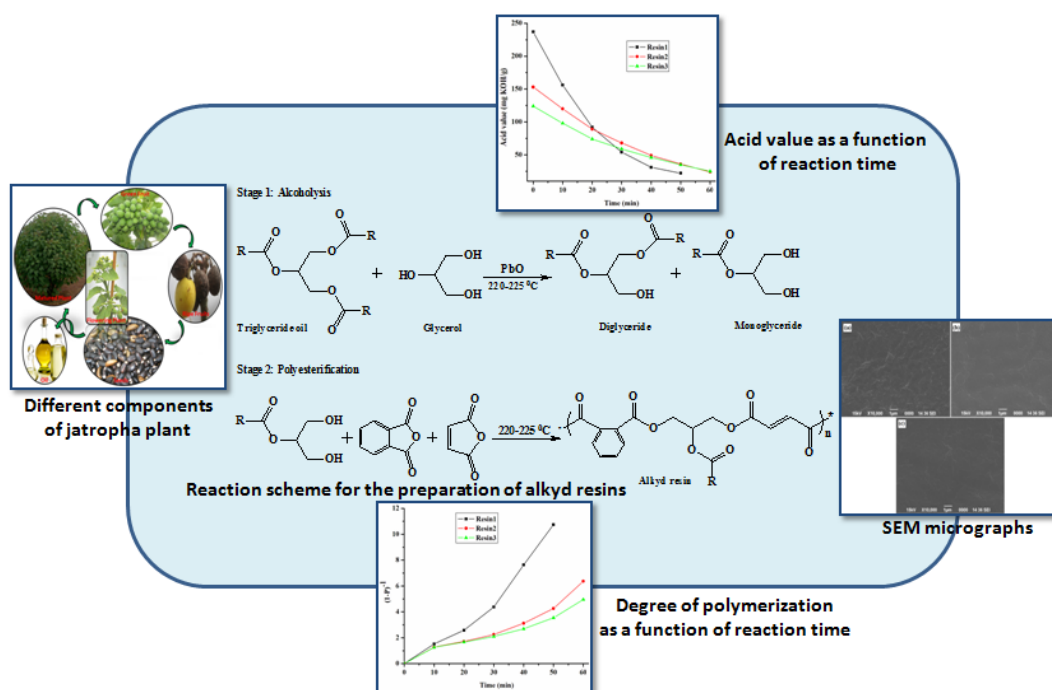# Chapter 2

Synthesis, characterization, and performance characteristics of Jatropha curcas oil based alkyd resins and their blends with epoxy resins

GRAPHICAL ABSTRACT

2.1 Introduction

The uses of renewable resources in different fields of applications of polymers have been proliferating day by day because of worldwide improvement of environmental concerns and depletion of world petroleum oil pool. Naturally renewable resources possess many advantages such as availability of feedstock, environment friendly nature, and low cost.[1-3] Polymers from renewable resources can form a basis for the replacement or substitution of petroleum-based polymers through the inventive design of new biodegradable polymer.[4]

Among the various vegetable oils based products, alkyd resins have attracted the interests of many chemists from both academia and industry. It can be seen from the huge number of scientific publications and patents covering this field. Alkyd resins have a wide range of industrial applications such as industrial finishes and maintenance, architectural uses and common surface coatings, etc.[5] Alkyd resins based on vegetable oil have number of advantages, including versatility in structure and properties, overall low cost, and ease of application.[6] In addition, alkyd resins are advantageous over acrylic resins in high solids coatings.

However, these alkyd resins suffer from some major drawbacks such as long drying time, low alkali resistance, low hardness, low mechanical strength, and low thermo stability, which limit their uses 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.[7] The presence of reactive functionalities like double bonds, hydroxyl groups, carboxyl groups, and ester linkages in alkyd resins provide tremendous potential for their modifications. Thus, alkyd resins with desired properties can be obtained by proper modification with varieties of reactive chemicals and other polymers. For instance, Dutta et al. reported the preparation of *Mesua ferrea* L. seed oil modified alkyd-epoxy blends for multipurpose coatings. The blends showed good performance with respect to drying time, hardness, flexibility, gloss, thermal stability, and alkali resistance.[8] Odetoye et al. reported the blending of jatropha oil-based alkyd with acrylic resins. The blended resins become hard within 5 min, which is comparable with that of the commercial standards. The white gloss paint formulated from the alkyd–acrylic blends (1:3) dried hard within 2 h at an outdoor temperature of 37 ± 2 °C.[9] Unpigmented polymer films of silicone acrylate–soya alkyd resins exhibit excellent mechanical properties and good exterior durability compared to silicone modified alkyd resin.[10]

The major seed oils used traditionally for preparation of such resins are linseed,[11] castor,[12] soyabean,[13] sunflower,[14] safflower, tung,[15] coconut, etc. These resins have been used in different fields of applications such as paint, coating, adhesives, binder for composites, etc. Non-traditional oils such as nahar oil,[16] rubber seed oil,[17] jatropha seed oil,[18] mahua oil,[19] melon seed oil, annona squmosa, African mahogany seed oil, African locust bean seed oil,[20], *Hura-crepitans* L. seed oil,[21] etc. are not exploited much for industrial applications.

Among the different vegetable oils, jatropha oil has drawn special attention to the scientific community with many attributes including multipurpose uses, and considerable potential of the crop. For instance, various parts of the jatropha are used in potential applications such as biodiesel, medicine, cosmetics, etc. The oil has also been used for making soap commercially in many countries.[22] 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 condition and the oil of these species having various characteristics is more suitable for biodiesel

production.[23] Thus, with the various potentially beneficial products and uses, *Jatropha curcas* can be regarded as a plant of high agro-industrial potential.

Although jatropha oil is exploited for different potential applications, it has not been getting so much interest in surface coating industry. The present study aims to investigate the preparation, characterization of the alkyd resins based on *Jatropha curcas* oil and their blending with epoxy resin. The performance characteristics such as, drying time, pencil hardness, gloss, chemical resistance, thermal stability, and mechanical properties of the cured blends were evaluated. The kinetics of polyesterification reaction was also studied.

2.2 Experimental

2.2.1 Materials

Jatropha curcas seeds were collected from the local area of Tezpur (Sonitpur district, Assam, India) and the oil was extracted from the seeds by solvent extraction and the extract was purified by heating and alkali refining (specific gravity 0.903 g/cm^3, saponification value 194 mg KOH/g, iodine value 105 g I$_2$/100 g, and acid value 1.03 mg KOH/g). The average molecular weight of the oil was found to be 884 g/mol and with polydispersity index 1.03.

Epoxy resin (epoxy eqivalent: 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 are used as received (Kumud Enterprise, Kharagpur, India). Glycerol, phthalic anhydride (PA), maleic anhydride (MA) and lead monoxide (PbO) were purchased from Merck and used without further purification.

2.2.2 Preparation of jatropha oil based alkyd resins

Jatropha oil based alkyd resins with different molar ratios of maleic and phthalic anhydrides were synthesized by a two-stage alcoholysis–polyesterification reaction. Scheme 2.1 presents the synthetic pathway for the preparation of alkyd resins. In a typical method 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 oil,

7.36 g (0.08 mol) of glycerol and 0.05 wt % of PbO with continuous stirring. The mixture was heated upto 225-230 °C for 45–60 min until monoglyceride was formed. Formation of monoglyceride was confirmed by its solubility in methanol (monoglyceride:methanol = 1:3, v/v) at room temperature. Then the reaction mixture was cooled to 125 °C and 0.12 mol of acid anhydride in the form of fine powder with 1.98 g of excess glycerol (27%) was added. Afterwards, the reaction temperature was raised to 230 °C and the progress of reaction was monitored by checking its acid value at a regular time interval. The reaction was continued until it reached acid value in the range of 20–40 mg KOH/g. The compositions of the three different batches of the resins are given in the Table 2.1.

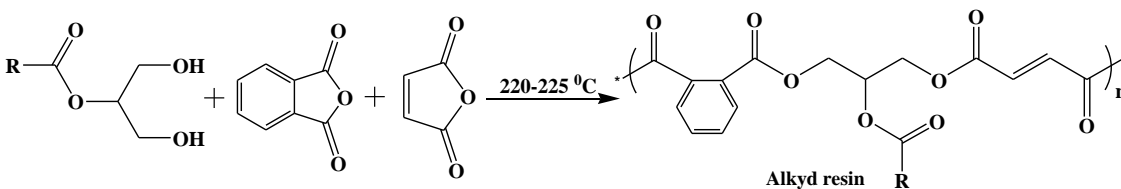**Table 2.1:** Mass (g) of each reagent used in resin formulations.

resins	compositions	oil	PA	MA	glycerol
Resin 1	100% PA	32.68	17.77	0	9.34
Resin 2	50% PA + 50% MA	32.68	8.88	5.88	9.34
Resin 3	25% PA + 75% MA	32.68	4.44	8.83	9.34

PA = phthalic anhydride. MA = maleic anhydride.

Stage 1: Alcoholysis
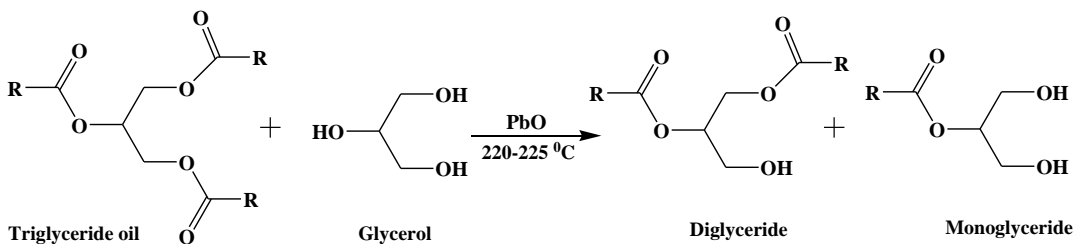
Stage 2: Polyesterification

Scheme 2.1: Schematic for the preparation of alkyd resins.

2.2.3 Preparation of alkyd/epoxy blends

The synthesized alkyd resins were blended with commercial grade epoxy resin in a predetermined ratio of 50:50 (w/w). Briefly, 2 g of alkyd resin and 2 g of epoxy resin were added and mixed thoroughly. To the mixture, MEKP (0.08 g, 4 wt % w.r.t. alkyd resin), cobalt octoate (0.02 g, 2 wt % w.r.t. alkyd resin), and poly(amido amine) (1 g, 50 wt % w.r.t. epoxy resin) were added with thorough mixing. The mixture was then uniformly coated over Teflon plate by an applicator and allowed to cure. Precaution was taken to avoid the air bubble formation during the curing process. The curing time of the blends were recorded. The blends prepared by this way with Resin 1, Resin 2, and Resin 3 are designated as Blend A, Blend B, and Blend C, respectively.

2.2.4 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,[24]

$$P = \frac{C_o - C_t}{C_o} \qquad \text{(Eqn. 2.1)}$$

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

$$DP = \frac{1}{1 - P} \qquad \text{(Eqn. 2.2)}$$

2.3 Instruments and methods

2.3.1 Fourier transform infrared spectrometer (FT-IR)

FT-IR is a useful method for the characterization of monomer and polymers. It is primarily used for the detection of functional groups, but analysis of spectra in the lower frequency finger print region can give evidence of degree of polymerization and the effect of substituents on the electronic properties of the polymer backbone.

Spectra were recorded from pressed KBr pellets using a Nicolet, Impact 410 FT-IR spectrometer in the range of 4000-400 cm^{-1} at room temperature.

2.3.2 Nuclear magnetic resonance spectrometer (^{1}H NMR)

NMR spectroscopy is one of the principal techniques used to obtain physical, chemical, electronic and structural information about molecules. Structure of compound can be determined by studying the peaks of NMR spectra. It is a very selective technique, distinguishing among many atoms within a molecule or collection of molecules of the same type but which differ only in terms of their local chemical environment. In proton NMR spectroscopy, structure of molecules is ascertained with respect to hydrogen nuclei within the molecule of a substance. ^{1}H NMR spectra were obtained on a Jeol FT-NMR spectrometer (400MHz) using TMS as the internal standard and CDCl$_3$ as the solvent.

2.3.3 Gel permeation chromatography (GPC)

The molecular weight of the particles were determined using a modular Waters 600 gel permeation chromatography (GPC) with three ultra styrogel columns of linear, 10^3 and 10^4 Å porosities and a 410 differential refractometer was used to determine the relative molecular weight of polymer samples as well as the distribution of molecular weights. Tetrahydrofuran (THF) was used as a mobile phase with a flow rate of 1.0ml/min. and the instrument was standardized with polystyrene standards.

2.3.4 Scanning electron microscope (SEM)

The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity.

SEM studies were performed to investigate the surface morphology or microstructure of the samples. JSM-6390LV, JEOL, Japan was used for analysis. The surface of the sample was coated with platinum before SEM analysis.

2.3.5 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) reveals the thermal characteristics of polymers including degradation temperature, absorbed moisture content the level of oligomer in polymer etc. It determines the weight loss with respect to temperature. Thermogravimetric analysis (TGA) was conducted on a Shimadzu TG 50 thermogravimetric analyzer with a heating rate of 10 °C/min under nitrogen atmosphere. The analysis was performed in the temperature range of 25- 600 °C.

2.3.6 Tensile property

The tensile properties of cured films such as tensile strength, and strain at break were examined using a universal testing machine (UTM, Zwick, Z010) at ambient temperature. Thickness and width of the rectangular films were controlled to be 0.5 mm and 10 mm, respectively. The sample gauge length was 4.5 cm and the cross-head speed was 50 mm/min. Three different measurements for each film sample were carried out to obtain averaged mechanical data.

2.3.7 Viscosity

Viscosity was determined by Brookfield viscometer, RVT model (#spindle 3, RPM 20) at room temperature.

2.3.8 Gloss

Gloss can be characterized by the angular distribution of light scattered from a surface and can be determined with a gloss meter. Paint films were drawdown on glass plate (wet film thickness 5-6 mm) and dried for 12 h and checked the gloss by using a digital mini gloss meter at an angle of incidence of 60°.

2.3.9 Chemical resistance

A weighted amount of the cured film (0.5 g) was kept in a 250 mL beaker containing 100 mL of different chemicals, viz. 10% 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 month. After that the samples were taken out of the solutions and dried in a vacuum oven until constant weight was achieved.

2.3.10 Evaluation of physicochemical properties

The physicochemical properties of the specimens such as acid value, saponification value, iodine value, adhesion, and flexibility were determined according to standard test methods.[25-28] The pencil hardness of the cured films was determined in scale of 6B to 6H of a standard set of pencils by dragging the pencil along the films using a pencil hardness tester. The relative amount of scratching is reported as the pencil number which offers the least scratching.

Determination of acid value

Acid value is the amount of free fatty acid (FFA) present in a sample. It is the quantity of base required to neutralize the FFA and it is expressed in mg KOH/g sample. In a typical method a known amount of the sample is dissolved in ethanol (neutralized) and titrated with an ethanolic KOH solution of known concentration using phenolphthalein as indicator. The volume of KOH (V mL) at the end point is recorded and acid value is calculated by following the equation:

$$\text{Acid value} \; = \; \frac{V \text{ x Equivalent weight of KOH}}{\text{Weight of the sample (g)}} \qquad \text{(Eqn. 2.3)}$$

Determination of saponification value

It is a measure of the average molecular weight or chain length of all the fatty acids present in oil. It represents the number of mg of KOH required to saponify 1 g of oil under specified conditions. For the determination of saponification value a weighted amount of oil is refluxed with 0.1 N ethanolic KOH solution. Afterwards, the mixture is titrated with 0.1 N HCl and the volume of HCl at the end point was recorded (A mL). A blank treatment was also run without sample and the volume of HCl at the end point was noted (B mL). The saponification value is calculated by the following equation:

$$\text{Saponification value} = \frac{\text{(B-A) x Normality of HCl x 56.1}}{\text{Weight of the sample (g)}} \qquad \text{(Eqn. 2.4)}$$

Determination of iodine value

Iodine value is the mass of iodine in grams that is consumed by 100 g of an oil or fat. It indicates the degree of unsaturation of the constituent fatty acids in oil and is thus a relative measure of the double bonds present in the oil. The higher the iodine value, the more C=C bonds are present in the oil. Iodine value is expressed in grams of iodine absorbed by 100 g of oil.

For the determination of iodine value a weighted amount of oil is dissolved in chloroform. To this mixture 20 mL of Wij's solution (iodine monochloride) is added with thorough mixing and allowed the flask to stand for half an hour incubation in dark. Afterwards, 10 mL of KI solution was added and titrated the solution against 0.1 N sodium thiosulphate solution until yellow color appeared. Then, 1 mL of starch indicator was added and again titrated against the sodium thiosulphate solution. The disappearance of the blue colour is recorded as the end point of the titration (A mL). In exactly the similar manner, the test was repeated without the oil and the corresponding reading at the end point was recorded (B mL).

$$\text{Iodine value} = \frac{\text{Normality of Na}_2\text{S}_2\text{O}_3 \text{ x (B}-\text{A) x 127 x 100}}{\text{Weight of the sample (g) x 1000}} \qquad \text{(Eqn. 2.5)}$$

2.4 Results and discussion

2.4.1 Kinetics of polyesterification reaction

During the course of the alkyd resin preparation the polyesterification reaction was monitored by measuring 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 Fig. 2.1. As the reaction progressed the acid value 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 from the different reactivities of the primary and secondary hydroxyl groups of the monoglyceride. As primary hydroxyl group reacts 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 group and increasing viscosity of the reaction mixture leads to relatively slow reduction in acid value at the later stages of the reaction.[20] The decrease in acid value is most rapid for the Resin 1 (100% PA) and the least for the Resin 3 (25% PA and 75% MA). This can be attributed to the presence of PA in Resin 1 which undergoes rapid esterification rather than MA present in Resin 3 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.[29] Moreover, the decreasing concentration of the acids also decreases the rate of polyesterification towards the end of the reaction.[4] The formation of cross linked 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 cross linked networks the viscosity of the alkyd resins was observed to be increased with increasing the reaction time.
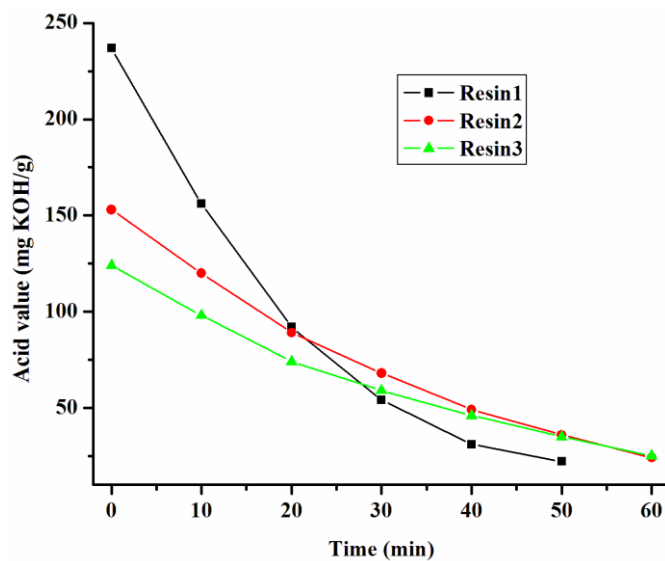
Fig. 2.1: Plots of acid value as a function of reaction time during polyesterification reaction.

The monofunctional and polyfunctional condensation reactions are considered to follow a second order rate law (Eqn. 2.6) as these condensation reactions essentially take place between the functional groups.[30]

$$(1-P)^{-1} = C_o k t + 1 \qquad \text{(Eqn. 2.6)}$$

where P is the extent of reaction, C_o is the initial concentration of the reactants, k is the rate constant, and t is the reaction time. In our study, concentration is substituted by acid value. As per the Eqn. 2.5, the plots of $(1-P)^{-1}$ against t should be linear if k is constant throughout the reaction. However, from Fig. 2.2 it is observed that the plots of $(1-P)^{-1}$ versus t for the alkyd resins are not linear throughout the reaction. Upto 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 cross linking of the alkyd chains can be expected. Similar results were observed in the polyesterification of African locustbean and jatropha seed oil.[18,20]
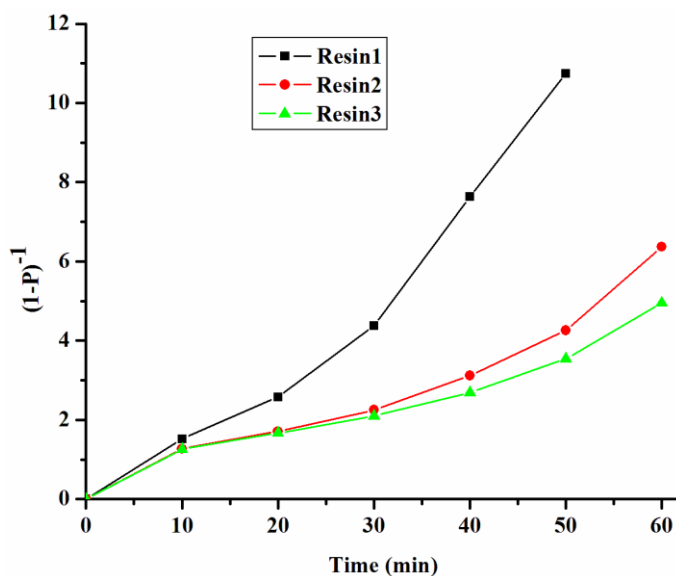

Fig. 2.2: Plots of degree of polymerization as a function of reaction time for the alkyd resins.

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 2.2. From the table, it is observed that the extent of the

reaction vary from 52.4 to 61.2 for the alkyd resins having different molar ratios of PA and MA. The alkyd Resin 1 having 100% PA showed the highest degree of polymerization (2.58), followed by Resin 2 (2.25) having 50% PA and 50% MA, and least for Resin 3 (2.10) having 25% PA and 75% MA. This can be attributed to the presence of PA in Resin 1 which undergoes rapid esterification rather than MA. The relatively low degree of polymerization as compared to the typical polyesterification reaction between PA and glycerol may be due to the formation of low molecular weight species at the point of deviation from linearity.[31] The second order rate constant found to be highest for Resin 1 (4.47 x 10^{-4} g (mg KOH)$^{-1}$ min^{-1}) followed by Resin 2 (2.87 x 10^{-4} g (mg KOH)$^{-1}$ min^{-1}) and least for Resin 3 (2.58 x 10^{-4} g (mg KOH)$^{-1}$ min^{-1}). It indicates that the rate of alkyd production depends on the nature of the anhydride used in the resin formulations. On the basis of these results, Resin 1 having 100% PA would best be prepared with *Jatropha curcas* oil.

Table 2.2: 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		
	Resin 1	Resin 2	Resin 3
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 x 10^{-4} g (mg KOH)$^{-1}$ min^{-1}	4.47	2.87	2.58

2.4.2 Spectroscopic (FT-IR and ^{1}H NMR) analysis

The FT-IR spectra of jatropha oil and the synthesized alkyd resins are shown in Fig. 2.3. In FT-IR spectrum of the oil (Fig. 2.3a), characteristic peaks are found at 3468 cm^{-1} due to -OH stretching vibration and at 2856-2924 cm^{-1} is due to aliphatic C-H stretching vibration. Peaks for C=O stretching vibration of triglyceride ester appears at 1744cm^{-1}, for C=C stretching vibration at 1655 cm^{-1} and that for C-H bending vibration is found at 1456

cm^{-1}. Also, peak at 1162 cm^{-1}is due to C-O-C stretching vibration of ester and that at 719 cm^{-1} is due to the methylene rocking vibration.
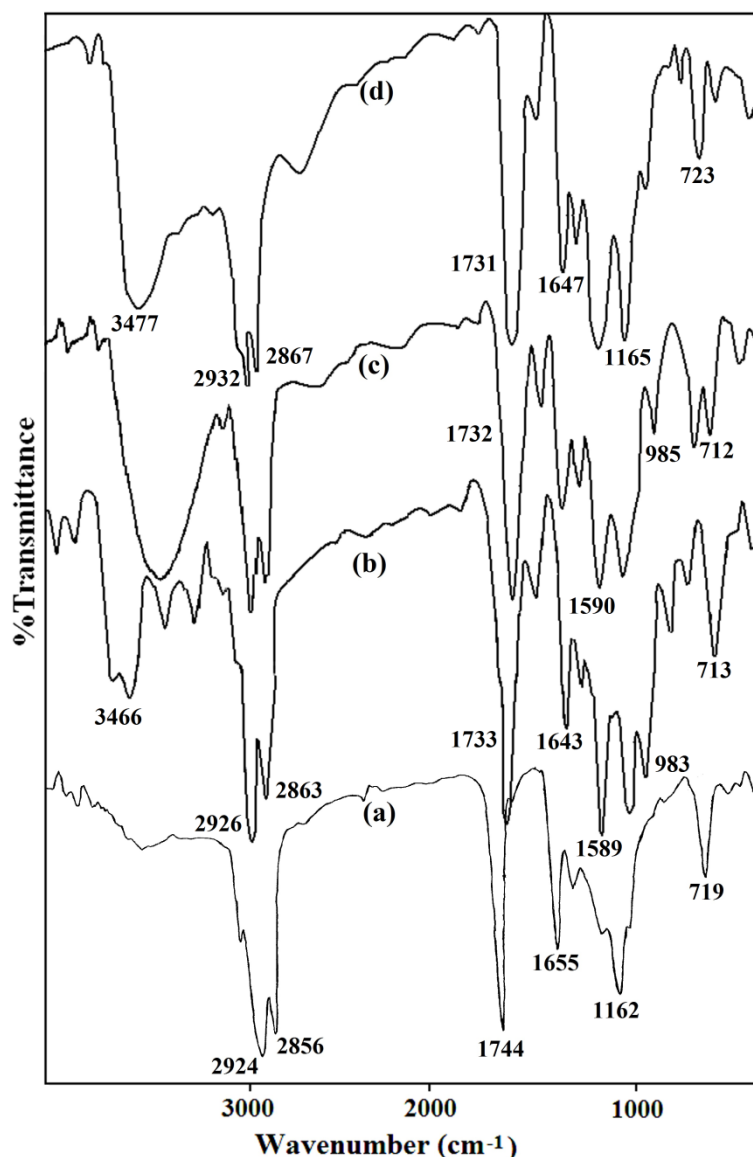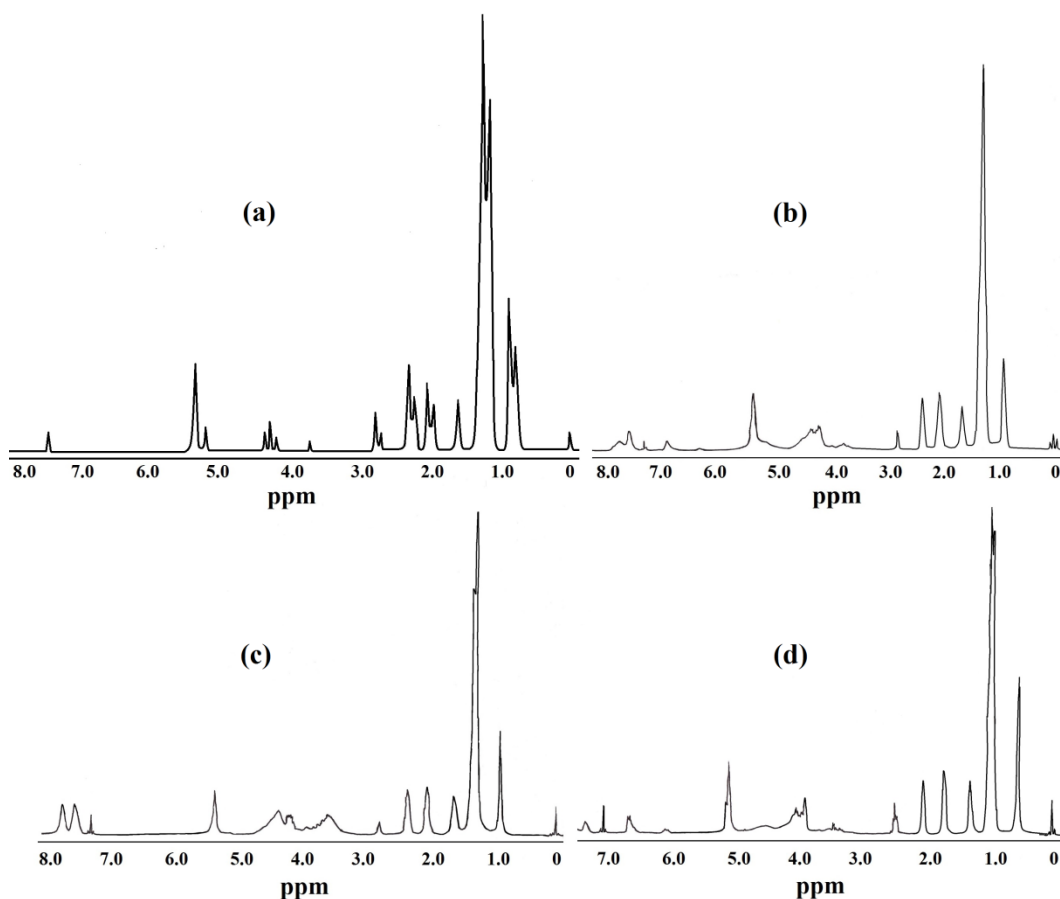

Fig. 2.3: FT-IR spectra of jatropha oil (a), Resin 1 (b), Resin 2 (c), and Resin 3 (d).

The FT-IR spectral data of the resins (Fig. 2.3b-d) indicate the presence of important linkages such as ester group, olefinic double bonds, ether linkages etc. The broad peaks at about 3466-3477 cm^{-1} can be assigned to -OH stretching vibration. The C-H asymmetric and symmetric stretching vibration appears at about 2925 cm^{-1} and 2865 cm^{-1}, respectively. In jatropha oil, the peak for C=O band appears at 1744 cm^{-1}, whereas in case

of synthesized resins, peaks for C=O band appears at 1731-1733 cm^{-1}, indicating some modification around the carbonyl group. The C-O-C stretching vibrations attached with aliphatic and aromatic moiety appears at around 1128-1165 cm^{-1} and 1269-1279 cm^{-1}. FT-IR absorption peaks for unsaturation of fatty acid and the aromatic ring of the phthalate groups correspond to the alkyd resin appears at 1589 cm^{-1} and for aromatic unsaturation at 1590 cm^{-1}. Thus, the polyesterification reaction is confirmed by FT-IR analysis.[29]

^{1}H-NMR spectrum of jatropha oil and the alkyd resins are shown in the Fig. 2.4. Peaks at ∂ 0.87-0.89 ppm due to the protons of terminal methyl group and that at ∂ 1.25-1.39 ppm for protons of all the internal -CH$_2$ groups. For all the internal protons of -CH$_2$

Fig. 2.4: ^{1}H NMR spectra of jatropha oil (a), Resin 1 (b), Resin 2 (c), and Resin 3 (d).

moiety present in the fatty acid chain peak arise at ∂ 1.60 ppm. Characteristic peaks at ∂ 2.01-2.05 ppm is for allylic protons of -CH$_2$, at ∂ 2.30-2.32 ppm for α-protons of ester

groups and at ∂ 2.75-2.78 ppm for double allylic protons of -CH$_2$. Peaks at ∂ 4.15-4.28 ppm for protons of glyceride moiety and ∂ 5.32-5.35 ppm for the protons of the -CH=CH- moiety.

^{1}H-NMR spectra of the resins peaks at ∂ 0.85-0.89 ppm appearing for the protons of terminal methyl group of the fatty acid chains and ∂ 1.60 ppm may be due to protons of -CH$_2$ group attached next to the above terminal methyl group. Peaks at ∂ 1.21-1.29 ppm are observed for protons of all the internal -CH$_2$ groups present in the fatty acid chain. For protons of unsaturated carbons, the characteristic peaks appear at ∂ 5.33-5.35 ppm and the same for methylene protons of glycerol moiety are found at ∂ 3.54-4.79 ppm. The protons for -CH- of same glycerol moiety are observed at very high value of ∂ 6.28-6.86 ppm. It may be due to the deshielding effect by the anhydride group possessing one unsaturation unit of MA or aromatic ring of PA, which are absent in the ^{1}H-NMR spectrum of the oil. The PA containing resin (Resin 1) shows aromatic protons at ∂ 7.54-7.83 ppm.

2.4.3 Physicochemical properties of jatropha oil based alkyd resins

The physicochemical properties such as acid value, saponification value, viscosity, volatile matter, and color are given in Table 2.3. As the resinification reaction was deliberately stopped at earlier stage to avoid gel formation, the acid value increases from 23 to 44 with increase in MA content in the resins. The moderate acid value of the

Table 2.3: Physicochemical properties of the synthesized alkyd resins.

serial no.	properties	Resin 1	Resin 2	Resin 3
1	acid value (mg of KOH/g)	23	25	44
2	saponification value (mg KOH/g)	383	392	399
3	viscosity (centipoise)	33	45	65
4	volatile matter (%)	3.25	3.80	4.18
5	color	dark brown	dark brown	dark brown

synthesized resins supports their moderate reactivity for surface coating applications. The saponification value of the resins is found to be in the range of 383 to 399. The viscosity

of the resins tends to increase with increasing MA content in the resins. It can be attributed to the increased molecular weight of the resins with MA content (Table 2.4). The amount of volatile matter for the synthesized alkyd resins is low (3.25 - 4.18) and hence they can find suitable applications in non-polluting surface coatings.[32]

2.4.4 GPC analysis

The average molecular weights and molecular weight distribution of jatropha oil and synthesized alkyd resins are given in Table 2.4. The benefits of narrow molecular weight distribution and low molecular weight of the alkyd resins are of a great interest in the formulation and application of the coating. The low average molecular weight of the alkyd resins influences the drying time, chemical resistance, and mechanical properties of the resins.[2] It is observed that the average molecular weights of the alkyd resins increase gradually with increasing MA content in the resins. In the second stage of alkyd resin preparation (Scheme 2.1), there is always possibility to occur some side reaction between maleate double bonds and -OH groups. This Michael addition reaction leads to increase in molecular weight of the alkyd resins with MA content.

Table 2.4: Molecular weight and molecular weight distribution of the alkyd resins.

sample	$\bar{M}_n$	$\bar{M}_w$	MWD
jatropha oil	883	927	1.05
Resin 1	1625	1833	1.13
Resin 2	1847	2158	1.16
Resin 3	2132	2718	1.27

$\bar{M}_n$ = number average molecular weight. $\bar{M}_w$ = weight average molecular weight.

MWD = molecular weight distribution ($\bar{M}_w/\bar{M}_n$).

2.4.5 Curing study of the resins

Jatropha oil based alkyd resins were cured by blending with commercially available epoxy resin and the curing characteristics are summarized in Table 2.5. Blending with epoxy resins significantly improved the curing time of the jatropha oil modified alkyd

resins. This is due to the high reactivity of the epoxy resins towards the anime hardener. The hydroxyl and/or epoxide groups of epoxy resin can react with the hydroxyl groups of the alkyd resins. In addition, besides the reaction of hydroxyl and ester group of alkyd resins, the amine group of the epoxy hardener can react with the ester groups.[8]

Table 2.5: Curing characteristics of the synthesized alkyd resins and the blends.

sample	curing temperature (°C)	tack-free time (min)	curing time
Resin 1	120	-	9 h
Resin 2	120	-	7 h
Resin 3	120	-	4.5 h
Blend A	90	40	60 min
Blend B	90	55	75 min
Blend C	90	50	70 min

2.4.6 Coating performance of the resins

To find suitability of the blends, coating characteristics such as gloss, flexibility, adhesion, and hardness of the cured films were investigated and the results are summarized in Table 2.6. The good gloss indicated that the cured films possess good

Table 2.6: Gloss, flexibility, adhesion, and pencil hardness of the cured blends.

sample	gloss(60°)	flexibility[a]	adhesion (100%)	pencil hardness
Blend A	76	P	100	3H
Blend B	64	P	100	2H
Blend C	57	P	100	2H

[a]P = Pass.

dimensional stability and smooth surface morphology. The resins exhibit excellent flexibility and adhesion. The flexibility is imparted by the long hydrocarbon chains of the fatty acid part of the oil and adhesion is conferred by the polar functionalities such as

ester, amine, amide, hydroxyl, ether, etc. of the resins. The higher pencil hardness of Blend A may be due to the presence of higher concentration of rigid aromatic moiety in the constituent alkyd resin. The results suggest suitability of the resins in surface coating application.

2.4.7 Chemical resistance

The results of chemical resistance for the resins are given in Table 2.7. It is observed that all the blends exhibit excellent resistance to water, salt solution, and HCl solution. But the alkali resistance of the resins are poor. The poor alkali resistance of the alkyd resins can be attributed to the presence of hydrolysable ester linkages in the resins. However, Blend A with higher concentration of PA is fairly resistant to alkali, which can be attributed to the presence of rigid aromatic moiety. The ester linkages of the aromatic moiety are less reactive towards hydrolysis.

Table 2.7: Chemical resistance of the blends.

sample	chemical environment			
	NaOH (5%)	HCl (10%)	NaCl aq. (25%)	water
Blend A	good	excellent	excellent	excellent
Blend B	peel off	excellent	excellent	excellent
Blend C	peel off	excellent	excellent	excellent

*Excellent = no weight loss.

2.4.8 Blend morphology

The surface morphology of the cured blends was investigated by SEM analysis. To produce blends with improved combination of properties depends on the degree of compatibility of the constituent resins. Good compatibility of jatropha oil based alkyd with epoxy resins can be confirmed from SEM study. The SEM micrographs of the blends are presented in Fig. 2.5. In all the cases, there is no observable phase separation and possess a smooth surface morphology. It is also reflected in the good gloss of the cured blends (Table 2.6).
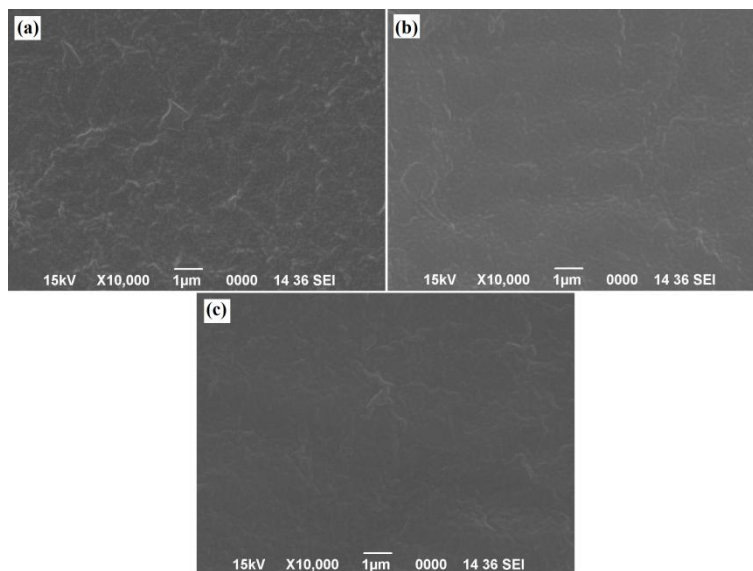
Fig. 2.5: SEM micrographs of (a) Blend A, (b) Blend B, and (c) Blend C.

2.4.9 Thermal and mechanical properties

The TGA curves for the cured resins are shown in Fig. 2.6. The initial 1-2% weight loss is attributed to the moisture loss. It is observed that all the resins showed fairly good
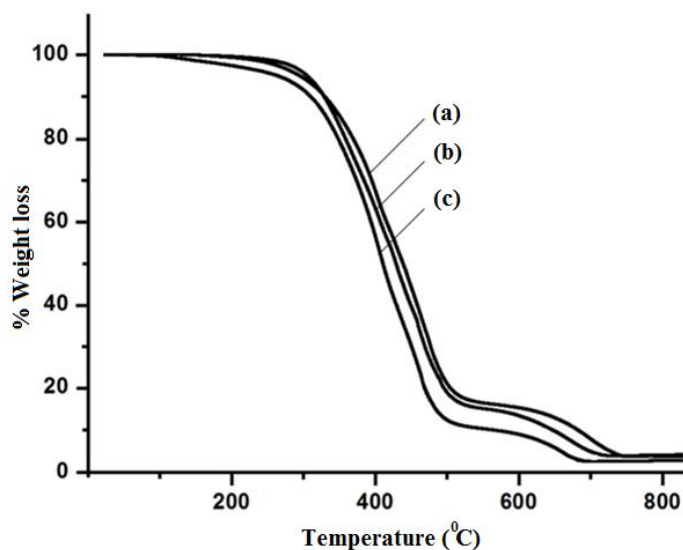

Fig. 2.6: TGA thermograms for the blends (a) Blend A, (b) Blend B, and (c) Blend C.

thermal stability. The major degradation of the resins occurred in the temperature range of 300-500 °C. The thermal stability of the blends increases in the order Blend A > Bland B

> Blend C. The relatively higher thermal stability 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.[8] Thus, jatropha oil modified alkyd and epoxy blends bear very good thermal stability 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.

The mechanical properties such as tensile strength and elongation at break (%) of the cured films are given in Table 2.8. It is observed that Blend A with 100% PA in the constituent alkyd resin formulation exhibits the highest tensile strength (22.7 MPa), followed by Blend B (18.5 MPa) with 50% PA and 50% MA. It can be attributed to the better compatibility of the epoxy resins with the alkyd resins having higher concentration of PA. The presence of polar aromatic moieties in the alkyd resins facilitates the strong electrostatic interaction with the epoxy resins. Higher the concentration of PA, more pronounced is the effect. In addition, higher concentration of MA resulted intramolecular cross-linking reactions within the alkyd resins and thereby leaving less functionality to react with the epoxy resins.[8] The decrease in elongation at break of the blends is justified by the increased cross-linking density of the polymer blends.

Table 2.8: Tensile strength and elongation at break for the cured films.

sample	tensile strength (MPa)	elongation at break (%)
Blend A	22.7	35
Blend B	18.5	47
Blend C	16.8	62

2.5 Conclusion

➢ Jatropha oil with semi drying nature is a suitable candidate for the preparation of alkyd resins.

➢ Kinetic study of alkyd resin preparation showed that the polyesterification reaction followed a second order rate law.

➢ The second order rate constant at the initial stage of polyesterification was found in the order of 10^{-4} g (mg KOH)$^{-1}$ min^{-1}. However, it depends on the nature of the anhydride used.

➢ An appreciable degree of conversion was noticed from the extent of reaction. The extent of reaction increases with increasing PA content in the resins and lies in the range of 52.4-61.2%.

➢ The curing characteristics of the jatropha oil modified alkyd resins were improved by blending with a fast drying epoxy resin.

➢ The performance characteristics such as gloss, adhesion, flexibility, hardness, and chemical resistance of the alkyd resins are quite satisfactory and make them suitable for use in surface coating applications.

➢ The alkyd/epoxy blends exhibit very good thermal stability (>250 °C) and tensile properties (22.7 MPa).

References

1. Ahmed, S., et al. *J. Appl. Polym. Sci.* **82** (8), 1855-1858, 2001.

2. Aigbodion, A.I., & Pillai, C.K.S. *J. Appl. Polym. Sci.* **79** (13), 2431-2434, 2001.

3. Mahapatra, S.S., & Karak, N. *Prog. Org. Coat.* **51** (2), 103-108, 2004.

4. Uyama, H., et al. *Chem. Mater.* **15** (13), 2492-2494, 2003.

5. Ogunniyi, D.S., & Odetoye, T.E. *Biores. Technol.* **99** (5), 1300-1304, 2008.

6. Al-Turaif, H., & Lepoutre, P. *Prog. Org. Coat.* **38** (1), 43-52, 2000.

7. Yin, X., et al. *Prog. Org. Coat.* **77** (3), 674-678, 2014.

8. Dutta, N., et al. *J. Appl. Polym. Sci.* **100** (1), 516-521, 2006.

9. Odetoye, T.E., et al. *Prog. Org. Coat.* **73** (4), 374-381, 2012.

10. Kanai, T., et al. *Prog. Org. Coat.* **58** (4), 259-264, 2007.

11. Makarewicz, E. *Prog. Org. Coat.* **28** (2), 125-132, 1996.

12. Onukwli, O.D., & Igbokwe, P.K. *J. Eng. Appl. Sci.* **3** (2), 161-165, 2008.

13. Wang, C., & Jones, F.N. *J. Appl. Polym. Sci.* **78** (9), 1698-1706, 2000.

14. Dullius, J., et al. *Prog. Org. Coat.* **57** (2), 123-127, 2006.

15. Thanamongkollit, N., et al. *Prog. Org. Coat.* **73** (4), 425-434, 2012.

16. Dutta, N., et al. *Prog. Org. Coat.* **49** (2), 146-152, 2004.

17. Ikhuoria, E.U., et al. *Prog. Org. Coat.* **59** (2), 134-137, 2007.

18. Kumar, M.N.S., et al. *J. Polym. Environ.* **18** (4), 539-544, 2010.

19. Tiwari, S., et al. *J. Sci. Ind. Res.* **61** (2), 110-116, 2002.

20. Aigbodion, A.I., & Okieimen, F.E. *Ind. Crop. Prod.* **13** (1), 29-34, 2001.

21. Ezeh, I.E., et al. *Ind. Crop. Prod.* **36** (1), 94-99, 2012.

22. Openshaw, K. *Biomass Bioenerg.* **19** (1), 1-15, 2000.

23. Jain, S., & Sharma, M.P. *Renew. Sust. Energ. Rev.* **14** (2), 763-771, 2010.

24. Kumar, M.N.S., et al. *J. Polym. Environ.* **18** (4), 539-544, 2010.

25. Annual Book of ASTM Standard, American Society for Testing Materials, Philadelphia, 1973.

26. AOAC International Method, 920.159, 1997a. Determination of acid value.

27. AOAC International Method, 969.17, 1997c. Determination of saponification value.

28. AOAC International Method, 920.160, 1997b. Determination of iodine value.

29. Bora, M.M., et al. *Ind. Crop. Prod.* **52**, 721-728, 2014.

30. Flory, P.J. *Chem. Rev.* **39** (1), 137-197, 1946.

31. Carothers, W.H. *Trans. Faraday Soc.* **32**, 39-49, 1936.

32. Aigbodion, A.I., et al. *Prog. Org. Coat.* **46** (1), 28-31, 2003.