

Studies on the Preparation of *Parinari polyandra* Benth Seed Oil Alkyd Resins

T. E. Odetoye,¹ D. S. Ogunniyi,¹ G. A. Olatunji²

¹Department of Chemical Engineering, University of Ilorin, P.M.B. 1515, Ilorin, Nigeria

²Department of Chemistry, University of Ilorin, P.M.B. 1515, Ilorin, Nigeria

Correspondence to: T. E. Odetoye (E-mail: todetoye@yahoo.com)

ABSTRACT: *Parinari polyandra* Benth seed oil was utilized in the preparation of four sets of alkyd resin (35%, 50%, 60%, and 75% oil formulations) using a two-stage alcoholysis-polyesterification method. The rate of polyesterification was depended on the amount of oil used during synthesis. The properties of the alkyds (drying times, film characteristics, water and acid resistances, and solubility) were evaluated using relevant standards. Inclusion of cobalt naphthenate drier in the alkyds and their exposure to outdoor temperature improved the drying properties. White gloss paints formulated from the alkyds, considering a pigment-volume concentration of 20.67% in the gloss paint formulation compare well with commercial standard. FTIR and ¹H-NMR analysis confirm the alkyd (glycerolphthalate) structure. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: parinari seed oil; alkyd resins; polyester; coatings

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INTRODUCTION

Utilization of seed oil as a source of raw materials is gradually gaining more grounds in the chemical industries. This trend has been a result of consideration for renewability and environmental friendliness.¹ The popular seed oils such as palm oil, groundnut oil, soya bean oil, and palm kernel oil have been widely used for both edible and industrial applications. The dual usage of some of these oils has caused a kind of scarcity and higher demand leading to a relatively higher price of crops like soya bean, whereas a lot of the locally available seeds that are potential sources of industrial oil are still largely underutilized.^{2–6} There is a pressing need to search for more seed oils for industrial application and expand the present vegetable oil supplies especially in Nigeria where there is the need to replace seed oils that constitute food sources with nonedible ones to alleviate the problem of food shortage. There are many tropical seed producing plants available in Nigeria, which are potential oil crops waiting to be harnessed. *Parinari polyandra* (*P. polyandra*) Benth seed oil is one of such underutilized nonedible seed oil of potential significance.

P. polyandra Benth (a.k.a. *Maranthes polyandra* Benth) belongs to the family *Rosaceae*. It is a savannah plant that is found in West Africa extending from Mali to Sudan. In Nigeria, it is found in the northern states, middle-belt region, and in some parts of the southern states.⁷ Although the fruit is scarcely edible, the leaves are said to be chewed like kola nut.⁸

The seed oil is considered not edible because of its high content of free fatty acid (FFA) value and relatively high concentration of eleostearic acid, a polyunsaturated fatty acid with a significant drying property.³ The endosperm has a yellowish white appearance with a thick seed coat containing the oily mass. The fresh seed kernel contains between 31 and 60% oil depending on the variety and the season of harvest.^{3,9,10}

Although other related species (e.g., *Parinarium capense*, *Parinarium laurium*, and *Parinarium rudolphic*) had been investigated as far back as 1961,¹¹ there is limited published work on *P. polyandra*. In one of the few available works on *P. polyandra*, Olatunji et al.³ reported the proximate chemical composition of the seed oil of *P. polyandra*. The analysis revealed the crude protein content as 18.33%, whereas the triacylglycerol content was obtained to be 31.1%. The major fatty acids of the triacylglycerol were determined using gas chromatographic analysis of methyl ester derivatives of extracted lipid. Studies^{9,10} on the variation in lipid concentration of the seed oil revealed that the oil yield of the seeds vary with the month of harvest, yielding up to 60% oil in the month of November in Nigeria. The plant is used in the trado-medicinal treatment of painful and inflammatory conditions, treatment of veneral diseases,^{8,12} and the leaves used as anti-malaria.¹³

Alkyd resins are thermoset-producing polyester products formed from the condensation of polyhydric alcohols, polybasic acids, and monobasic fatty acids.¹⁴ Alkyds are used in the formulation

of paints, varnishes, lacquers, and other finishes; alkyd resins have become an indispensable raw material. These finishes are extensively used for decorative and protective purposes. They are used as industrial coatings for manufactured items in various manufacturing industries. They are of enormous importance in the building industry, where they are used for interior and exterior architectural finishes.¹⁴

Oil is one of the important raw materials used in the production of oil-modified alkyd resins in the surface coatings industry. Linseed oil, soya bean oil, and dehydrated castor oil are the popular seed oils used for the production of alkyd resins.¹⁴ In Nigeria, many tropical plants produce seeds that are potential sources of industrial oil, which if well-harnessed can enhance renewable supply of oils in the oleochemical industry without competing with food sources. *P. polyandra* B. is one of such plants.

This work reports the preparation and evaluation of *P. polyandra* B. oil-modified alkyd resins.

MATERIALS AND METHOD

Materials

The mature seeds of *P. polyandra* B. were obtained from trees at University of Ilorin, Nigeria. They were removed from their enclosing fruits (by cutting into halves) dried, winnowed, and crushed with laboratory mortar and pestle, while the oil was extracted with purified petroleum ether (40–60°C) in a Soxhlet apparatus. The residual solvent was removed by distillation and in vacuo.

The nonfatty materials (gum), the FFAs, and some coloring matter were removed from the seed oils by successively using the methods of degumming, neutralization, and bleaching described in literature.¹⁵ Analytical grade phthalic anhydride, calcium carbonate, and glycerol were obtained from commercial sources BDH chemicals and used without further purification, while the reference alkyd was a commercial medium oil alkyd purchased from the open market at Sango Otta in Nigeria.

Methods

Physicochemical Properties. After refining, some physicochemical properties of the parinari oil sample were determined according to the methods described in literature.^{16–20} Acid value,¹⁶ saponification value,¹⁷ and iodine value¹⁸ were determined according to ASTM methods. The specific gravity was determined using a specific gravity bottle at 32°C, whereas viscosity was determined using a suspended level viscometer (type BS/IP/SL). Viscometer flow times are proportional to kinematic

Table I. Compositions of the Prepared Alkyd Resins

	PN-AKD-1 (35% oil length)	PN-AKD-2 (50% oil length)	PN-AKD-3 (60% oil length)	PN-AKD-4 (75% oil length)
Parinari oil (g)	25.0	50.0	50.0	50.0
Phthalic anhydride (g)	25.7	30.0	19.2	10.0
Glycerol (g)	20.7	20.0	14.2	6.67
CaCO ₃ (g) ^a	0.125	0.25	0.25	0.25

^aCaCO₃ (g) is 0.5% w.r.t. weight of oil.

Table II. Some Properties of *Parinari polyandra* B.

Properties	^a Result
Refractive index (25°C)	1.464 ± 0.002
Specific gravity (32°C)	0.889 ± 0.04
Viscosity, 31°C (mPa s)	48.35 ± 2.14
Acid value(mg KOH/g)	2.24 ± 0.13
Free fatty acid (mg/g)	1.14 ± 0.11
Saponification value (mg KOH/g)	246.1 ± 1.4
Iodine value(g I ₂ /100g)	168.5 ± 1.3

^aProperties expressed as mean value of three replicates ± standard deviation.

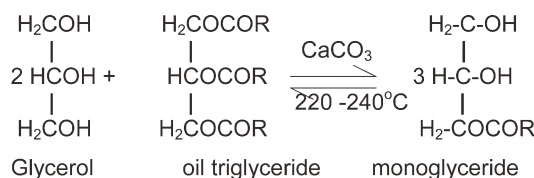
viscosity^{19,20}; therefore, the flow times were multiplied by the viscometer constant. Refractive index was determined using a refractometer.

Preparation of Alkyd Resins

Four classes of alkyds were prepared and labeled as follows: PN-AKD-1 (35% oil), PN-AKD-2 (50% oil), PN-AKD-3 (60% oil), and PN-AKD-4 (75% oil).

For each preparation, a known mass of seed oil was heated to between 220 and 240°C. Calculated amounts of glycerol and calcium carbonate depending on the class of alkyd (Table I) were added while maintaining the temperature at about 240°C. Completion of alcoholysis was checked by taking samples of reaction mixture every 5 min and mixing it with anhydrous methanol in a volume ratio of 1 : 1. End of alcoholysis process was indicated when the mixture gave a clear solution.¹⁴

At the completion of alcoholysis stage, a calculated amount of phthalic anhydride (depending on the class of alkyd) was added, maintaining the reaction temperature at about 240°C. The reaction was carried out under nitrogen atmosphere. The reaction was quenched when the acid number was ~ 10 by immersing the reaction vessel in warm water.¹⁴



Evaluation of Alkyd Resins

The solubility, viscosity, color, drying performance, solidification time, and film characteristics (e.g., thickness and hardness) of the alkyds prepared were determined by standard methods as reported earlier.^{21–23}

¹H-NMR and infrared analyses of the alkyds were also carried out. The NMR spectra were recorded on the Varian Mercury 200BB, Fourier Transform NMR spectrometer operating at 200

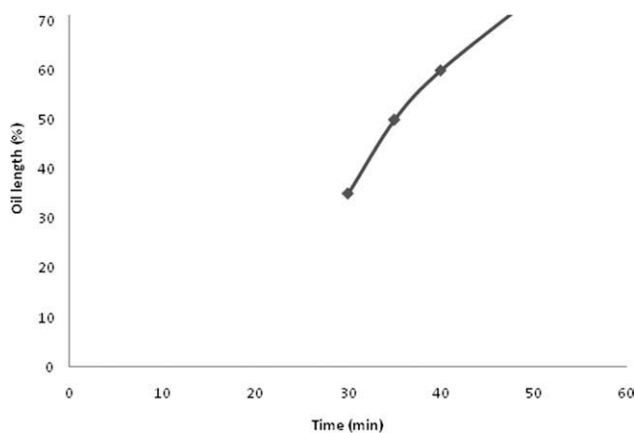


Figure 1. Percentage oil content versus time of alcoholysis.

MHz, the “s2pul” pulse sequence was used, having the following parameters; relax-delay time: 1.000 s; pulse: 64.8°; acquisition time: 1.994 s; number of repetitions: 16; pulse width: 3000.3 Hz; data processing FT size 16384. Also, IR spectra of the oils and alkyds were recorded on the FTIR spectrometer Nicolet AV-ATAR 330 FT-IR (Thermoelectron Corporation). Thin films of the samples were spread between two transparent NaCl cells and recorded on region 400–4000 cm^{-1} . The spectral resolution was set at 4 cm^{-1} and 32 scans.

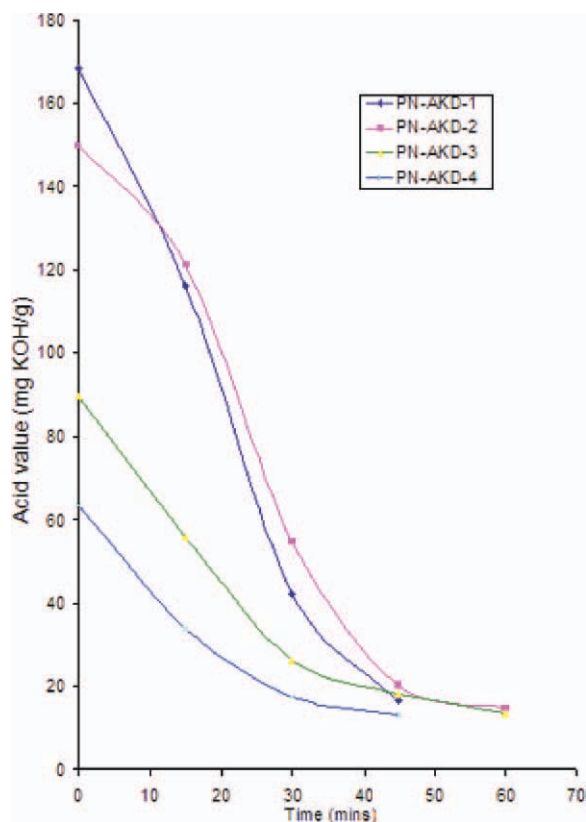


Figure 2. Changes in acid value with time in Parinari alkyds. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Chemical Shifts of Alkyd Samples Measured in CDCl_3 Solution

Number	NMR Chemical shifts (δ)			
	$^1\text{H-NMR}$		$^{13}\text{C-NMR}$	
	PN-AKD-2	C-AKD-2	PN-AKD-2	C-AKD-2
1	-	-	-	173.5
2	2.28 (2H, m)	2.32(2H)	34.2	
3	1.48(2H)	1.63(2H)	27.3	25.9
4-7	1.22(14H)	1.32(28H)	29.8	29.
8	1.92(2H)	2.06(2H)	32.0	37.6
9	5.25(3H, m)	5.39	128.1	
10	,	5.39	130.3	
11	1.92	2.06	37.0	37.4
12	5.25(2H, m)	1.32	130.1	
13	5.25	1.32	128.0	
14	1.48(2H)	1.32	31.6	
15	1.20(14H, s)	1.32	29.8	23.0
16,17	1.20	1.32	22.8	22.8
18	(0.833H, t)	0.84	14.2	14.6
1'	7.42(2H, s)	7.73(2H, s)	129.8	130.4
2'	7.63(2H, s)	7.50(2H, s)	130.3	129.5
3'	7.63	7.50	130.3	129.5
4'	7.42	7.73	129.8	130.0
5'	-	-	131.6	131.7
6'	-	-	131.6	131.7
7'	-	-	167.8	167.5
8'	-	-	167.8	167.5
1''	4.25(8H, m)	4.4(4H, m)	60.6	65.3
2''	4.25	3.73(1H)	69.8	70.7
3''	4.25	4.4	60.6	63.8
-OH				

The alkyd prepared and commercial alkyds were formulated into gloss paint considering the pigment-volume-concentration of 20.67%. The weight percentage composition of the paint is as follows: alkyd resin: 49.6%, talc powder: 21.9%, turpentine 15.0%, titanium dioxide: 12.9%, and cobalt naphthenate: 0.5%.

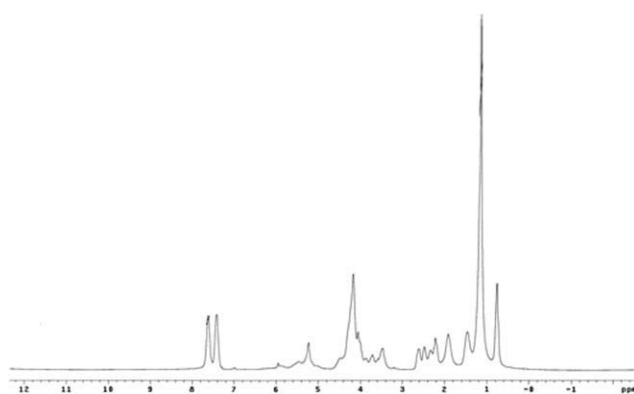


Figure 3. $^1\text{H-NMR}$ spectrum of PN-AKD-2 alkyd.

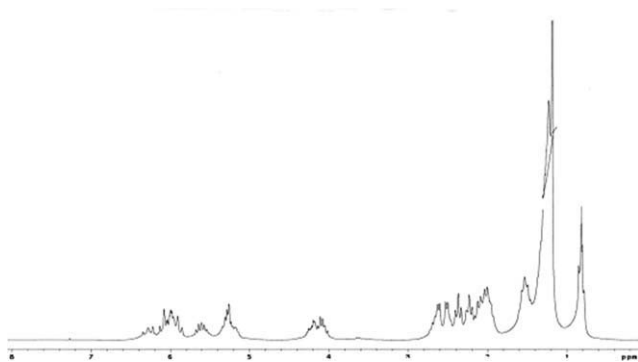


Figure 4. $^1\text{H-NMR}$ spectrum of Parinari oil.

RESULTS AND DISCUSSION

Physicochemical Properties of *P. polyandra* B. Oil

The properties of *P. polyandra* B. oil obtained by solvent extraction are indicated in Table II. The yield of oil was 59.1%, and it compares well with the value 60% obtained in an earlier work.⁹ The oil has a fairly high level of unsaturation, as indicated by its iodine value which classifies it as a drying oil. The iodine value of parinari oil was 168.48 (Table II). This value is comparable with the iodine values of some other drying oils like linseed (170–204) and tung (160–175).¹⁴ Iodine value is an important property to be considered in the choice of oil for the synthesis of drying alkyds because the degree of unsaturation of the oil will subsequently affect the rate of drying of the resulting alkyd resins. The higher the level of unsaturation contents, the faster the drying rates of the alkyds.¹⁴ Also, the viscosity value of Parinari oil, 48.35 mPa s is quite comparable with that of linseed oil of about 50 mPa s.²⁴

Preparation of *P. polyandra* B.-Modified Alkyds

The four different types of alkyds were prepared using a two-stage, alcoholysis-polycondensation method. The relationship between the percentage of oil used in the alkyd preparation and the time taken for alcoholysis stage is shown in Figure 1 and can be used to estimate the time of alcoholysis reaction of Parinari oil for different percentages of oil. This relationship can be used to prevent prolonged alcoholysis reaction time, which can lead to aggravation of side reaction such as the formation of polyglycerols.²⁵ In the alcoholysis stage, two moles of glycerol

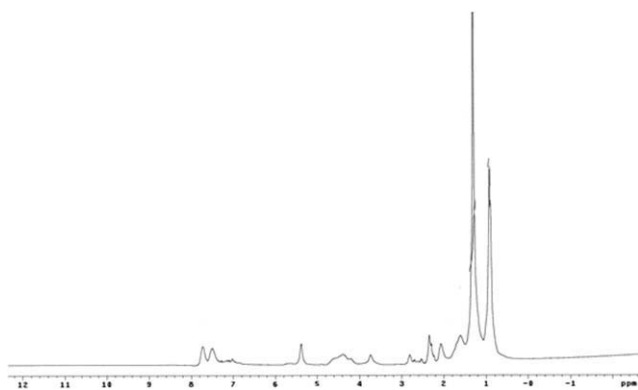


Figure 5. $^1\text{H-NMR}$ spectrum of C-AKD-2.

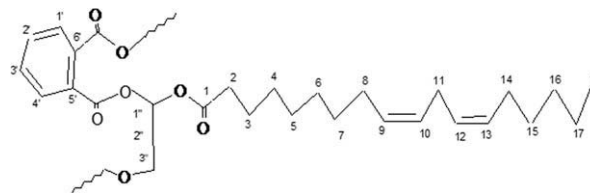


Figure 6. Proposed structure of C-AKD-2.

react with one mole of oil; however, the alcoholysis product may be expected to contain α -monoglyceride as major constituent and β -monoglycerides, γ -diglyceride, triglyceride, and glycerol as minor constituents. Notwithstanding, when two volumes of the reaction mixture were mixed with anhydrous methanol, it gave a clear solution which was an indication of a satisfactorily high amount of conversion of the triglycerides into α -monoglycerides, which is about 60%.²⁵ Prolonged alcoholysis time result in undesirable formation of polyglycerols. Generally, the initial acid value of the reaction mixture decreased with increasing oil content. Also, the rate of polyesterification decreased toward the end of the reaction as the concentration of the free acid decreased during the course of reaction. The change in acid value with time is shown in Figure 2.

Evaluation of Alkyd Resins

$^1\text{H-NMR}$ spectra were obtained for Parinari oil, 60% (medium oil) alkyd PN-AKD-2, and C-AKD-2 (Commercial medium oil alkyd of unknown composition). The data are summarized in Table III. NMR spectra signals (Figures 3–5) confirm the structure of alkyd resin (phthalate ester). The two sets of protons at positions 4',5' and 3',6' (Figures 6 and 7) of the phthalic acid moiety are indicated at δ 7.42, δ 7.63 ppm in the $^1\text{H-NMR}$ spectrum of PN-AKD-2 and δ 7.44, δ 7.65 ppm in the $^1\text{H-NMR}$ spectrum of C-AKD-2, respectively.

The peak at δ 0.83 in $^1\text{H-NMR}$ spectra of PN-AKD-2 is assigned to the terminal methyl groups of the fatty acid chains

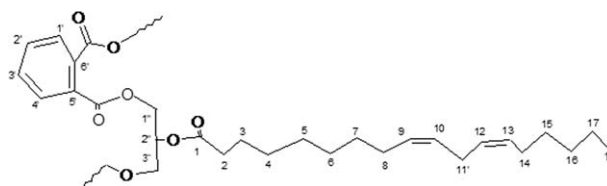


Figure 7. Proposed structure of Parinari oil alkyd.

Table IV. Main IR Peaks and Assignment in Parinari Oil

Peaks/Bands (cm^{-1})	Assignments
2930, 2865	C—H stretching frequency of alkane
1745	C=O stretching frequency of ester
1625	C=C stretching frequency
1464	C—H bending frequency
1170	C—O stretching frequency
860	C—C stretching frequency
795	—(CH ₂) _n —, n ≥ 4 group vibration

Table V. Main IR Peaks and Assignment in Alkyd Samples

Peak/Band (cm ⁻¹)		Assignment
PN-AKD-1	C-AKD	
1729	1734	C=O stretching frequency
1646	1646	C=C stretching frequency
989	988	C—C stretching frequency
742	742	Aromatic C—H stretching frequency
2924, 2855	2924, 2854	Aliphatic C—H stretching frequency
1480	1489,	Characteristic frequency of phthalic anhydride moiety
1072	1282, 1123, 1071	C—O—C stretching vibration
1580, 1599	1580, 1599	Characteristic frequency of ortho-substituted aromatic hydrocarbon

incorporated into the alkyds. In the case of C-AKD-2, the peak at 0.84 corresponds to both the CH₃— protons of the fatty acid chain and perhaps the CH₃— protons of the solvent (e.g., *n*-hexane, xylene used by the manufacturer). The peaks at δ 1.22 and 1.32 ppm in the ¹H-NMR spectra of PN-AKD-2 and C-AKD, respectively, show the —CH₂— of the fatty acid chain. The protons attached to the unsaturated carbons are registered at δ 5.25 ppm for PN-AKD-2 and δ 5.39 ppm for C-AKD-2 in their ¹H-NMR spectra. The protons of the carbon (next to the ester linkage on the fatty acid chain) —CO—CH₂— appeared at δ 2.28, δ 2.32 ppm in the ¹H-NMR spectra of P-AKD and C-AKD, respectively. The protons attached to carbon 3, —CO—CH₂—CH₂—, featured at δ 1.48, 1.63 ppm, respectively. Furthermore, the allylic protons of the fatty acid chain, —CH₂—CH= and protons of the α and β hydroxyl —OH groups of the glycerol moiety overlap²⁶ and appear at δ = 1.92, 2.06 ppm, respectively.

In the alkyd spectra, the signals of the protons attached to the α and β position of the glycerol moiety (CH₂—, CH—) overlap

appearing at δ 4.25 ppm in the ¹H-NMR spectra of PN-AKD. δ = 3.73 ppm in C-AKD ¹H-NMR spectra is attributed to primary OH in line with the structure for C-AKD (Figure 6), implying that the phthalic anhydride moiety is attached to the secondary position of the glyceryl backbone.

The IR spectra of the oil and the alkyds are also summarized in Tables IV, V and Figures 8 and 9.

The alkyds were tested for solubility, viscosity, colour, drying performance, solidification time, and film characteristics, e.g., thickness, hardness, adhesion, and flexibility. Tables VI and VII show some properties of the alkyds. PN-AKD-1 was partially soluble in toluene after 20 min and did not dissolve further appreciably even after about 24 h. However, PN-AKD-2, PN-AKD-3, and PN-AKD-4 were completely soluble after about 3, 1.5, and 1 min, respectively. Only PN-AKD-4 was completely soluble in turpentine. This is because aliphatic hydrocarbons are generally better solvents for longer oil alkyds²⁷ because of relatively higher concentration of aliphatic carbon (fatty acid) chain constituent of the alkyd. However, all the prepared alkyds and the commercial standard were soluble in xylene, suggesting xylene as the most suitable for diluting the prepared alkyds. Parinari oil alkyds generally have darker colors considering the number of reds and yellow. The color in PN-AKD alkyds is partly due to the residual pigment matter in the oil.

The prepared alkyds all have higher viscosities and solidification time values than the commercial alkyd indicating higher extents

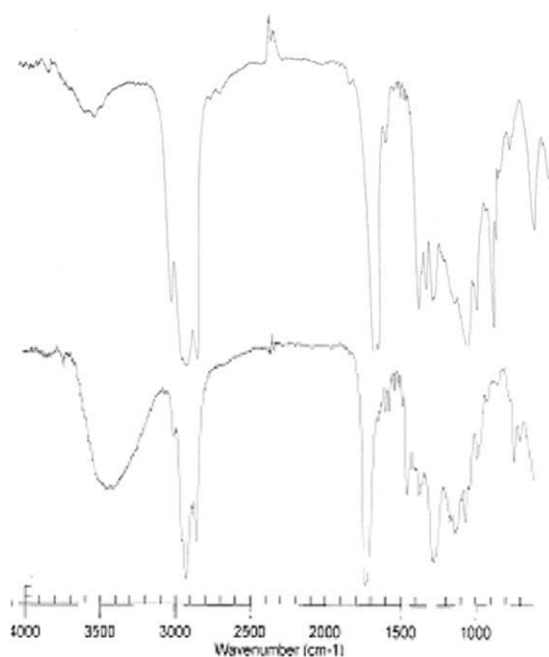
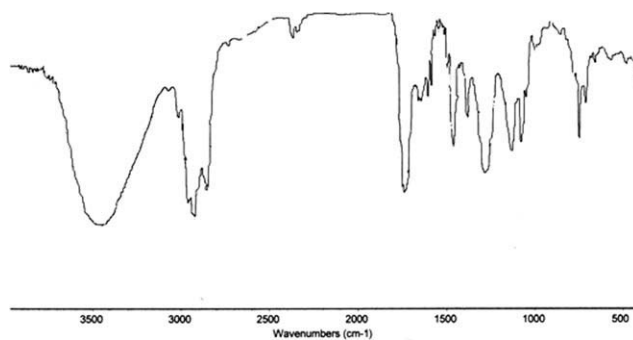
**Figure 8.** FTIR spectra of Parinari oil and PN-AKD-2.**Figure 9.** FTIR spectra of C-AKD.

Table VI. Some Properties of the Alkyd Solutions

Alkyd samples	Color (Lovibond)	Color (B.S 2660) ^b	Viscosity (mPa s) (29°C)	Film thickness (mm)	Solidification time (s)
PN-AKD 1	10.0R + 74.6Y	3-045 Mid brown	32.99	0.195	25
PN-AKD 2	10.0R + 77.7Y	3-045 Mid brown	26.39	0.175	45
PN-AKD 3	7.4R + 77.0Y	3-044 Hazelnut	18.24	0.135	62
PN-AKD 4	10.6R + 77.0Y	3-045 Mid brown	4.97	0.125	78
C-AKD ^a	0.2R + 3.6Y	4-053 Lemon	4.910	0.04	103

^aC-AKD is a commercial reference medium oil alkyd.^bSample undiluted.**Table VII.** Some Film Properties of the Alkyds

Alkyd samples	*Water resistance	*Acid resistance	Impact resistance (1 Kg)	Scratch hardness (6H pencil)
PN-AKD 1	4	4	5	5
PN-AKD 2	4	4	5	5
PN-AKD 3	3	4	5	5
PN-AKD 4	3	5	5	5
C-AKD	5	5	5	5

*0 = completely removed.

1 = cracked, partially removed.

2 = partially cracked but not removed.

3 = loss of gloss.

4 = slight loss of gloss.

5 = visibly unaffected.

of polymerization. The solidification time values of the alkyds are indicative of good stability.

Tables VIII and IX show the drying characteristic of the alkyd resin solutions, with and without cobalt naphthenate drier, that were tested both indoors and outdoors. When PN-AKD alkyds were applied as films, without inclusion of drier and placed outdoor, the drying performance improved slightly comparable to those of alkyds dried indoors. Dust free-time of prepared alkyds is about 7 min. C-AKD dried hard outdoor after about 6 h without inclusion of cobalt naphthenate drier and after about 2 h with inclusion of the drier.

Furthermore, even with the inclusion of cobalt naphthenate drier, PN-AKD-2 generally showed better drying characteristics than the commercial 60% oil alkyd. The tack free time of PNAKD-2 is desirably slightly shorter than that of C-AKD (Figure 10). However, PN-AKD-2 exhibited a relatively longer

Table VIII. Drying Performance of Nonpigmented Alkyds with Drier (Indoors and Outdoors)

Alkyd samples	TSTT(min)		TDTT (min)		TDF		TDH (h)	
	I	O	I	O	I (h)	O (min)	I	O
PN-AKD 1	13	7	25	15	7.83	30	Overnight	3.08
PN-AKD 2	14	8	50	16	6.83	28	"	3.68
PN-AKD 3	16	9	55	17	5.33	27	"	3.83
PN-AKD 4	18	10	52	18	4.25	25	"	1.6
C-AKD	91	30	150	20	15.4	3.28	"	1.5

TSTT, set-to-touch-time; TDF, dust-free-time; TDTT, dry-to-touch-time; TDH, dry-hard-time.

Table IX. Indoors and Outdoors Drying Performances of Nonpigmented Alkyds Without Cobalt Naphthenate Drier

Alkyd samples	TSTT (min)		TDTT (min)		TDF		TDH	
	I ^a	O	I	O	I (h)	O (min)	I	O
PN-AKD 1	20	18	122	58	7.5	2.20	Overnight	5
PN-AKD 2	23	19.5	140	66	7.0	2.25	"	6.6
PN-AKD 3	26	21	160	72	6.83	2.17	"	7.0
PN-AKD 4	30	23	170	75	6.0	2.67	"	7.5
C-AKD	90	17	230	60	3.89	2.25	Overnight	5.17

I = Indoor (temp = 30°C ± 2), O = Outdoor (temp = 37°C ± 2).

^aI = Indoor.

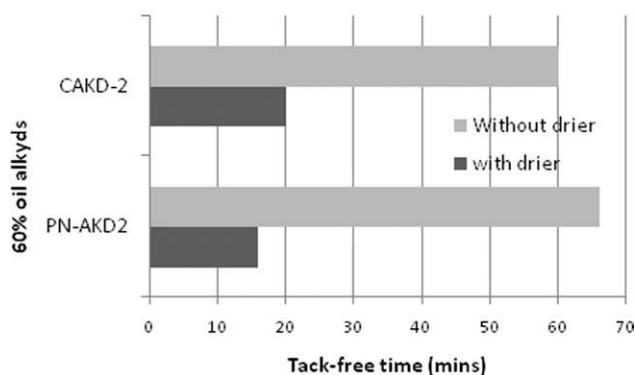


Figure 10. Effect of drier on tack-free time (outdoors).

dust-free-time and dry-hard-time when applied indoors though the longer TDF and TDH may be attributed to the higher film thickness of PN-AKD-2 which gave an advantage to the commercial alkyd to absorb oxygen “more easily” for the oxidative drying because of its (C-AKD) relative larger surface area exposed. PN-AKD alkyds contain considerable amount of linoleic and eleostearic fatty acid moieties.³

Generally, conjugated oils have faster drying rates because of their drying mechanism, which is slightly different from that of nonconjugated oils. Although the drying of conjugated oils is less well-understood,²⁸ the reaction between oxygen taken from the air (or free radicals) and conjugated fatty acid moieties of the Parinari alkyds can be said to occur with loss of unsaturation and the first reaction is possibly by the attack of oxygen on conjugated double bonds, by direct addition to form free radicals with two unsatisfied valencies (i.e., diradicals).^{14,28}

Also, all the formulated paints dried faster than the corresponding plain alkyds. The pencil hardnesses of the prepared alkyd were comparable to that of C-AKD as they all passed up to 6H pencil scratch without failing (Table VII).

CONCLUSIONS

This study described the preparation of parinari oil-modified alkyds. Thus, the oil extracted from the seeds of *P. polyandra* B. is a potential renewable, nonedible, raw material for the coatings industry. The drying properties of the alkyds compare favorably and competitively with those of the commercial standard. Parinari oil alkyds are generally more viscous and faster drying.

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