

Preparation and Characterization of Alkyd Resins Based on *Citrullus colocynthis* Seed Oil

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ABSTRACT: In this study, different samples of alkyd resins based on *Citrullus colocynthis* seed oil (CCSO)—which has a high content of linoleic acid—were prepared as a renewable raw material. Short (I), medium (II), and long (III) alkyd resins were synthesized using oil, glycerol, and phthalic anhydride (PA) in different proportions. *Prunus mahaleb* seed oil (PMSO), which contains conjugated linolenic acid, was blended with CCSO in different proportions to examine the effect of PMSO on the film properties of alkyd resins (IV and V). All synthesized resins were characterized by FTIR and ¹H NMR spectroscopic analysis. These resins were also cured by an epoxy resin and their film properties (pencil hardness, adhesion, gloss, and chemical resistance) were determined. Analysis of these alkyds reveals that CCSO can be used as a new potential raw material for coating applications.

KEYWORDS: *Citrullus colocynthis* seed oil, *Prunus mahaleb* seed oil, alkyd resin, alcoholysis-polyesterification, renewability

1 INTRODUCTION

Today, paints and coatings are widely used in our everyday life. Due to the continuously increasing demand, depletion of petroleum resources, and increasing price of conventional raw materials, efforts have been devoted to the exploration of new sustainable, environment-friendly resources and end-products for many industrial applications. It is expected that the demand will continue to increase every year over the next decade, in spite of the increased price of conventional raw materials. Therefore, there is an increasing interest in using renewable resources like plant oils for coating applications because of the limited supply of petroleum-based products and their long-term effects on the environment. Moreover, a life-cycle analysis of alkyd emulsion paints showed less effect on the environment than those based on acrylic dispersions [1]. Alkyd paints are very attractive materials because they offer the possibility of obtaining versatile, low cost,

renewable, and low volatile organic compound emission products. Thus, in spite of the challenges associated with many new coating resins developed over the decades, alkyd resins—as a family—continue to remain of interest. There are two major reasons for the popularity of alkyds. First, alkyds are extremely versatile. An alkyd technologist can choose from a large variety of reaction ingredients and at widely different ratios to tailor the structure and properties of the resin or to obtain similar resin properties from different ingredients, as their availability or cost dictate. The second reason is that alkyd resins can be prepared at relatively low cost. Most of the raw materials are fairly low-cost commodity items, and major capital investment and high processing costs are not needed to produce the resins [2]. Alkyd resins have been the workhorse of the coating industry over the last half century. The coatings with drying oils have superior appearance, chemical resistance, and outstanding physical properties. However, the properties of the coating are mainly dependent on the type of drying oil. Therefore, an understanding of drying oil chemistry is necessary in order to develop coating properties that satisfy the requirements of a particular application. The

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major challenge in efforts to further develop the coatings industry will undoubtedly be ensuring low costs, to retain alkyds as the major candidate in the coatings industry. All these facts highlight that there is a need to find other unconventional oils that can replace some of the conventional oils and thus lower their price. Oils occur naturally in a wide range of sources, with each source providing a separate and distinctive material. Plant sources, including oilseeds, are the major source of oils. Most seeds and fruits contain oil; however, only a few of these sources are of economic importance. *Citrullus colocynthis* is a member of the genus *Citrullus* from the Cucurbitaceae family, which is well known as melons. The majority of *Citrullus colocynthis* are grown in the Saharo-Arabian phylogeographic region of Africa, in the Mediterranean region, and other regions of tropical Asia. Nearly 90% of the total dried crops are seeds, and Schafferman *et al.* [3] reported that the oil yield is approximately 400 l/ha. CCSO has a high percentage of linoleic acid (up to 66%) and the total unsaturated fatty acids constituted over 80% of the seed oil [4]. Silva *et al.* [5] reported that the addition of karawila seed oil, which contains α -eleostearic acid (*cis*, *trans*, *trans*-octadecatrienoic acid), improves the physical properties of alkyds and films of blends. PMSO is rich in α -eleostearic acid ($\approx 38\%$) and contains linoleic acid ($\approx 23\%$). Its level of saturated fatty acid is low [6]. Grown in the Mediterranean region and in parts of central Asia, the oil is being used in cosmetic formulation. Different oils have been applied for the synthesis of alkyd resins. However, till today, there has been practically no information available for the synthesis of alkyds using CCSO. In this study, the objective is divided into two sections. In the beginning, we have used pure CCSO and a blend with *Prunus mahaleb* as a substitute for fatty acids in order to synthesize a new alkyd resin. The resins were synthesized with varying amounts of oil, PA, and glycerol. In the second section, we studied their physicochemical and film properties, and the effect of blending PMSO on the film properties of alkyd resins prepared from CCSO.

2 EXPERIMENTAL

2.1 Materials

Citrullus colocynthis fruits were collected in December 2015 from Wadi Hanifa in the Al-Diriyah region (Riyadh, Saudi Arabia) and *Prunus mahaleb* seeds were purchased from a local market in Riyadh (Saudi Arabia). All chemicals and reagents (analytical grade) were obtained from Merck (Darmstadt, Germany), Sigma-Aldrich (Steinheim, Germany), Acros Organics (New Jersey, USA), and Fisher Scientific Co. (Leicestershire, UK) and used as received.

2.2 Oil Extraction and Purification

From the mixture, good quality seeds were chosen, and the damaged, oversized particles or undersized seeds were removed. The seeds were oven-dried at 60 °C for 24 h and then milled using an IKA-WERKE M20 grinder (Germany). The oil fraction of the oleaginous seeds was separated from the seeds using a Soxhlet method with hexane. The solvent was eliminated by rotary evaporation (Büchi R-210, Flawil, Switzerland), and then the residue was dried under vacuum.

2.3 Physicochemical Properties of the Extracted Oil

Acidity (percent oleic acid), acid value, and saponification value were determined according to the ISO standard [7, 8]. The iodine number was calculated using the method described by Ham *et al.* [9]. The density of the oil was measured using a density meter DM40 (Mettler-Toledo, Columbus, USA). The refractive index of the extracted oils was determined using an Abbe refractometer (Bellingham and Stanley Ltd, Kent, England). The kinematic viscosity was determined using an Ubbelohde type viscometer size 2 (Koehler, Bohemia, New York, USA).

2.4 Fatty Acid Composition

The fatty acid analysis was carried out using a GC-MS (QP2010 Ultra, Shimadzu, Japan) equipped with a FID detector and Rxi-5Sil MS column (30 m \times 0.25 mm internal diameter, 0.25- μ m film thickness). The fatty acid methyl esters were prepared using the method described by Nehdi *et al.* [4]. The detector and injector temperatures were programmed at 275 and 220 °C, respectively. The column temperature gradient ranged from 150 to 180 °C at 15 °C/min followed by an increase to 210 °C at 1 °C/min. Helium was used as the carrier gas. The MS was operated in the electron ionization (EI) mode at 70 eV. The peaks were identified by matching their mass spectra to peaks in the Wiley library database (NIST 11, Shimadzu, Japan).

2.5 Characterization of Alkyd Resins

The ^1H NMR spectra were recorded in deuterated chloroform (CDCl_3) containing a small amount of tetramethylsilane at the resonance frequency of 400 MHz using a JEOL ECLIPSE 400 spectrometer. The infrared spectra were recorded on a Shimadzu Fourier transform infrared spectrometer at a scan rate of 4 cm^{-1} .

2.6 Synthesis of Alkyd Resin

After the selection of oil content (pure CCSO or a blend of CCSO and PMSO), synthesis of alkyd resin was conducted using an alcoholysis process. This synthesis was performed in a three-necked round bottom flask fitted with a magnetic stirrer, a Dean-Stark trap fitted with a water-cooled condenser and a nitrogen inlet tube. The first step of the procedure, alcoholysis reaction, is the production of monoacylglycerols from oils. In the first reaction, oil was heated to 150 °C under a nitrogen atmosphere. Glycerol and NaOH—which is used as a catalyst (0.4 wt% of total oil)—were added to the reactor. The reaction temperature was increased to 220 °C. The reaction time was 90 min. The product is a mixture of mostly monoacylglycerol with small amounts of diacylglycerol and triacylglycerol. The completion of the reaction was monitored by the methanol test [10].

In the second step, after cooling the mixture, PA was added and the temperature was kept at 220–230 °C. The previously added NaOH was still in the reactor and it also catalyzed the alkyd production. Toluene was added (≈5 mL) to remove water. The reaction was followed up by determining the acid value. To obtain low viscosity, the reaction was stopped at an acid value of 15–30 mg KOH/g of alkyd. The overall formulation of the synthesized long oil alkyd is given in Table 1.

2.7 Curing of Alkyd Resins

Curing of the synthesized alkyd resins was performed according to the procedure reported in the literature [10]. In a typical procedure, the alkyd resins were cured by blending with commercial epoxy resin (EPON™ 1001, Hexion). Two grams of each resin and 1.33 g of epoxy were mixed well with stirring. To this, 0.6 g of epoxy hardener (Aradur® 450 BD, Huntsman) and 0.04 g of accelerator (cobalt-octoate) were added,

followed by stirring for 10 min. This homogeneous mixture was uniformly coated over steel and glass panels and kept at room temperature for 15 min. Prior to coating, surface preparation of these panels was done by using organic solvents such as alcohol and acetone. Also, commercially available cleaners like DUSTER BR (Cramolin®, Germany) and granite and stones (Parker & Bailey, USA) were used. These cleaners can be used where externally clean surfaces are needed without scratching or streaking, as claimed by the manufacturer. The resin mixture was then directly applied, without surface activator, to the panels using a four-sided Bird applicator (80 mm width, gap sizes 30/60/90/120 μm, Sheen Instruments Ltd, UK) with 90 μm gap size. The coated samples were adjusted to have a uniform wet film thickness. Initially, these blends were heated at 60 °C for half an hour in the oven and then the temperature was changed to 110 °C at a heating rate of 10 °C/30 min. The hardness of the films was checked at various time intervals. The films were used for further analysis once a suitable hardness was attained. The average dry thickness of the film was found to be 90–100 μm.

2.8 Pencil Hardness Test

The pencil grade (from soft to hard) that did not scratch or rupture the coating is termed the pencil hardness of the test specimen. This is carried out at room temperature with a pencil hardness tester (Sheen Instruments model SH720N) according to ASTM D3363-05. The set of pencils from soft to hard (9B to 9H) was used.

2.9 Gloss Test

Gloss of the cured resin was determined with a tri-gloss meter (Sheen Instruments, model 260). The calibrated interment was placed on the sample surface and operated automatically. It determines the gloss values at refraction angles of 20°, 60°, and 85° [11].

Table 1 Formulation of the different alkyd resin.

Recipe	Alkyds				
	I	II	III	IV	V
<i>Citrillus colocynthis</i> seed oil (g)	30	30	30	27	21
<i>Prunus mahalab</i> seed oil (g)	0	0	0	3	9
Glycerol (g)	14.21	11.052	7.89	7.89	7.89
Phthalic anhydride (g)	22.84	17.77	15.21	15.21	15.21
NaOH (g)	0.12	0.12	0.12	0.12	0.12
Oil length (%)	44	51	57	57	57

2.10 Pendulum Test

The pendulum test [12] consists of measuring the damping time of a pendulum oscillating on a test surface. The hardness is a function of the oscillation amplitude detected by electronic, optical cells from two specified pendulum deflection positions. It decreases faster on a medium soft surface.

2.11 Adhesion Test

To measure the strength of the bond formed between the coating material and the applied surface, an adhesion test was performed as per ASTM D3359-2009. The films on the substrate were cut by crosshatch and cleaned using a brush. Scotch tape was adhered on the film and peeled off quickly at 180° angle. The peeled off grid areas on the tape were observed by a magnifier and the results were reported in terms of % of the film removal.

2.12 Water and Chemical Resistance of the Blends

The water and alkali resistance test was determined according to ASTM D1647-89. The chemical resistance of the blended resins was determined on dried coated glass panels in order to evaluate their properties under these conditions. To prevent water absorption from the open end of the panels they were coated with a small amount of the wax. These plates were then accurately weighed and dipped in distilled water for one week. The samples were removed at various time intervals, dried at room temperature, and weight loss was measured. The weight loss of the coating was calculated as follows:

$$\text{Weight loss} = \frac{W_0 - W_1}{W_0} \times 100\% \quad (1)$$

where W_0 is the initial weight of the sample, and W_1 is the sample weight after one week of immersion. Similar analysis was carried out on dried coated glass panels in alkali solution (0.5 N NaOH), acid solution (10% aqueous HCL), and salt solution (10% aqueous NaCl). [13]. This analysis was carried out in triplicate and the average of the three readings is presented in Table 7.

3 RESULTS AND DISCUSSION

3.1 Fatty Acid Composition

The fatty acid compositions of CCSO and PMSO are given in Table 2. The fatty acid profile of CCSO reveals

that the major acid is linoleic acid (C18:2Δ9,12; 65.25%) followed by oleic (C18:1Δ9; 16.37%), palmitic (C16:0; 9.72%) and stearic (C18:0; 7.26%) acids. The total saturated and unsaturated fatty acids present in CCSO are 17.43% and 82.56%, respectively. The main fatty acid in PMSO is α-eleostearic (C18:3Δ9c,11t,13t). Other fatty acids present in significant concentration comprised linoleic acid (C18:2Δ9,12; 23.85%) and oleic acid (C18:1Δ9; 33.32%).

3.2 Physicochemical Properties of Seed Oils

A comparison of the physicochemical properties of CCSO and PMSO are given in Table 3. The high acid value of CCSO (3.7 mg KOH/g) indicates that it contains a higher amount of free fatty acids compared to PMSO (0.9 mg KOH/g). The saponification values of CCSO and PMSO are 192.35 and 191.91 mg KOH/g respectively. These values are approximately similar due to the nearly equal average molecular mass of the two oils (874.93 and 876.97 g/mol respectively). The specific gravities of CCSO and PMSO are 0.9231 and 0.9276 respectively. These values are within the range of specific gravities of commonly used vegetable oils. The value of kinematic viscosity of PMSO (40.5 mm²/s) is much higher than CCSO (23.55 mm²/s). Blayo *et al.* [14] reported that the viscosities of oils containing α-eleostearic acid, such as Tung oil, are significantly

Table 2 Fatty acid (%) composition of CCSO and PMSO.

CCSO		PMSO	
Fatty acid	%	Fatty acid	%
C16:0	9.724	C8:0	0.044
C16:1Δ9	0.026	C14:0	0.031
C17:0	0.063	C16:0	4.168
C18:0	7.267	C16:1Δ9	0.227
C18:1Δ9	16.373	C17:0	0.069
C18:1Δ11	0.513	C18:0	2.351
C18:2Δ9,12	65.256	C18:1Δ9	33.325
C20:0	0.318	C18:1Δ11	0.890
C20:1Δ11	0.168	C18:2Δ9,12	23.853
C18:3Δ9,12,15	0.053	C20:0	0.427
C22:0	0.060	C20:1Δ11	0.183
C20:3Δ8,11,14	0.176	C18:3Δ9,12,15	0.072
		C22:0	0.092
		C18:3Δ9c,11t,13t	34.262

higher. The higher values are explained by the more polar character of conjugated fatty acids, which yielded a higher cohesive energy and led to an increased viscosity. Moreover, *PMSO* (160.92 g/100 g oil) shows a higher iodine value than *CCSO* (128.26 g/100g oil). The high iodine value observed for *PMSO* is due to the presence of a large quantity of linolenic acids. Based on their iodine value, *CCSO* is classified as a semidrying oil (125–140) and *PMSO* is classified as a drying oil (> 140) [2].

3.3 Synthesis of Alkyd Resin

Many researchers have studied the effects of various catalysts for both the alcoholysis and polyesterification

Table 3 Physicochemical properties of *CCSO* and *PMSO*.

	<i>CCSO</i>	<i>PMSO</i>
Color	Yellow	Light yellow
Free fatty acid (as oleic)	1.85	0.45
Acid value (mg KOH/g)	3.70	0.9
Iodine value (g/100g oil)	128.26	160.92
Saponification value (mg KOH/g)	192.35	191.91
Refractive index (25 °C)	1.4725	1.4763
Density (25 °C)	0.9231	0.9276
Kinematic viscosity (40 °C) (mm ² /s)	23.55	40.50
Molecular weight	874.939	876.971

reactions. Base catalysts such as alkali hydroxide are widely used in alcoholysis reactions [15]. According to Uzoh *et al.* [16], the alcoholysis reaction is usually completed within an hour or two after the batch reaches operating temperature. In the first step of this work, we used several catalysts for the alcoholysis reaction, and the solubility tests of the mixture in anhydrous methanol are grouped in Table 4. It was observed (Table 4) that most of the samples of the alcoholysis mixture are only partially soluble in anhydrous methanol even after 2 h of reactions carried out using CaO and CaCO₃. From Table 4, NaOH (0.4 wt%) is selected as a suitable catalyst. It can be explained by the relatively high amount of free fatty acid present in *CCSO*. Lin [2] reported that if an oil has a high acid value, the reaction can be severely retarded. The reaction required a long time or an additional amount of catalyst and both are undesirable for alcoholysis.

When heated with glycerol in the presence of NaOH at 220 °C (first step), *CCSO* (or blended *PMSO*) undergoes alcoholysis, yielding a mixture composed mainly of monoacylglycerol [10]. In the second step, the addition of PA undergoes polyesterification, which yields the alkyd resin. The polyesterification reaction was monitored by measuring the acid value at different time intervals.

The plot of acid value against reaction time during the polyesterification reaction of the synthesized alkyd resins is shown in Figure 1. The plots indicate that as the reaction progressed the acid value decreased. The decrease in acid value is more rapid during the early stage of the reaction. These changes in acid value

Table 4 First stage alcoholysis reaction.

<i>Alcoholysis Catalyst</i>	<i>Catalyst % (wt)</i>	<i>Reaction time (min)</i>	<i>Completion of alcoholysis reaction</i>
CaCO ₃	0.1	120	Not complete
	0.2	120	Not complete
	0.3	120	Not complete
	0.4	120	Not complete
	0.5	120	Not complete
CaO	0.1	120	Not complete
	0.2	120	Not complete
	0.3	120	Not complete
	0.4	120	Not complete
	0.5	120	Not complete
NaOH	0.1	120	Not complete
	0.2	120	Not complete
	0.3	120	Complete
	0.4	90	Complete
	0.5	90	Complete

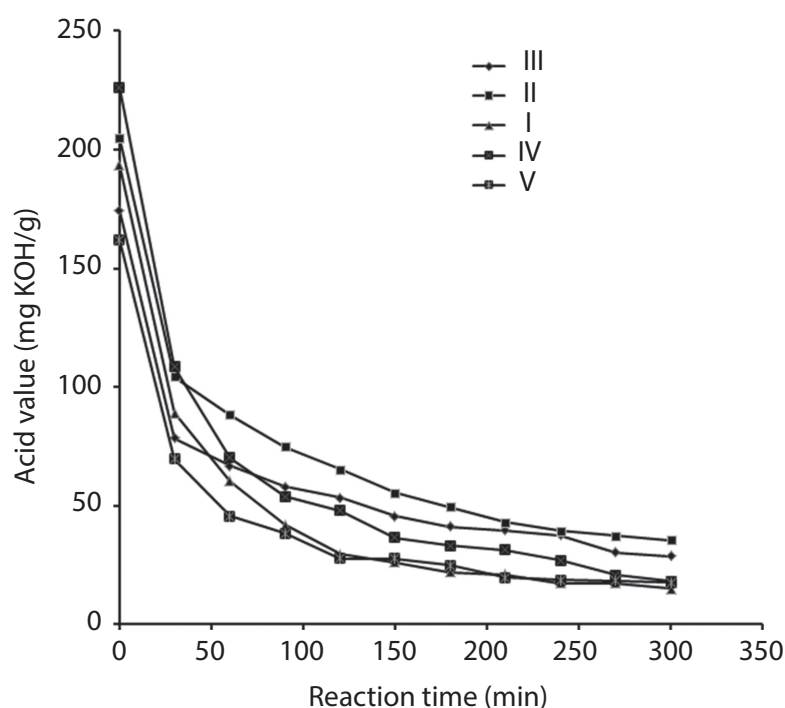


Figure 1 Plot of acid value vs time for alkyd resins.

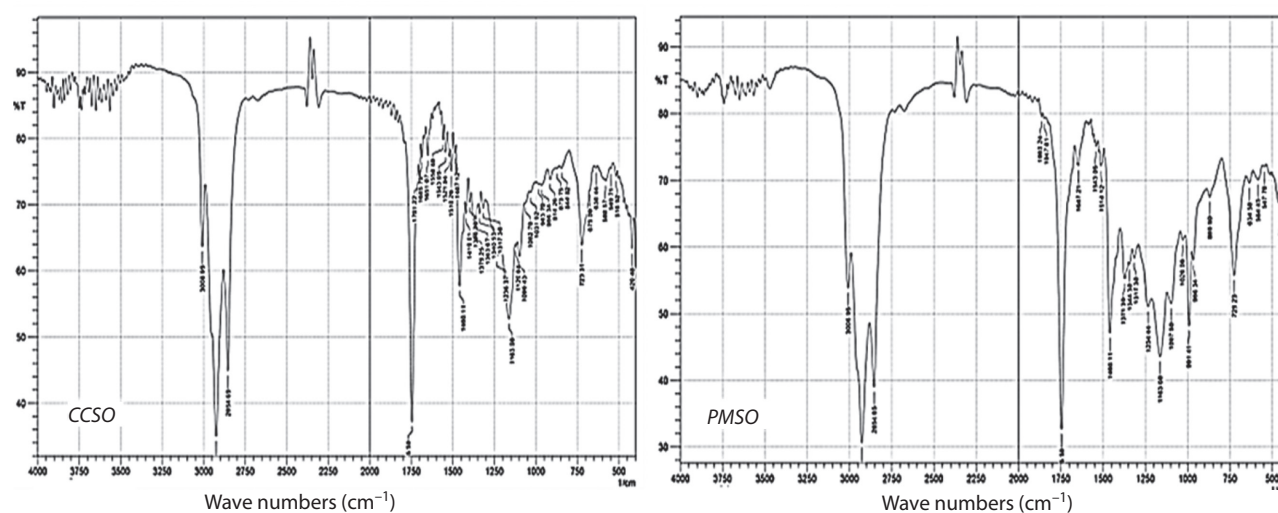


Figure 2 Infrared spectra for CCSO and PMSO.

have been explained by the different reactivities of the hydroxyl groups of glycerol [17]. Since a primary alcohol reacts faster than a secondary hydroxyl group, the early stage corresponds when primary hydroxyl groups react while the later stage presents the period when secondary hydroxyl groups react [17]. It was observed that the initial acid value of the reaction mixture decreased with decreasing PA content in the alkyd resin containing the highest concentration of PA.

3.4 Characterization of Alkyd Resins

Alkyd resins based on CCSO and a blend of CCSO and PMSO were characterized by FTIR and ^1H NMR spectroscopy. The FTIR spectra of the oils and the synthesized alkyd resins are shown in Figures 2 and 3, respectively. The FTIR of PMSO exhibited a characteristic doublet at 991.41 and 966.34 cm^{-1} due to the presence of α -eleostearic acid (*cis:trans:trans*).

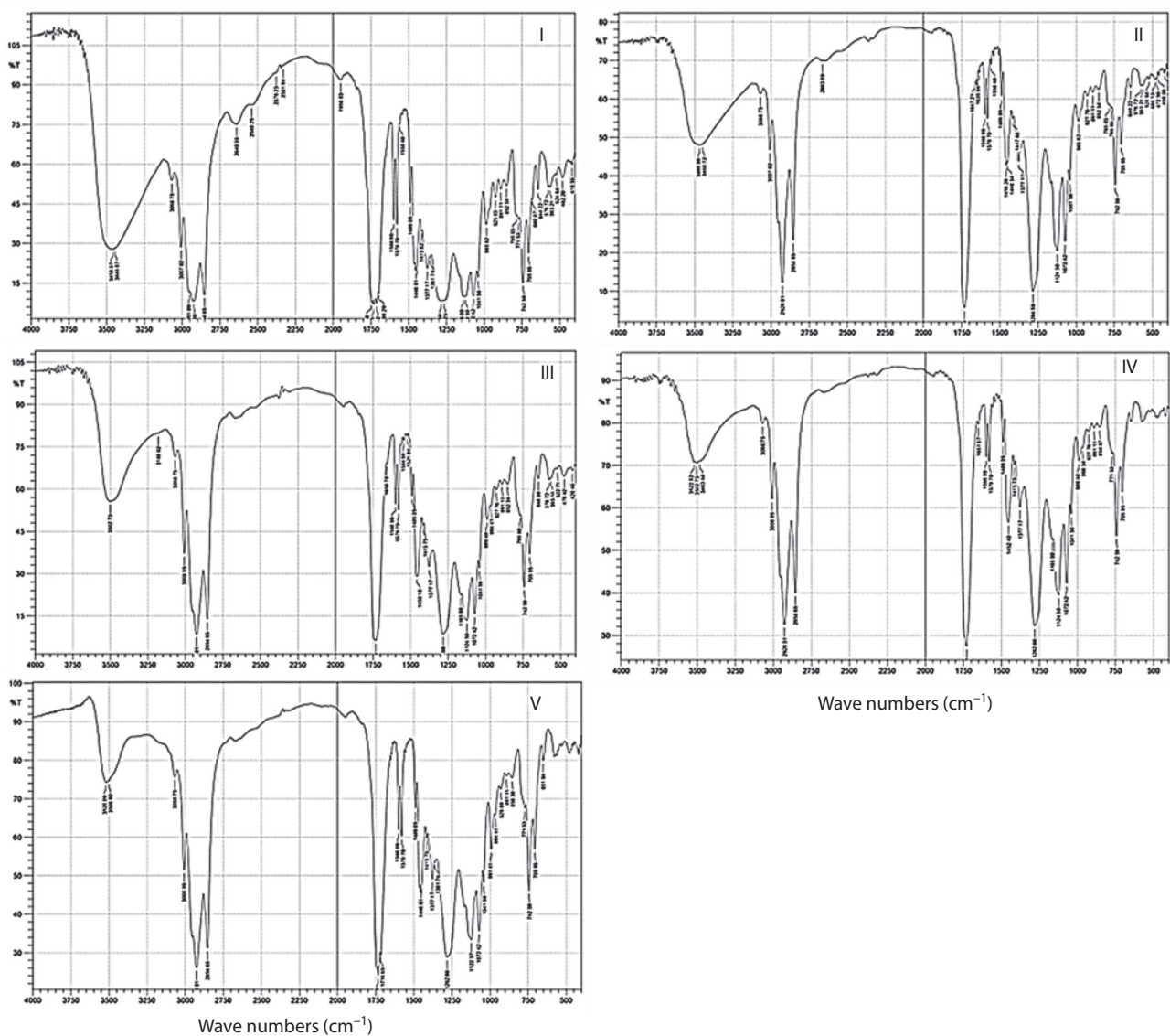


Figure 3 Infrared spectra for alkyd resins.

The similar functional groups present in *CCSO* and *PMSO* are: the peaks at 3008 cm^{-1} corresponding to olefinic C-H stretching; the peaks around $3000\text{--}2800\text{ cm}^{-1}$ corresponding to an aliphatic C-H stretching band. The C=O stretching band appears at 1745 cm^{-1} . The peak for C-H bending vibration appears at 1460 cm^{-1} . The characteristic peaks at $110\text{--}1300\text{ cm}^{-1}$ correspond to C-O-C stretching vibrations. The peak at 725 cm^{-1} corresponds to methylene rocking vibrations.

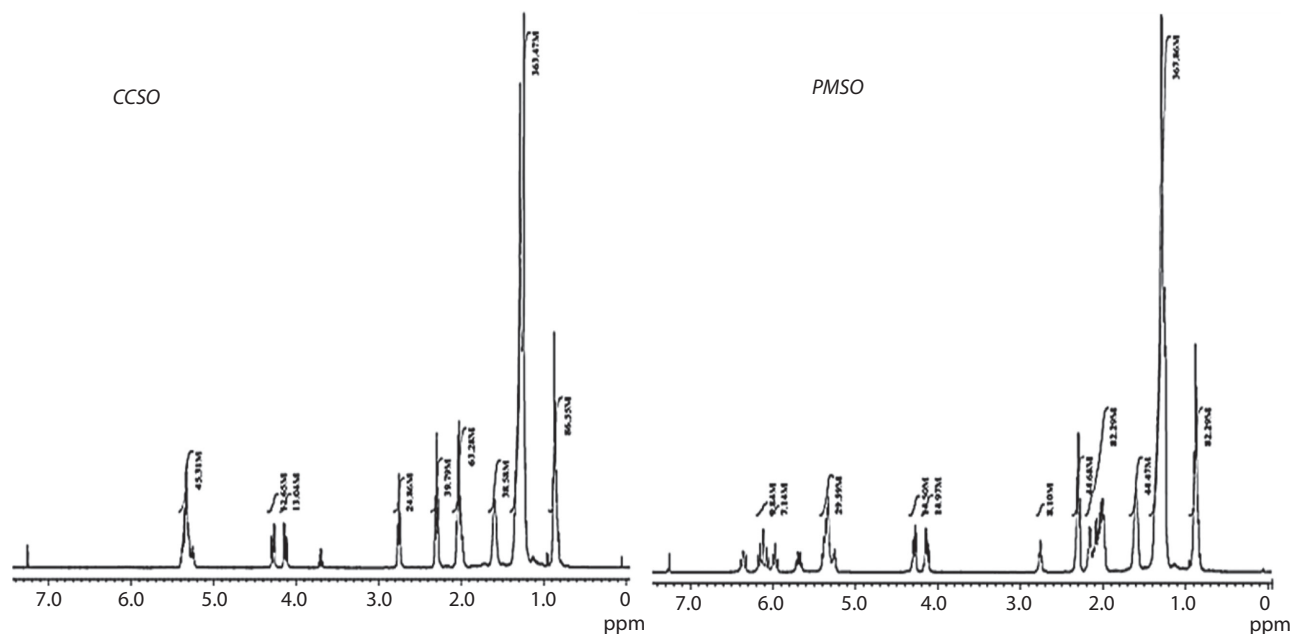
The polyesterification reaction is confirmed by FTIR analysis. The FTIR spectra of *CCSO*-based alkyd resin and blend with *PMSO* support the presence of ester and olefinic double bonds in alkyd resins (Table 5). In oil spectra, the peak for C=O appears at 1745 cm^{-1} , whereas in the case of the synthesized resin, peaks

for C=O appear at $1732\text{--}1728\text{ cm}^{-1}$. Furthermore, the peaks are broadened with respect to that of oil, indicating the difference in structural environment around the ester carbonyl group [17]. It is important to note the presence of the characteristic peaks (991 and 966 cm^{-1}) corresponding to the conjugated triene of eleostearic acid chain of *PMSO* in the alkyd resins **IV** and **V**. All the spectra showed two peaks centered at 1598 and 1579 cm^{-1} , which corresponded to the C=C stretching of the aromatic ring in the phthalate groups corresponding to the alkyd resins.

The ^1H NMR spectrum of the oils is shown in Figure 4. Peaks at $0.8\text{--}0.9\text{ ppm}$ are due to the protons of the terminal methyl group. Peaks of all protons of the internal CH_2 groups present in the fatty acid chain appear at $\delta = 1.2\text{--}1.4\text{ ppm}$. Characteristic peaks

Table 5 Characteristic peaks in FT-R spectra of alkyd resins.

Functional groups	Alkyd resins				
	I	II	III	IV	V
O-H stretching vibration	3460.3	3466.08	3502.73	3502.73	3518.16
Olefinic C-H stretching vibration.	3007.02	3007.02	3008.95	3008.95	3008.95
C-H aliphatic stretching vibration.	2951.09–2854.65	2926.01–2854.65	2926.01–2854.65	2926.01–2854.65	2926.01–2854.65
C=O stretching frequency of ester.	1730.15	1732.08	1732.08	1728.22	1728.22
C=C stretching frequency of alkene and aromatic band.	1598.99–1579.70	1598.99–1579.7	1598.99–1579.7	1598.99–1579.7	1598.99–1579.7
Symmetric and asymmetric bending of methyl groups.	1359.82 and 1454.33	1377.17 and 1454.33	1377.17 and 1458.18	1377.17 and 1452.4	1377.17 and 1452.4
C-O-C stretching vibrations attached with aliphatic and aromatic moiety.	1284.59–1072.42	1284.59–1072.42	1282.66–1072.42	1282.66–1072.42	1282.66–1072.42
(CH) in CH=CH wagging conjugated <i>cis, trans, trans</i>				989.48 and 966.34	991.41 and 966.34
Out of plane aromatic C-H bending vibration.	744.52–705.95	742.59–705.95	742.59–705.95	742.59–705.95	742.59–705.95

**Figure 4** ^1H NMR spectra of CCSO and PMSO.

at $\delta = 1.9\text{--}2.1$ ppm are for allylic protons of CH_2 , at $\delta = 2.2\text{--}2.4$ ppm for α -protons of the ester groups and at $\delta = 2.7\text{--}2.8$ ppm for the CH_2 of double allylic protons. Peaks at $\delta = 4.1\text{--}4.4$ ppm are for the protons of the triglyceride moiety and $\delta = 5.2\text{--}5.5$ ppm are for the protons of the $\text{CH}=\text{CH}$ moiety [17]. Furthermore, the ^1H NMR spectrum of PMSO contains peaks in the 5.9–6.4 ppm region corresponding to the protons of the conjugated trienes of α -eleostearic acid. The ^1H NMR

spectra of the resins are shown in Figure 5, which confirmed the synthesis of the alkyd resins. The characteristic peaks at $\delta = 7.2\text{--}7.3$ ppm are for the proton for $-\text{CH}-$ of the glycerol moiety [18]. It was observed due to the deshielding effect of the anhydride group acquiring the aromatic ring, which is absent in the ^1H NMR spectra of oils. The peaks at $\delta = 7.4\text{--}7.8$ ppm are observed for the aromatic protons of phthalic anhydride-containing resins.

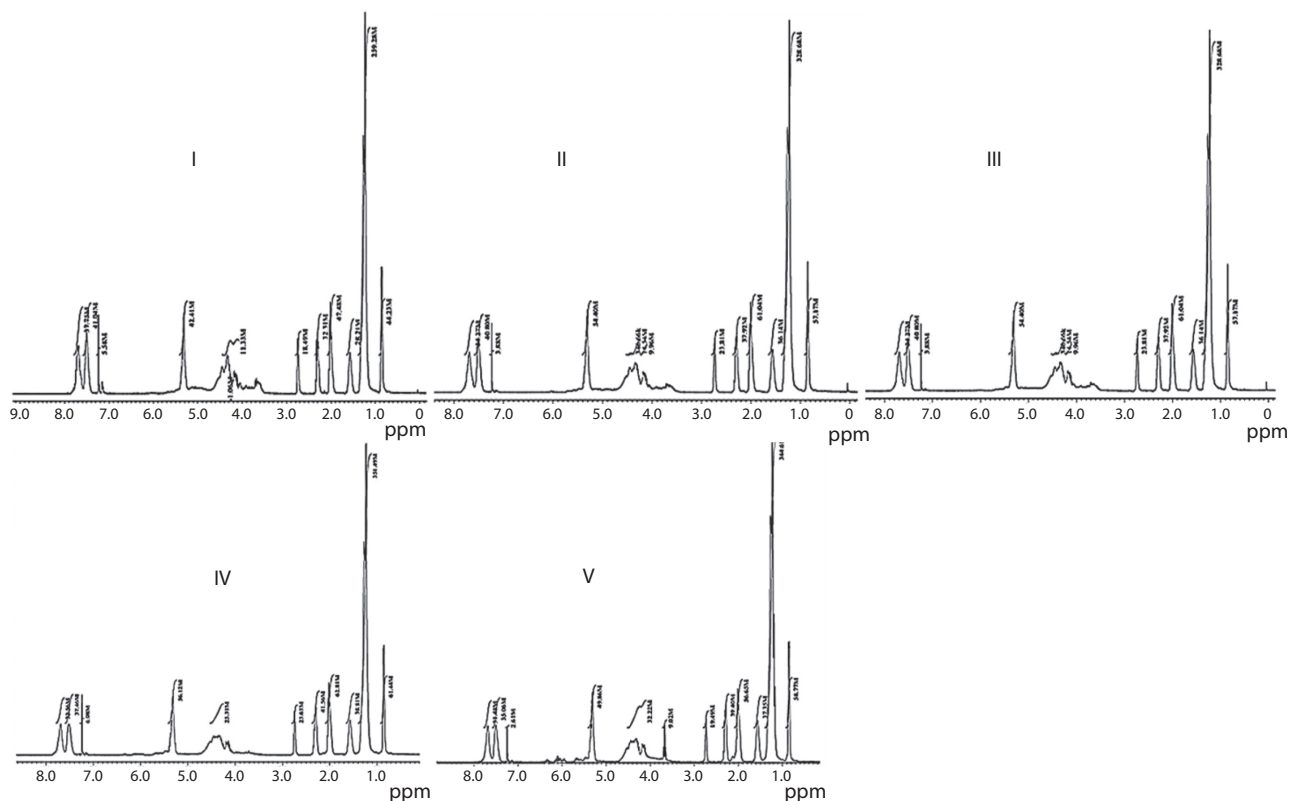


Figure 5 ^1H NMR spectra of alkyd resins.

Table 6 Pencil hardness, adhesion, gloss and pendulum characteristics of the cured epoxy-blended resins.

Sample	Color	Pencil hardness	Gloss grade			Pendulum test removal (%)	Adhesion	
I	Pale yellow	2H	31.3	88.6	83.1	20	4B	4
II	Pale yellow	2H	23.4	83.7	93.3	33	3B	8
III	Pale yellow	F	22.6	84.1	93.9	13	5B	0
IV	Dark brown	5B	21.9	74.9	84.4	17	4B	2
V	Dark brown	5B	44.4	78.5	88.2	9	5B	1

3.5 Physical Properties of the Cured Alkyd Resins

Table 6 shows some of the physical properties of the cured epoxy-blended films of CCSO and a blend of CCSO and PMSO. The pencil hardness was tested with 9B to 9H, of which 9H has the highest hardness. On the basis of the hardness value of the testing pencil, the pencil hardness value was found to be highest for I and II, which contain high amounts of PA. Bora *et al.* [10] reported that the increase of phthalic anhydride increases the pencil hardness value due to the presence of the rigid aromatic moiety in the polymer chain. Furthermore, the addition of PMSO decreases the hardness value for resins IV and

V. The gloss measurement is an important property of a coating, which results from the interaction between light and the surface of the coating film. The gloss is enhanced due to the presence of the aromatic moiety of phthalic anhydride in the alkyd resins [19]. The glosses of all the resins are found to be good. According to Table 6, the pendulum hardness value of pure CCSO is higher than that found in blended alkyd resins with PMSO. The film adhesion of the coating recorded a grade of 5B to 3B. It is observed that the % of the film removed was in the range of 5–10% area of lattice. This adhesion is still considered to be reasonably good. The adhesion characteristics of all the resins are due to the presence of the polar ester bonds [20].

Table 7 Chemical resistance of the cured resins.

Sample	The weight loss of film ,wt.% (STDEV)			
	10% HCl (aq)	1% NaOH (aq)	10%NaCl (aq)	Distilled water
I	2.51 (±0.31)	13.47 (±1.41)	5.12 (±2.25)	1.30 (±0.40)
II	1.81 (±0.73)	9.43 (±2.50)	4.87(±1.48)	2.40 (±1.14)
III	1.21 (±0.30)	19.94 (±2.88)	3.57(±1.51)	2.97 (±1.53)
IV	2.24 (±0.83)	17.27 (±4.15)	3.30 (±0.14)	2.80 (±0.48)
V	2.27(±1.19)	14.47 (±4.09)	4.40 (±1.06)	2.12 (±0.89)

STDEV: Standard Deviation

3.6 Water and Chemical Resistance of the Blends

The performances of the cured epoxy-blended resins under different chemical environments are given in Table 7. It was found that the majority of epoxy-blended alkyds are highly resistant to dilute HCl, aqueous NaOH solution, and distilled water. Resins IV and V show fair resistance to aqueous NaCl solution due to the presence of PMSO. The resins are fairly resistant to alkali solution due to the presence of alkali hydrolyzable aliphatic ester groups [19].

4 CONCLUSION

From this study, it can be concluded that alkyd resins based on pure CCSO and its blend with PMSO with varying amounts of PA and glycerol have been successfully synthesized. The FTIR and ¹H NMR spectra confirmed the chemical structures of both the raw oils and the resins with the functional groups present. The study established that CCSO-modified alkyd resins show excellent adhesion, pencil hardness, gloss (60°) and pendulum hardness. These resins show good chemical resistance toward dilute HCl, NaCl solution, and distilled water. Moreover, the blend-modified alkyd with PMSO shows different physical properties compared to that obtained with CCSO due to the decrease in the number of crosslinking sites. *Citrullus colocynthis* is a low cost and widely available biomass in Saudi Arabia. This study indicates that CCSO can be used as novel biobased raw material for coating applications.

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REFERENCES

1. J. Beetsma and A. Hofland, Life cycle analysis of alkyd emulsion based paint. *Surf. Coat. Int.* **81**, 491–494 (1998).
2. K. Lin, Paints, varnishes, and related products, in *Bailey's Industrial Oil and Fats Products*, F. Shahidi (Ed.), 6th ed., pp. 320–352, John Wiley & Sons, Inc., New Jersey (2005).
3. D. Schafferman, A. Behazav, E. Shabelsky, and Z. Yaniv, Evaluation of *Citrullus colocynthis*, a desert plant native in Israel as a potential source of edible oil. *J. Arid Environ.* **40**, 431–439 (1998).
4. I.A. Nehdi, H. Sbihi, C.P. Tan, and S.I. Al-Resayes, Evaluation and characterisation of *Citrullus colocynthis* (L.) Schrad seed oil: Comparison with *Helianthus annuus* (sunflower) seed oil. *Food Chem.* **136**, 348–353 (2013).
5. S.H.U.I. De Silva, A.D.U.S. Amarasinghea, B.A.J.K. Premachandra, and M.A.B. Prashantha, Effect of karawila (*Momordica charantia*) seed oil on synthesizing the alkyd resins based on soya bean (Glycine max) oil. *Prog. Org. Coat.* **74**, 228–232 (2012).
6. H.M. Sbihi, I.A. Nehdi, and S.I. Al-Resayes, Characterization of white mahlab (*Prunus mahaleb*) seed oil: A rich source of α -eleostearic acid. *J. Food Sci.* **79**, 795–801 (2014).
7. Animal and vegetable fats and oils – Determination of acid value and acidity, ISO 660 (1996).
8. Animal and vegetable fats and oils – Determination of saponification value, ISO 3657 (2002).
9. B. Ham, R. Shelton, B. Butler, and P. Thionville, Calculating the iodine value for marine oils from fatty acid profiles. *J. Am. Oil Chem. Soc.* **75**, 1445–1446 (1998).
10. M.M. Bora, P.G. Dibakar, C. Deka, and D.K. Kakati, Synthesis and characterization of yellow oleander (*Thevetia peruviana*) seed oil-based alkyd resin. *Ind. Crop Prod.* **52**, 721–728 (2014).
11. 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**, 596–602 (2012).
12. Standard test methods for hardness of organic coatings by pendulum test, ASTM D 4366-95 (1984).
13. H. Jiajian, Y. Teng, Y. Xiyun, M. Limin, Z. Chuang, H. Yang, Z. Chaoqun, and Y. Zhuohong, Study on the UV curing

- behavior of tung oil: Mechanism, curing activity and film-forming property. *Ind. Crops Prod.* **112**, 61–69 (2018).
14. A. Blayo, A. Gandini, and J.F. Le Nest, Chemical and rheological characterizations of some vegetable oils derivatives commonly used in printing inks. *Ind. Crops Prod.* **14**, 155–167 (2001).
 15. H. Nosal, J. Nowicki, M. Warzała, E. Nowakowska-Bogdan, and M. Zarebska, Synthesis and characterization of alkyd resins based on *Camelina sativa* oil and polyglycerol. *Prog. Org. Coat.* **86**, 59–70 (2015).
 16. C.F. Uzoh, N.J. Obodo, and O.D. Onukwuli, Exploring the effect of styrene and anhydride ratio on the coating properties of non-drying vegetable oil based alkyd resin. *J. King Saud Univ. Eng. Sci.* (2016). (In press)
 17. I.E. Ezeh, S.A. Umoren, E.E. Essien, and A.P. Udoh, Studies on the utilization of *Hura crepitans* L. seed oil in the preparation of alkyd resins. *Ind. Crop Prod.* **36**, 94–99 (2012).
 18. D.L. Pavia, G.M. Lampman, G.S. Kriz, and J.R. Vyvyan, *Introduction to Spectroscopy*, 4th ed., Cengage Learning, Belmont, USA (2008).
 19. P.C. Pranali and A.P. Pratap, Utilization of sunflower acid oil for synthesis of alkyd resin. *Prog. Org. Coat.* **93**, 61–67 (2016).
 20. S.S. Mahapatra and N. Karak, Synthesis and characterization of polyesteramide resins from Nahar seed oil for surface coating applications. *Prog. Org. Coat.* **51**, 103–108 (2004).