostability of the blends was improved significantly (up to 20°C) as compared to the neat alkyd resins. Morphological study of the blends showed good interaction between the alkyd and epoxy resin. This indicates that *Jatropha curcas* oil-based alkyd and epoxy resins have good compatibility and thus have potential uses in surface coatings. From this study it is observed that Blend A without maleic anhydride moiety shows optimum performance.

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## REFERENCES

1. G.J.L. Griffin, *Chemistry and Technology of Biodegradable Polymers*, Chapman & Hall, Glasgow (1994).
2. H. Uyama, M. Kuwabara, T. Tsujimoto, M. Nakano, A. Usuki, and S. Kobayashi, Green nanocomposites from renewable resources: Plant oil–clay hybrid materials. *Chem. Mater.* **15**, 2492 (2003).
3. D.S. Ogunniyi and T.E. Odetoeye, Preparation and evaluation of tobacco seed oil-modified alkyd resins. *Biores. Technol.* **99**, 1300 (2008).
4. H. Turaif and P. Lepoutre, Evolution of surface structure and chemistry of pigmented coatings during drying. *Prog. Org. Coat.* **38**, 43 (2000).
5. C.D. Diakoumakos and F.N. Jones, A new class of high-solids low-gloss mar resistant pigmented coatings prepared from an isophthalate-based oligoester, a melamine resin and various talcs. *Surf. Coat. Technol.* **150**, 37 (2002).

6. X. Yin, H. Duan, X. Wang, L. Sun, W. Sun, H. Qi, and L. Ma, An investigation on synthesis of alkyd resin with sorbitol. *Prog. Org. Coat.* **77**, 674 (2014).
7. D.A. Raval and V.M. Patel, Modified karanja oil based curing of acid functional acrylic copolymer resin for anticorrosive coating. *Paint India* **3**, 51 (2005).
8. N. Dutta, N. Karak, and S.K. Dolui, Synthesis and characterization of polyester resins based on Nahar seed oil. *Prog. Org. Coat.* **49**, 146 (2004).
9. A.I. Aigbodion, F.E. Okieimen, E.O. Obazee, and I.O. Bakare, Utilisation of maleinized rubber seed oil and its alkyd resin as binders in water-borne coatings. *Prog. Org. Coat.* **46**, 28 (2003).
10. F.S. Guner, Y. Yagci, and A.T. Erciyas, Polymers from triglyceride oils. *Prog. Polym. Sci.* **31**, 633 (2006).
11. M.T. Rodriguez, J.J. Gracenea, J.J. Saura, and J.J. Suay, The influence of the critical pigment volume concentration (CPVC) on the properties of an epoxy coating: Part II. Anticorrosion and economic properties. *Prog. Org. Coat.* **50**, 68 (2004).
12. L.M. Cano-Asseleih, R.A. Plumbly, and P.J. Hylands, Purification and partial characterization of a hemagglutinin from seeds of *Jatropha curcas*. *J. Food. Biochem.* **13**, 1 (1989).
13. A. Kumar and S. Sharma, An evaluation of multipurpose oil seed crop for industrial uses (*Jatropha curcas* L.): A review. *Ind. Crop. Prod.* **28**, 1 (2008).
14. E.T. Akintayo, Characteristics and composition of Parkia biglobbosa and *Jatropha curcas* oils and cakes. *Biores. Technol.* **92**, 307 (2003).
15. L. Yu, S. Petinakis, K. Dean, A. Bilyk, and D. Wu, Green polymeric blends and composites from renewable resources. *Macromol. Symp.* **249**, 535 (2007).
16. K. Openshaw, A review of *Jatropha curcas*: an oil plant of unfulfilled promise. *Biom. Bioenerg.* **19**, 1 (2000).
17. S. Jain and M.P. Sharma, Prospects of biodiesel from *Jatropha* in India: A review. *Renew. Sus. Energ. Rev.* **14**, 763 (2010).
18. M. Boruah, P. Gogoi, B. Adhikari, and S.K. Dolui, Preparation and characterization of *Jatropha curcas* oil based alkyd resin suitable for surface coating. *Prog. Org. Coat.* **74**, 596 (2012).
19. M.N.S. Kumar, Z. Yaakob, S. Maimunah, Siddaramaiah, and S.R.S. Abdullah, Synthesis of alkyd resin from non-edible *Jatropha* seed oil. *J. Polym. Environ.* **18**, 539 (2010).
20. B. Sarma, S.K. Dolui, and A.K. Sharma, Comparative evaluation of the effect of butylated and isobutylated derivatives of M-F resins as wood finish properties. *J. Sci. Ind. Res.* **60**, 153 (2001).
21. Indian Standard 101, Part 5/Section 2, Clause 2 (1988) Methods of Sampling and Test for Paints, Varnishes and Related Products. Indian Standards Institution, New Delhi.
22. American Society for Testing Materials, *Annual Book of ASTM Standards*, Philadelphia (1973).
23. A.I. Aigbodion and F.E. Okieimen, An investigation of the utilisation of African locustbean seed oil in the preparation of alkyd resins. *Ind. Crop. Prod.* **13**, 29 (2001).
24. M.M. Bora, P. Gogoi, D.C. Deka, and D.K. Kakati, Synthesis and characterization of yellow oleander (*Thevetia peruviana*) seed oil-based alkyd resin. *Ind. Crop. Prod.* **52**, 721 (2014).
25. P.J. Flory, Fundamental principles of condensation polymerization. *Chem. Rev.* **39**, 137 (1946).
26. W.H. Carothers, Polymers and polyfunctionality. *Trans. Faraday Soc.* **32**, 39 (1936).
27. N. Dutta, N. Karak, and S.K. Dolui, Alkyd-epoxy blends as multipurpose coatings. *J. Appl. Polym. Sci.* **100**, 516 (2006).
28. N.L. Thomes, The barrier properties of paint coatings. *Prog. Org. Coat.* **19**, 101 (1991).