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Karanja (*Millettia pinnata* (L.) Panigrahi) seed oil as a renewable raw material for the synthesis of alkyd resin

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ABSTRACT

Non-edible vegetable oils are an important class of bio-resource for producing polymeric materials due to their large abundance, low cost and renewability. Karanja (*Millettia pinnata*) tree is an evergreen, drought resistant, nitrogen fixing tree belonging to Leguminaceae family. Karanja seed oil (~27 wt%) mainly consisting of triglycerides is a good source of non-edible vegetable oil for synthesizing alkyd resin. Triglyceride was first converted to monoglyceride by glycerolysis process. The monoglyceride was then reacted with phthalic and/or maleic anhydride to produce alkyd resins. The synthesized resins were characterized by FT-IR and ^{1}H NMR spectroscopy. The surface characteristic of the cured resins was studied by SE microscopy. The physico-chemical properties of the resins such as colour, acid value, free fatty acid content and iodine value were evaluated. The coating performance of the cured resins was tested by measuring chemical resistance, thermal stability, pencil hardness, gloss and adhesion.

1. Introduction

Sustainable economic growth requires guaranteed sources of raw materials for the industrial production. Today's most important source of industrial chemicals is the petroleum, a non-renewable resource. It is neither sustainable, because limited, nor environmentally friendly. So effort is directed towards biomass as an alternative source of raw materials for sustainable growth. Polymers are an important class of industrial product and the polymer chemists are also in the lookout for alternative source of biobased raw materials. One such industrial polymer is alkyd resin, widely used in surface coating, is a key ingredient of all surface-coating products like paint, primer, adhesive and printing ink (Uzoh et al., 2013) due to their good attributes such as strength, flexibility, gloss retention, good thermal stability and low price (Ling et al., 2014). Alkyd resins are tough resinous polymeric materials prepared via an esterification reaction between polybasic acids, polyols and monoacids (commonly fatty acids from vegetable oils or fats) (Parker, 1965) and can be synthesized from both edible and non-edible vegetable oil sources. Non-edible vegetable oil due to its lack of food value is considered as a highly promising alternative source for synthesis of alkyd resins.

In India, a wide variety of non-edible oils are produced such as neem (Khandelwal and Chauhan, 2012), mahua (Khandelwal and Chauhan, 2012), jatropha (Kumar et al., 2010), nahar (Dutta et al., 2004), yellow oleander (Deka and Basumatary, 2011), tobacco (Ogunniyi and Odetoye, 2008), cotton seed oil(Agarwal et al., 2003) and rubber seed oil (Kumar and Purushothaman, 2012). Bora et al. (2014), Dutta et al. (2004) and Boruah et al. (2012) reported synthesis of alkyd resins from yellow oleander (*Thevetia peruviana*), nahar (*Mesua ferrea*) and *Jatropha curcas* seed oil respectively. *Millettia pinnata* seed oil, commonly called karanja oil, is a good source of non-edible vegetable oil for synthesizing alkyd resin. Glycerol, the other raw material for the synthesis of alkyd resin is obtained as byproduct during transesterification for the production of biodiesel (Sharma and Singh, 2008).

Karanja (Fig. 1) is a medium sized evergreen, drought resistant, semi-deciduous tree belonging to the Leguminaceae (Pappilonaceae) family (Bobade and Khyade, 2012a,b; Atabani et al., 2013). It grows fast and matures after 4–7 years yielding fruits which are flat, elliptical and ~7.5 cm long. Each fruit contains 1–2 kidney shaped brownish red kernels (Fig. 2). A single tree is said to yield 9–90 kg seed per tree, indicating a yield potential of 900-9000 kg seed/ha (assuming 100 trees/ha), 25% of which might be rendered as oil (Karmee and Chadha, 2005). It is one of the few nitrogen fixing trees that produce seeds with a significant oil content of 30–40% (Atabani et al., 2013; Bobade and Khyade, 2012a,b). The oil contains primarily seven fatty acids viz. palmitic, stearic, oleic, linoleic, lignoceric, arachidic and behenic (Lakshmikanthan,

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Fig. 1. Mature karanja tree grown in Gauhati.

Fig. 2. Karanja seed.

1978). Karanja oil contains oleic acid (44.5–71.3%) as the major fatty acid followed by linoleic (10.8–18.3%), stearic (2.4–8.9%), palmitic (3.7–7.9%), behenic (4.2–5.3%), arachidic (2.2–4.7%) and lignoceric (1.1–3.5%) acid (Karmee et al., 2004). The oil (Fig. 3) is reddish brown in colour and rich in unsaponifiable matter and oleic acid (Sanford et al., 2009). India is a tropical country and offers most suitable climate for the growth of karanja tree (Sharma and Singh, 2008). It is found in abundance in rural areas and forests of entire India, especially in Eastern India, Assam and Western Ghats. The tree is also widespread in China, Japan, Australia, New Zealand and USA. Karanja oil has been reported to contain furanoflavones, furanoflavonols, chromenoflavones, flavones and furanodiketones which make the oil non-edible (Sharma and Singh, 2008) and hence encourages its application for the synthesis of alkyd resin. In India owing to its low cost and ready availability karanja oil is popular among the farmers, who use it to run pumps that irrigate their fields (Karmee et al., 2004). Karanja oil has found applications in body oils, salves, lotions, soaps, hair tonics, shampoos and pesticides (Kesari et al., 2010). Karanja oil is considered to be less toxic and cheaper than jatropha oil (Khayoon et al., 2012).

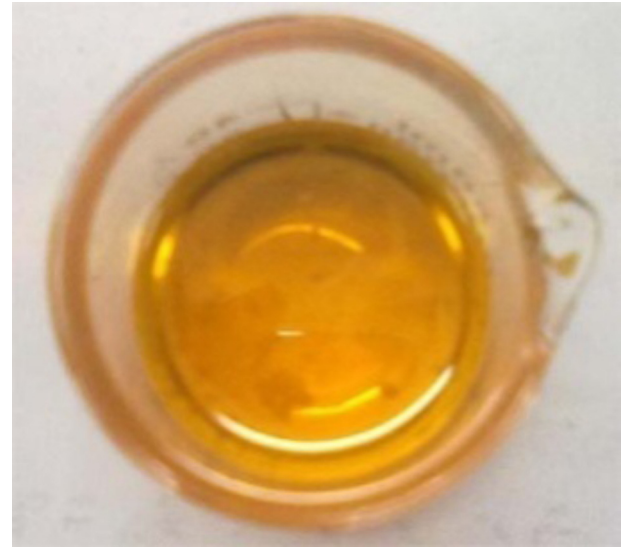

Fig. 3. Karanja seed oil.

This work reports for the first time the synthesis of alkyd resins from karanja oil.

2. Materials and methods

2.1. Materials

Karanja (*Millettia pinnata*) seeds were collected in summer season, 2013 from Gauhati University campus, Guwahati, Assam, India. Mature seeds were deshelled, dried in sunlight and the kernels were crushed using a grinder.

Analytical grade phthalic anhydride (Merck, Mumbai, India), maleic anhydride (SRL, Mumbai, India), litharge (PbO) (Qualigens, Mumbai, India) and glycerol (Fisher scientific, Mumbai, India) were used without purification. Commercial grade epoxy resin, epoxy hardener and cobalt-octoate (Archana Enterprise, Kharagpur, India) were used as received. Silica gel (60–120 mesh), petroleum ether (40–60 °C) and ethyl acetate (Merck, Mumbai, India) were also used as received.

2.2. Oil extraction and purification

The oil was extracted with petroleum ether from the crushed kernel in a soxhlet extractor. The solvent was then removed at 45 °C using a rotary vacuum evaporator to get the crude oil. Crude oil was purified by column chromatography over silica gel using a mixture of 98% petroleum ether and 2% ethyl acetate as eluent. Column chromatography separates triglycerides, the major constituent (95–98%) of the oil from the complex mixture of minor compounds (2–5%) of wide range of chemical nature. The minor components are mono- and diglycerides, free fatty acids, phosphatides (or phospholipids), sterols, protein fragments, various resinous and mucilaginous materials (Aluyor et al., 2009; International Conference on Palm and Palm Products, 1989).

2.3. Synthesis of alkyd resins

Six different alkyd resins viz. K-AR 1, K-AR 2, K-AR 3, K-AR 4, K-AR 5 and K-AR 6 were synthesized by following a two stage alcoholysis-polyesterification procedure (Fig. 4) (Runk, 1952; Igwe and Ogbobe, 2000; Bora et al., 2014) varying the amount of phthalic anhydride (PA) and maleic anhydride (MA). The amounts of various ingredients are shown in Table 1. In the two stage process the oil

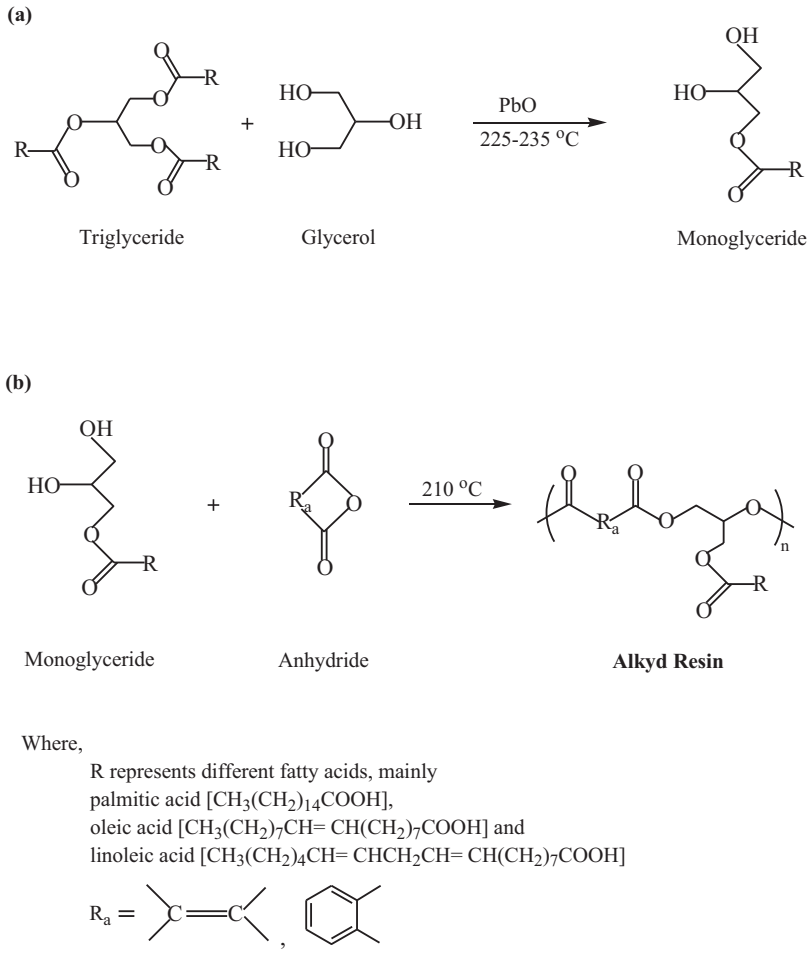

Fig. 4. Schematic route for synthesis of (a) karanja oil monoglyceride and (b) karanja oil alkyd resin.

Table 1
Compositions of different alkyd resins.

Resins	Compositions	Oil (g)	PA (g)	MA (g)	Glycerol (g)
K-AR 1	100% PA + 0% MA	32.08	17.774	0	9.36
K-AR 2	90% PA + 10% MA	32.08	15.997	1.177	9.36
K-AR 3	80% PA + 20% MA	32.08	14.219	2.353	9.36
K-AR 4	70% PA + 30% MA	32.08	12.442	3.529	9.36
K-AR 5	60% PA + 40% MA	32.08	10.664	4.706	9.36
K-AR 6	50% PA + 50% MA	32.08	8.887	5.883	9.36

was first converted to a monoglyceride precursor, by reaction with glycerol. This was then reacted with PA and MA to synthesize the alkyd resin. When percentage of MA exceeds 50%, gelling occurs.

The alcoholysis-polyesterification reaction was carried out in a three necked round bottomed flask equipped with a mechanical stirrer (Heidolph, Germany), a thermometer and a nitrogen gas inlet. A mixture of 32.08 g (0.04 mol) of karanja oil, 7.36 g (0.08 mol) of glycerol and 0.05 wt% (with respect to the oil) of PbO was heated at 230 °C (±5 °C) with continuous stirring maintaining a constant speed of 900 rpm under nitrogen atmosphere for 30 min until monoglyceride is formed. Monoglyceride formation was confirmed by methanol solubility test. One part of the product was mixed with three parts of methanol in a sample vial at room temperature. Complete dissolution in methanol giving a clear liquid indicated the formation of monoglyceride (Runk, 1952). The reaction mixture was then cooled to 120 °C and 0.12 mol of acid anhydride in finely divided form was added along with 1.98 g excess glycerol (27%). After that the reaction temperature was raised to 210 °C (±5 °C) and the heating was continued until it reached acid value in the range of 20–30 mg KOH/g.

2.4. Instrumentation and measurements

2.4.1. Determination of specific gravity

Specific gravity of the purified oil was determined according to ASTM D5355-95 Standards.

2.4.2. Determination of refractive index

Refractive index of the purified oil was determined according to AACC International Method 58-20.02.

2.4.3. Determination of acid value and free fatty acids

Acid value *and free fatty acids* (% FFA) of the oil and synthesized alkyd resins were determined by AACC International Method 58-15.01.

2.4.4. Determination of saponification value

Saponification value of the oil was determined by AACC International Method 58-50.01.

2.4.5. Determination of iodine value

Iodine value of the oil and synthesized alkyd resins were determined by AACC International Method 58-30.02.

Table 2
Physico-chemical properties of karanja, *Thevetia peruviana*, *Jatropha curcas* and *Mesua ferrea* seed oil.

Property	Karanja	*Thevetia peruviana*[a]	*Jatropha curcas*[b]	*Mesua ferrea*[c]
Colour	Reddish brown	Pale yellow	Faint yellow	Pale yellow
Odour	Repulsive	Odd odour	Unpleasant odour	-
Percentage yield (%)	27.25	61.7	63.16	-
Refractive index (30 °C)	1.467	1.4645	-	1.4739
Specific gravity (g/cm^3)	0.938	0.912	0.9032	0.9292
Acid value (mg KOH/g)	11.518	0.658	-	11.87
Free fatty acid (% oleic acid)	6.235	0.35	2.23	5.96
Iodine value (g I_2/100 g)	89.9	71.4	103.62	91.17
Saponification value (mg KOH/g)	182	121	193.55	200.82

[a] Values from Bora et al. (2014).
[b] Values from Akbar et al. (2009).
[c] Values from Sayeed et al. (2004).

2.4.6. Determination of the fatty acid composition

Analysis of the fatty acids was carried out using a Perkin Elmer Clarus 600 GC–MS equipped with a 60.0 m × 250 μm capillary column. The oven temperature was maintained at 110 °C for 2 min, increased to 280 °C at 5 °C min^{-1} and then held for 9 min. Temperatures of the injector, transfer and source were 250 °C, 200 °C and 180 °C respectively. Helium was used as a carrier gas and total scan time was 30 min. MS was scanned from 40 to 550 Da. For identification of fatty acids of karanja oil, library search was carried out.

2.4.7. Fourier transform infrared (FT-IR) spectroscopic analysis

Chemical compositions of the oil and synthesized alkyd resins were evaluated by Fourier transform infrared (FT-IR) analysis in a Shimadzu FT-IR spectrophotometer using KBr pellet at wavelengths between 4000 and 400 cm^{-1}.

2.4.8. ^{1}H NMR analysis

^{1}H NMR spectra of the oil and synthesized alkyd resins were recorded in $CDCl_3$ at 300 MHz using Bruker Advance III 300 MHz/54 mm NMR spectrometer.

2.4.9. Scanning electron microscopic (SEM) analysis

The surface morphology of the cured resins was studied by scanning electron microscope (SEM) of model of JSM-6390LV, JEOL, Japan at an accelerating voltage of 5–15 kV. The surface of the resins was coated with platinum before the SEM analysis.

2.4.10. Curing of alkyd resins

The synthesized alkyd resins were cured by blending with epoxy resin. 2 g of the resin was taken in a Petri dish and agitated with 1.33 g of epoxy resin, 0.6 g of epoxy hardener and 0.04 g of cobalt-octoate as accelerator for 10 min. Then the resinous mixture was uniformly coated over Teflon sheet and heated at 40 °C for 1/2 h in an oven and then temperature was gradually raised to 100 °C by increasing at a rate of 10 °C/30 min. The film was taken out from the oven and checked for hardening at different interval of time. When the film had attained the suitable degree of hardness the heating was stopped.

2.4.11. Thermogravimetric analysis (TGA)

Thermal stability of the cured resins was investigated by thermogravimetric analysis (TGA) in an inert nitrogen atmosphere with TGA/DSC 1 Mettler Toledo at 10 °C min^{-1}.

2.4.12. Pencil hardness test

The test was done with an Erichen scratch hardness test kit (model 291) according to ASTM D3363-92a under room temperature and the hardest pencil grade from soft to hard (6B to 6H) that did not scratch or rupture the coating was termed the pencil hardness of the test specimens.

2.4.13. Water resistance

Blended resins were coated on glass plates and set to dry with the sides coated with wax to prevent water absorption from open ends. Plates were dipped in water for 30 days and then water resistance was determined according to ASTM D1647-89.

2.4.14. Chemical resistance

The chemical resistance of the blended resins were determined on dried coated glass plates. The plates were immersed in alkali solution (0.5 N NaOH), acid solution (10% aqueous HCl) and salt solution (10% aqueous NaCl) for 30 days and then investigated for any change (Dutta et al., 2004).

2.4.15. Gloss test

Gloss of the cured resin was determined with a digital gloss metre (S.C. Dey & Co., Kolkata) at 60° (Boruah et al., 2012).

Table 3
Fatty acid composition (%) of some non-edible vegetable seed oil.

Fatty acid	Chemical name	Formula	Structure	Karanja	*Thevetia peruviana*[a]	*Jatropha curcas*[b]	*Mesua ferrea*[c]
Myristic	Tetradecanoic	$C_{14}H_{28}O_2$	14:0	–	–	0.1	2.13
Palmitic	Hexadecanoic	$C_{16}H_{32}O_2$	16:0	13.8	23.28	14.2	10.87
Palmitoleic	*cis*-9-Hexadecenoic	$C_{16}H_{30}O_2$	16:1	–	–	0.7	–
Stearic	Octadecanoic	$C_{18}H_{36}O_2$	18:0	7.97	10.71	7.0	14.19
Oleic	*cis*-9-Octadecenoic	$C_{18}H_{34}O_2$	18:1	53.52	43.72	44.7	55.93
Linoleic	*cis*-9, *cis*-12-Octadecadienoic	$C_{18}H_{32}O_2$	18:2	15.64	19.85	32.8	13.68
Linolenic	*cis*-9, *cis*-12, *cis*-15-Octa-decatrienoic	$C_{18}H_{30}O_2$	18:3	–	–	0.2	–
Arachidic	Eicosanoic	$C_{20}H_{40}O_2$	20:0	2.89	02.41	0.2	2.92
Behenic	Docosanoic	$C_{22}H_{44}O_2$	22:0	3.93	–	–	–
Lignoceric	Tetracosanoic	$C_{24}H_{48}O_2$	24:0	1.58	–	–	–

[a] Values from Bora et al. (2014).
[b] Values from Akbar et al. (2009).
[c] Values from Sayeed et al. (2004).

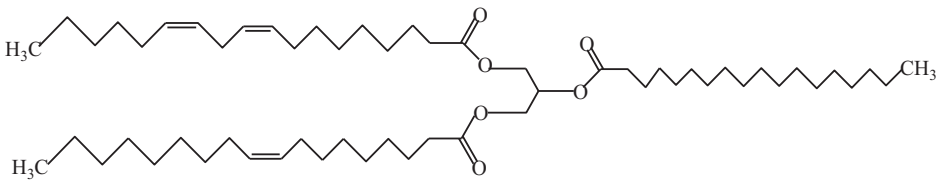

Fig. 5. Probable chemical structure of karanja (*Millettia pinnata*) oil.

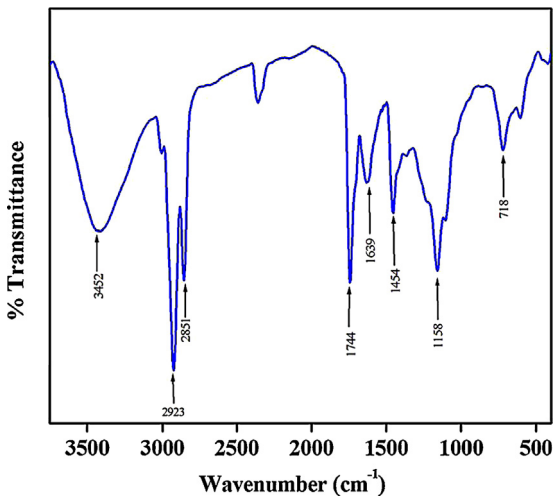

Fig. 6. FT-IR spectrum of karanja oil.

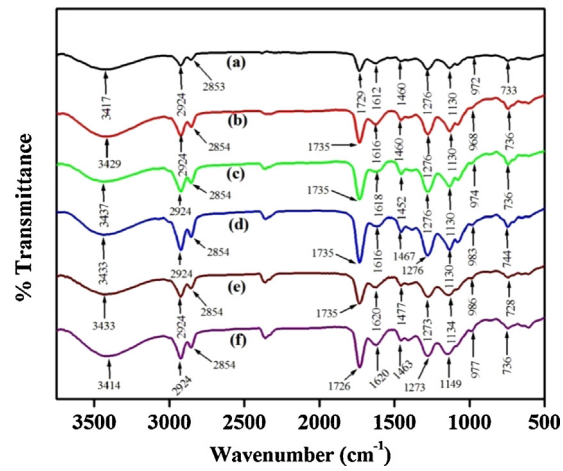

Fig. 7. FT-IR spectra of the synthesized resins: (a) K-AR 1, (b) K-AR 2, (c) K-AR 3, (d) K-AR 4, (e) K-AR 5 and (f) K-AR 6.

2.4.16. Adhesion test

Films of 100 μ size were prepared on metal and stainless steel surface to carry the adhesion test with cello tape (Boruah et al., 2012).

2.4.17. Solubility test

Solubility of the resin was investigated in butanol, toluene, acetone and xylene. 2 g of the resin was taken in 5 mL of the solvent and shaken for a few minutes until complete dissolution occurs (Bora et al., 2014).

3. Results and discussion

3.1. Physico-chemical properties of karanja seed oil

The comparison of physico-chemical characteristics of karanja seed oil with *T. peruviana*, *J. curcas* and *M. ferrea* seed oil are shown in Table 2.

Lower iodine value of karanja oil indicates the presence of less number of unsaturated bonds and hence can be classified as non drying oil and may have application in paints as well as surface coating industry. However due to its lower iodine value a thin film of karanja seed oil is not capable of drying into a hard film by the process of auto-oxidation on exposure to air. Higher saponification value of karanja oil indicates that oil can be used in the production of soaps. The physico-chemical properties of karanja seed oil conform to the already reported data (Bobade and Khyade, 2012a,b).

3.2. Fatty acid composition

The fatty acid composition of the karanja seed oil is shown in Table 3. The fatty acid profile reveals that the major acid is oleic acid (53.52%), followed by other constituents: viz. linoleic acid (15.64%), palmitic acid (13.8%), stearic acid (7.97%), behenic acid (3.93%), arachidic acid (2.89%) and lignoceric acid (1.58%). The total saturated and unsaturated fatty acids present in karanja oil are found to be 30.17% and 69.16% respectively. Based upon the fatty acid composition, the probable structure of the oil is given in Fig. 5. The karanja seed oil is found to have two acids viz. behenic and lignoceric which are not present in *T. Peruviana*, *J. curcas* and *M. ferrea* oils.

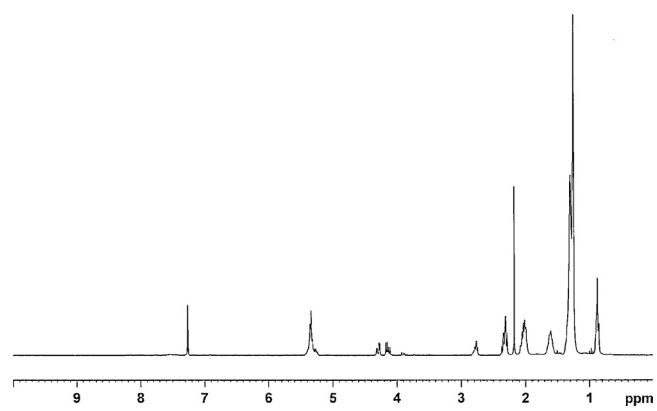

Fig. 8. ^{1}H NMR spectrum of karanja oil.

3.3. Synthesis of karanja seed oil based alkyd resins

Karanja seed oil alkyd resins were prepared following the general procedure in Bora et al. (2014). Karanja oil was transesterified at 230 °C with glycerol in the presence of PbO (litharge) to produce a mixture containing monoglycerides as major components (Runk, 1952; Igwe and Ogbobe, 2000). The mixture was then reacted with phthalic anhydride and/or maleic anhydride at 210 °C to yield the desired alkyd resin (Table 1).

As the reaction progressed the acid value is decreased. The decrease in acid value is more rapid during the early stages of the reaction than at the later stage of the reaction. This pattern

Table 4
Physico-chemical properties of the karanja oil based alkyd resins.

Properties	K-AR 1	K-AR 2	K-AR 3	K-AR 4	K-AR 5	K-AR 6
Acid value (mg KOH/g)	34.68	29.22	32.13	35.62	38.25	42.92
Free fatty acid (% oleic acid)	35.31	28.93	29.72	40.31	44.25	57.86
Iodine value (g I_2/100 g)	42.86	45.24	46.74	52.26	53.92	59.25
Colour	Dark brown	Dark brown	Dark brown	Dark brown	Dark brown	Dark brown

of changes in acid value during polycondensation reaction has been explained on the basis of different reactivities of primary and secondary hydroxyl groups of glycerol (Goldsmith, 1948). Since a primary hydroxyl group reacts faster than a secondary hydroxyl group, it is believed that the rapid decrease in acid value at the early stages of the reaction corresponds to the period when primary hydroxyl groups react, while the later stage represents the period when secondary hydroxyl groups react (Aigbodion and Okieimen, 2001). The decrease in acid value is most rapid for K-AR 1 and the least for K-AR 6. This may be due to the presence of 100% PA in K-AR 1which undergoes rapid esterification rather than 50% PA + 50% MA present in K-AR 6. Thus, the rate of decrease in acid value could be said to depend on the nature of anhydride used. It has been reported that the period when the decrease in acid value during polycondensation reaction is less rapid, it probably indicates the beginning of formation of three-dimensional network as a result of crosslinking of alkyd chains (Aigbodion and Okieimen, 1996). Thus, it can be inferred from these results that during the later stage of the reaction when secondary hydroxyl groups react, there is probably crosslinking of alkyd chains, resulting in increased viscosity of the reaction medium (Aigbodion and Okieimen, 2001). Further the rate of polyesterification also decreases towards the end of the reaction as the concentration of free acids decreased (Ogunniyi and Odetoye, 2008).

3.4. Characterization and evaluation of alkyd resins

Alkyd resins based on karanja seed oil were characterized by FT-IR and ^{1}H NMR spectroscopy. The FT-IR spectra of the oil and synthesized alkyd resins are shown in Figs. 6 and 7 respectively.

In the FT-IR spectrum of the oil characteristic peaks are found at 3452 cm^{-1} due to O—H stretching vibration and at 2851-2923 cm^{-1} due to aliphatic C—H stretching vibration. Peaks for C=O stretching vibration of triglyceride ester appears at 1744 cm^{-1}, for C=C stretching vibration at 1639 cm^{-1} and that for C—H bending at 1454 cm^{-1}. Also peaks at 1158 cm^{-1} due to C—O—C stretching vibration of ester and that at 718 cm^{-1} due to the methylene rocking vibration are also observed.

The FT-IR spectra (Fig. 7) of the resins indicate the presence of important linkages, viz. ester group, olefinic double bonds and other characteristic peaks. The polyesterification reaction is confirmed by FT-IR analysis. In karanja oil, the peak for C=O appears at 1744 cm^{-1}, whereas in case of synthesized resin, peaks for C=O appears at 1726–1735 cm^{-1}. Further, the peaks are broadened with respect to that of oil, indicating the difference in structural environment around the ester carbonyl group (Pavia et al., 2008).

^{1}H NMR spectrum of the oil is shown in Fig. 8. Peaks at δ 0.888–0.899 ppm are due to the protons of terminal methyl group. For all the protons of internal —CH_2 groups present in the fatty acid chain peaks appear at δ 1.607–1.63 ppm. Characteristic peaks at δ 1.998–2.058 ppm are for allylic protons of —CH_2, at δ 2.287–2.347 ppm for α protons of ester groups and at δ 2.77 ppm for —CH_2 of double allylic protons. Peaks at δ 4.152–4.282 ppm are for the protons of glyceride moiety and δ 5.324–5.361 ppm are for the protons of the —CH=CH— moiety (Pavia et al., 2008).

^{1}H NMR spectra of the resins are shown in Fig. 9. Peaks at δ 0.856–0.877 ppm are for the protons of terminal methyl group of

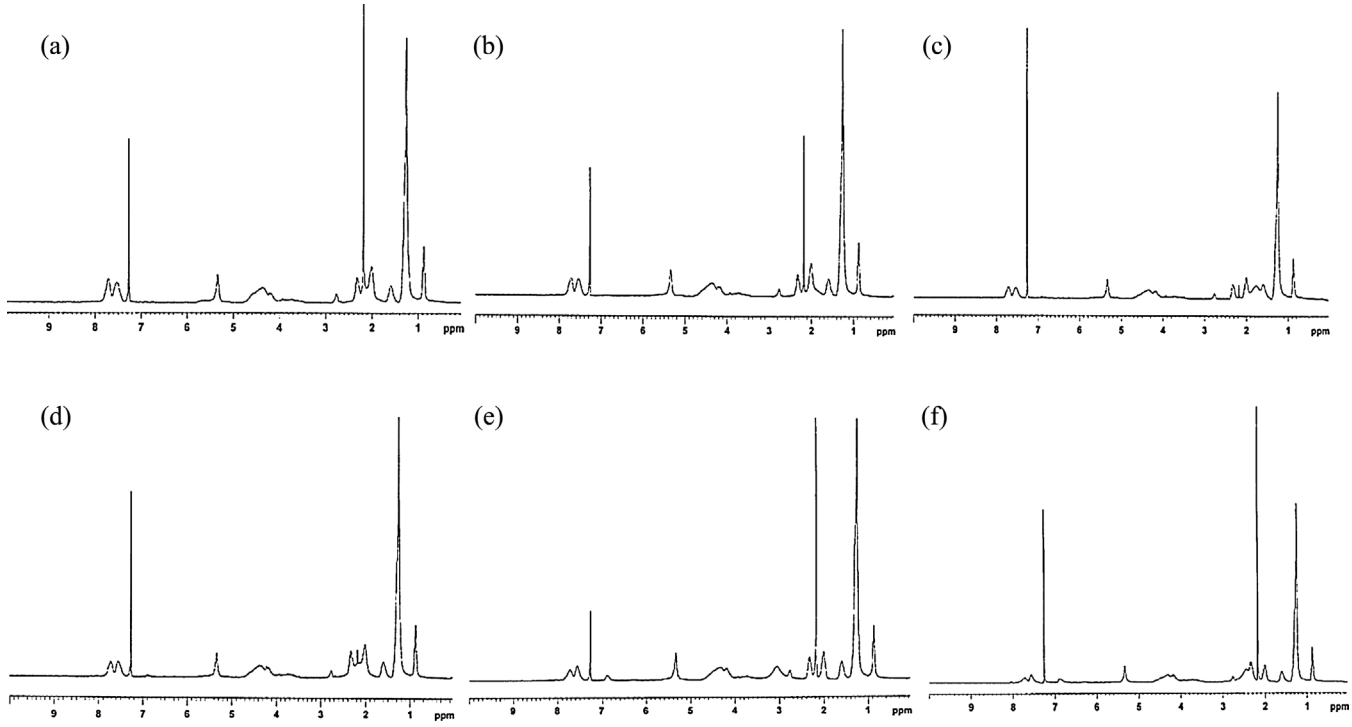

Fig. 9. ^{1}H NMR spectra of the synthesized resins: (a) K-AR 1, (b) K-AR 2, (c) K-AR 3, (d) K-AR 4, (e) K-AR 5 and (f) K-AR 6.

Table 5
Drying performance of the synthesized alkyds.

Alkyd sample	Curing time (min)	Curing temperature (°C)
K-AR 1	270	100
K-AR 2	250	95
K-AR 3	225	90
K-AR 4	210	85
K-AR 5	200	80
K-AR 6	180	70

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

Alkyd sample	Pencil hardness	Adhesion (%)	Gloss (60°)
K-AR 1	4H	100	70
K-AR 2	2H	100	65
K-AR 3	HB	100	72
K-AR 4	B	100	75
K-AR 5	2B	100	80
K-AR 6	4B	100	83

the fatty acid chains and that at δ 1.583–1.606 ppm may be due to protons of $-CH_2$ groups attached next to the above terminal methyl group. Peaks at δ 1.249– 1.251 ppm are observed for the protons of all internal $-CH_2$ groups present in the fatty acid chain. For protons of unsaturated carbons, the characteristic peaks appear at δ 5.34–5.345 ppm and for methylene protons of glycerol moiety are found at δ 4.157–4.385 ppm. The resins show aromatic protons at δ 7.255–7.725 ppm (Pavia et al., 2008). The intensity of aromatic proton signals was found to be lowest for sample K-AR 6 having lowest percentage of phthalic anhydride in the reactant composition.

The surface characteristics of the cured alkyd resins were investigated by SEM. The SE micrographs of the resins: (a) K-AR 1, (b) K-AR 2, (c) K-AR 3, (d) K-AR 4, (e) K-AR 5 and (f) K-AR 6 are presented in Fig. 10. The SEM images show a smooth surface in all cases. Similar SEM images were reported for polyester resin from yellow oleander oil by Bora et al. (2014). However a distinct difference in the motif was visible as the nature of the acid-anhydride was changed.

Some physico-chemical properties of the karanja oil based alkyd resins are given in Table 4.

The dark brown colour of the synthesized alkyd resins may be attributed to the colour of the seed oil. Bleaching of the coloured seed oil may improve the alkyd colours as reported by Odetoye et al. (2010), when they observed that bleaching of the faint yellow colour of *J. curcas* seed oil led to an improvement of alkyd colours.

Alkyds K-AR 1, K-AR 2, K-AR 3, K-AR 4, K-AR 5 and K-AR 6 were soluble in acetone, butanol, toluene and xylene (2 g alkyd resin/5 mL solvent). Alkyds were highly soluble in acetone and toluene while lowest solubility was observed in butanol. With decrease in percentage of aromatic moiety the solubility of resins also decreased in the respective solvent.

The drying performance of the alkyd is one of the most important requirements for their applications in surface coating, adhesive and binder. The results showed that the films of the alkyd resins remained sticky even after a long time exposure (~96 h) to air. This attributes to the absence of linolenic acid in the oil which was confirmed from its fatty acid composition (Aigbodion and Okieimen, 2001). As a consequence karanja seed oil may be classified as non-drying oil. Thus the alkyds investigated in this study are required to be blended with fast-drying film forming resins such as epoxy resin.

3.5. Curing of alkyd resins

Table 5 shows the drying characteristics of karanja seed oil alkyd resins at different curing time and temperature.

From the data given in the table it is clear that the curing time as well as the required temperature decrease with the increasing MA content in the resin. K-AR 6 (50% MA) possesses the lowest curing time (180 min at 70 °C) whereas the K-AR 1 (0% MA) has the highest curing time (270 min at 100 °C). This is attributed to the fact that with the increase of MA content in resin, the degree of unsaturation increases, which results in decrease in the curing time as the unsaturation is the main component for crosslinking reaction by free radical mechanism (Oldring, 2nd edition, 2000).

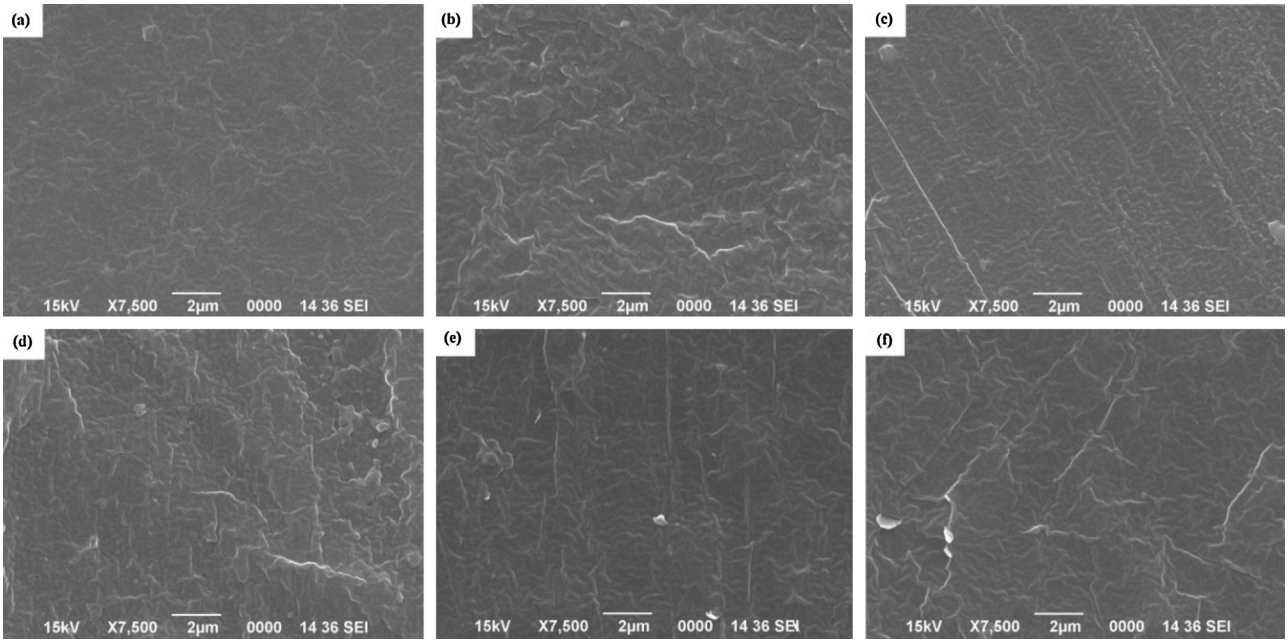

Fig. 10. SEM images of the synthesized resins: (a) K-AR 1, (b) K-AR 2, (c) K-AR 3, (d) K-AR 4, (e) K-AR 5 and (f) K-AR 6.

Table 7
Chemical resistance of the cured epoxy-blended alkyd resin.

Alkyd type	10% HCl (aq)	0.5 N NaOH (aq)	10% NaCl (aq)	Distilled water
K-AR 1	Excellent	Fair	Excellent	Excellent
K-AR 2	Excellent	Fair	Excellent	Excellent
K-AR 3	Excellent	Fair	Excellent	Excellent
K-AR 4	Excellent	Fair	Excellent	Excellent
K-AR 5	Excellent	Poor	Excellent	Excellent
K-AR 6	Excellent	Poor	Excellent	Excellent

3.6. Physical properties of the cured alkyd resins

Table 6 shows some of the physical properties of cured epoxy-blended films of karanja oil based alkyd resins. The pencil hardness value was tested with 6B to 6H of which 6H has the highest hardness. On the basis of hardness value of tested pencil, the pencil hardness value was found to be highest for K-AR 1 with 100% PA due to the presence of rigid aromatic moiety in the polymer chain (Oldring, 2nd edition, 2000). The adhesion characteristics of all the resins are very good due to the presence of polar ester bonds (Mahapatra and Karak, 2004). The gloss property of the resins is also found to be good. These results indicate that the resins have the potential for surface coating application.

3.7. Chemical resistance

The performances of the cured epoxy-blended resins under different chemical environments are given in Table 7. Equal amount of each cured epoxy-blended film was dipped in the reagents and after 1 month, weight change was measured. More the weight change less is the resistance of the resin to the respective reagent and vice-versa.

It was found that epoxy-blended alkyds are highly resistant to dilute HCl, aqueous NaCl solution and distilled water. Alkyds K-AR 1, K-AR 2, K-AR 3 and K-AR 4 are fairly resistant to alkali, which may be due to the low rate of hydrolysis of aromatic ester groups (Boruah et al., 2012). But the alkyds with increased percentage of maleic anhydride show poor resistance to alkali. This poor alkali resistance of the alkyds may be due to the presence of alkali hydrolysable aliphatic ester groups (Mahapatra and Karak, 2004).

3.8. Thermal analysis

The thermogravimetric analysis (TGA) of the cured epoxy-blended resins was carried out in an inert atmosphere (N_2 atmosphere) to measure the thermal stability of the cured alkyd resins. The TGA curves of the alkyds are given in Fig. 11. The initial decomposition of all the resins approximately starts at 280 °C. As it is clear from the figure, the overall thermal stability of the alkyds follows the order K-AR 1 > K-AR 2 > K-AR 3 > K-AR 4 > K-AR 5 > K-AR 6. The presence of rigid aromatic ring contributes to higher thermal stability. The major weight loss temperature is above 300 °C. Thus karanja oil based polyester resins bear very good thermostability under the nitrogen atmosphere.

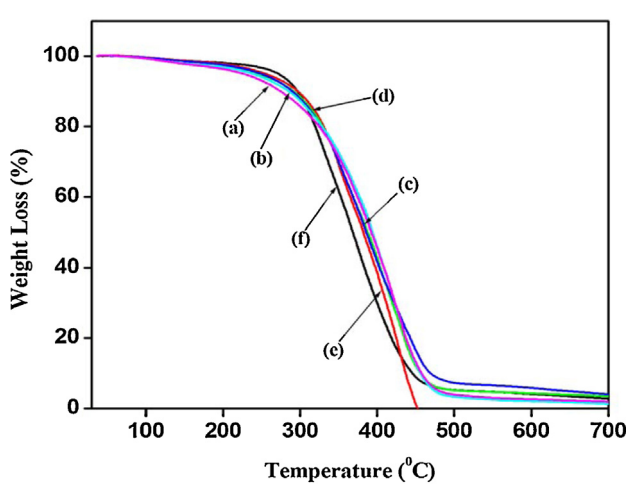

Fig. 11. TGA thermogram of the cured alkyds: (a) K-AR 1, (b) K-AR 2, (c) K-AR 3, (d) K-AR 4, (e) K-AR 5 and (f) K-AR 6.

4. Conclusion

The karanja seed oil possesses the characteristics of a non-drying oil, for which the successful application of its alkyd resins as coating materials requires its blending with epoxy resin and epoxy hardener and curing. The physical properties of the cured epoxy-blended resin conform to the required standard for suitable application as coating material. Hence, karanja seed oil, a non-edible oil, provides a renewable source of raw materials for production of alkyd resin, for subsequent use as coating material.

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