

Synthesis of Alkyd Resin from Jatropha and Rapeseed Oils and Their Applications in Electrical Insulation

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ABSTRACT: Alkyd Resin based on Jatropha and Rapeseed oils using glycerol, phthalic, and maleic anhydride were synthesized to obtain the resins suitable for electrical applications. These resins were characterized for the physical and electrical properties. Varnishes were prepared using these resins and characterized as per standard methods. In general, both the varnishes prepared from alkyd resin from jatropha and rapeseed oils meet

the standard requirements. However, the varnish prepared from rapeseed oil was found to be superior in terms of adhesion, break down voltage, and volume resistivity. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1724–1729, 2008

Key words: alkyd resin; electrical insulation; varnish; jatropha; rapeseed oil

INTRODUCTION

The oil from various seeds specially, waste fruit seeds has been used in the synthesis of different kinds of polymeric resins like alkyds, epoxies, polyurethanes, polyester amides and amides, and other polymers.^{1–6} The use of renewable but nonedible oils provides an opportunity for the utilization of waste seeds to make value added products including polymeric resins for paint for coating industries.^{7–10}

The use of petroleum based monomers in the manufacture of polymers is expected to decline in the coming years because of spiraling prices and the high rate of depletion of the stocks. This has inspired the technologists all over the world to investigate renewable natural materials as an alternate source of monomers for the polymer industry as substitute for the petroleum-based monomers to manufacture of polymers.^{11–14} These resins hold considerable scope for applications in the paint and coating industries.^{15–18}

Alkyd resins are the reaction products of an oil or fatty acid, polyols, and polyacids, such as phthalic and maleic anhydrides. These polymers are supplied in solvents and can be cured by reaction with oxygen or amino-based cross linking resins to form tough, durable films. The choice and amount of oil in the polymers determines the dry rate and solubility of the polymer in solvents. Long and medium oil alkyds are supplied in low odor aliphatic solvents. They are suitable for architectural

and maintenance finishes. Short oil alkyds are supplied in aromatic solvents and are used in fast air drying and bake finishes. Alkyds can also be modified or co-reacted with many other resins such as rosin, phenolic, urethane, vinyl monomers etc. The different combination of ingredients, and precise control of the reaction parameter, influences the final properties of the alkyd resins. Because of this reason, there are a large number of alkyd resins available for the coatings formulators. Synthesis and electrical application of varnishes based on jatropha and rapeseed oil alkyd resin yet has not been reported. In the present studies, attempts have made to synthesize alkyd resins suitable for making varnishes for electrical insulation applications. The work on synthesis and evaluation of alkyd resins and varnishes has been reported.

EXPERIMENTAL

Materials

1. Jatropha oil: Dahod mill, Dahod.
2. Rapeseed oil: Dahod mill Dahod.
3. Phthalic anhydride: National chemicals, Baroda.
4. Glycerol: National chemicals, Baroda.
5. Catalyst (PTSA): National chemicals, Baroda.
6. Thinner: Uma Paint, Mmakarpura GIDC, Baroda

Apparatus

The polymerization reaction was carried out in a four-necked flask equipped with Dean-stark apparatus, condenser, temperature controller, and stirring device.

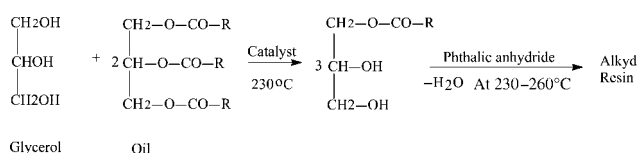
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PROCEDURE

Alkyd resins were synthesized by esterification of jatropha oil and rapeseed oil with phthalic anhydride and glycerol. About 100 g of oil, 20 g of glycerol, and 0.05 g of PTSA as catalyst was added to glass reaction vessel. The mixture was then heated up to 230°C and continued for 1 h. The completion of reaction was verified by mixing one part of reaction mixture in three parts of methanol at room temperature. The mixture was completely dissolved in methanol and gave a clear liquid; it indicates that the reaction is completed. Thereafter, the mixture was cooled down to 150°C, and 50 g of Phthalic anhydride was added to the mixture and heated to 230°C again. It was maintained in this condition for 5 h. The completion of reaction was checked by quantitative water removal from reaction in dean-stark. The alkyd resins were characterized by acid value, viscosity and infra red spectrophotometric analysis. Finally, it was cooled down to room temperature and stored in airtight container.

A typical esterification reaction is given below.



Glycerol

Oil

Where R = $-(\text{CH}_2)_7-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{CH}_3$

Preparation of varnish

A total of 6.5 g of Alkyd resin was mixed with 0.32 g Co-Naphthanate, 0.12 g Lead-Naphthanate, 0.1 g Calcium Naphthanate, and 4 g thinner in a 100 mL beaker and mixture was gently warmed to about 60°C. It was stored in air tight container after cooling. The varnishes were characterized for physical and electrical properties.

CHARACTERIZATION

The resin was tested for density, viscosity, and non-volatile matter. The characterization of the varnish prepared and tested as per the methods given in the Indian standard IS 10026.¹⁹ For electrical test, the varnish was coated on to 0.1 mm thick copper sheet and cured at 130°C for 3 h and used.

Density

The density of the varnish was determined by weighing a sample of varnish in a 25 cm³ capacity, wide-mouth pycnometer and dividing the mass of varnish by the mass of an equal volume of distilled water at the room temperature.

Viscosity

The viscosity was determined at $27 \pm 2^\circ\text{C}$ using Brookfield viscometer using different spindle and speed.

Nonvolatile matter

Three specimens were placed in the oven within 30 min after preparation of varnish in previously weighed metal dishes and heated for 2 h at 135–140°C. The nonvolatile matter was calculated from the difference in initial and final weights of the metal dishes. The mean value of the three results was reported as the percentage nonvolatile matter.

Drying time of thin films

The copper plates of $50 \times 50 \times 0.1 \text{ mm}^3$ dimension were coated by dipping in varnish at temperature $27 \pm 2^\circ\text{C}$. The specimens were allowed to stand immersed in varnish until free from bubbles and suspended for drying in dust free atmosphere. A piece of filter paper was placed on the panel after drying and a weight was placed on the paper in the vicinity of the center of the specimen, with a rubber disk interposed between the paper and weight to distribute the pressure equally. After 1 min the paper was removed to check whether it is tack free.

Flash point

The flash point of the varnish was determined using closed-cup apparatus as specified in IS197.

Dilution ability or compatibility

About 20 mL of the filtered varnish was poured into a 100 mL capacity-measuring cylinder with stopper. About 10 mL of Xylene was added and shaken vigorously. The mixture was allowed to rest for few minutes and was observed for cloudiness or separation. This was repeated until the mixture becomes cloudy or a separation was observed by adding 5 mL Xylene repeatedly.

Varnish ability to cure in considerable thickness

Two containers of aluminum foil having a base area of 45 mm \times 45 mm and height of 25 mm were prepared by bending the aluminum foil. There were cleaned with a mixture of xylene and anhydrous ethanol before using. A total of 20 g of varnish was filled in aluminum container at room temperature. The containers were placed in the drying oven. It was dried for 3 h at 130°C. The varnish blocks were freed from the foil and conditioned for 16 h at temperature of ($27 \pm 2^\circ\text{C}$) and a relative humidity of ($50 \pm 5\%$). The specimens were checked as per IS specification.

Softening test for varnish

A sample specimen was prepared as per condition given above. It was kept standing on its edge for one hour in a laboratory drying oven at 150°C. The specimen was checked for any deformation or softening.

Test of varnish reactivity with copper

The copper wire of 0.5 mm diameter, 120 mm in length were taped three places with cotton tape. This bundle of wire was dried for 1 h in an oven at 105°C. It was then cooled to room temperature in desiccators and immersed for 10 min in filtered varnish. The varnish was allowed to drain for 5 min and dried for 3 h at 130°C. After cooling, the bundle of copper wire was immersed again in varnish and repeated the foregoing cycle. After cooling, the cotton tape was removed and the copper wire was examined for any change in color.

Effect of varnish on enameled wires (pencil hardness)

The test specimens of 150 mm in length and 0.8 mm diameter copper wire was heated for 10 min at 130°C. A glass cylinder containing sufficient varnish to immerse a substantial portion of the test specimens was used. The temperature of the varnish was kept at $(60 \pm 3)^\circ\text{C}$. The specimens were immersed in the varnish within the specified limits of testing. After 30 min, the specimens were removed from the varnish and the hardness of the film was determined as pencil hardness. The sharpened edge of the pencil was pressed slowly along the surface with a force of ~ 5 N. Tests on three specimens were carried out to see whether varnish film was removed or not.

Flexibility test

A sample of varnish was prepared as per procedure as described in No-4. After cooling the sample to room temperature in a desiccators, the specimens were inserted, into the test fixture and bent 180°

around the mandrel. The specimens were observed for any cracks.

Resistance to insulating liquids

A sample of varnish was prepared as per procedure given in No 4. The test specimens of 10 mm \times 10 mm size were immersed in the insulating liquid as prescribed chemical in IS 10026 for 48 h. The specimens were wiped with cotton batting and the effect of the insulating liquid was observed, whether the varnish film dissolved, blistered, wrinkled, loosened or was physically affected in a visible manner.

Volume resistivity in air and after immersion in water

Three specimens were prepared as per above procedure No-4. The thickness of film was 0.05 mm \pm 0.005 mm. Three specimens were tested with a layer of conducting rubber placed between it and the metal electrode. Then they were immersed in distilled water at $(27 \pm 2)^\circ\text{C}$ for the 24 h. The specimens were removed from water and dried with filter paper before repeating the test for resistivity.

Electric strength in air and after immersion in water

The test specimens were prepared according to IS 2584. Five tests were carried out on the dried specimens and same tests were conducted after immersion in water for 24 h.

Dielectric constant and dissipation factor

The specimens were prepared according to procedure as per No. 4. The specimens were cut in size of 90 mm diameter and the dielectric constant and dissipation factor was measured using Schering bridge (Model No 2801).

Thermal rating

The specimen was prepared as per procedure No. 4 as described above and the varnish film was care-

TABLE I
Esterification of Jatropa Oil with Phthalic Anhydride

Sr. No	Oil (mole)	Glycerol (mole)	Phthalic anhydride (mole)	Isophthalic anhydride (mole)	Malic anhydride (mole)	Catalyst conc. (%) of oil	Time (h)	Acid value in g of KOH/g	Viscosity in cps
1	1	2	0.5	–	–	1	5	22.8	1,48,000
2	1	2	1.5	–	–	1	5	29.8	17,6,000
3	1	2	0.5	–	–	0.25	5	11.16	1,86,000
4	1	2	1.0	–	–	0.05	5	1.01	1,66,000
5	1	2	–	1	–	0.05	5	30.14	4,80,000
6	1	2	–	–	1	0.05	–	Reaction run out	Reaction run out

TABLE II
Esterification of Rapeseed Oil with Phthalic Anhydride

Sr. no	Oil (mole)	Glycerol (mol)	Phthalic anhydride (mol)	Catalyst conc. (in g)	Time (h)	Acid value in gm of KOH/g of oil	Viscosity in cps
1	1	2	0.5	1	5	20.8	1,48,000
2	1	2	1.5	1	5	25.14	1,76,000
3	1	2	0.5	0.25	5	10.01	1,86,000
4	1	2	1.0	0.05	5	0.98	1,66,000

fully removed. This film was subjected to Thermo Gravimetric Analysis using Mettler Toledo TGA/SDTA851 instrument. The thermal rating was determined from the thermogram as per a method developed at the authors' laboratory. Details of the method have been published elsewhere.²⁰

RESULTS AND DISCUSSION

The alkyd resins from Jatropha oil and Rapeseed oil were synthesized by esterification process using glycerol and anhydrides. The mole ratio of Jatropha/Rapeseed oil was taken considering the 48% oleic acid, since it is major content of oils. The molecular weight of fatty acid was taken as 326 and the content of anhydride was taken considering its purity 99%.

The fatty acid to anhydride ratio was changed from 1 : 0.5 to 1 : 1.5. The esterification temperature was kept in the range of 230–260°C. The reaction was very slow below 200°C. The extent of esterification, was checked by acid value, which ranged between 0.9 and 30 gm KOH/g.

The esterification conditions were optimized to achieve a suitable product for electrical applications. Jatropha oil, glycerol, and phthalic anhydride were in the mole ratios of 1 : 2 (0.5 : 1.0), respectively, and catalyst concentration was taken of 0.05 to 1.0% of oil content. The complete curing of resin basic requirement for electrical application, which was, obtained at mole ratio of oil, glycerol and phthalic anhydride 1 : 2 : 1. Similarly, in the case of rapeseed oil, best curing properties were obtained for the same mole ratio. The resin prepared using iso-

phthalic acid was not cured fully so it was not suitable for electrical application. In case of malic anhydride the esterification reaction were run out. The results are given in Tables I and II.

The resin was characterization by acid value and viscosity measurement. The FTIR spectra analysis was carried out by using perkin elmer-spectrum BX FTIR. The Infrared spectra of the resin show in Figures 1 and 2. The structure of alkyd was conformed by the Infra red spectroscopy. A broad band at 3540–3200 cm^{-1} indicates the presence of free OH group. A strong absorption in the region of 3030–2855 cm^{-1} is due to the long chain alkyl group and 2850–2840 cm^{-1} due to the crystalline type long chain alkyl group present in polymeric chain. Strong absorption band at 1620–1575 cm^{-1} attribute to carbonyl group. A strong absorption in the region at 1740–1720 cm^{-1} is due to the phthalate type ester group present in polymeric chain.

The comparison of physical and electrical properties of varnishes prepared from alkyd resin synthesized from Jatropha and Rapeseed oil are shown in Tables III and IV. It is observed that most of electrical properties such as break down strength; surface resistivity, dielectric constant, dissipation factor etc. were meeting the requirement. The adhesion strength on copper plate is 0.4 kg/cm^2 and 2.5 kg/cm^2 in case of resins prepared from jatropha and rapeseed oil respectively. However, incorporating suitable additives the adhesion on copper can be enhanced.

The comparisons of physical and electrical properties of varnishes prepared from alkyd resin from

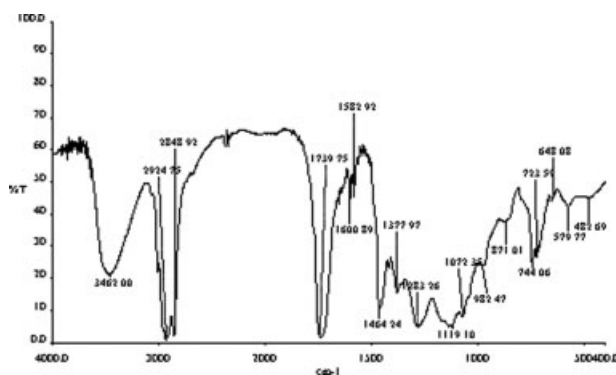


Figure 1 FTIR spectrum of alkyd resin from jatropha oil.

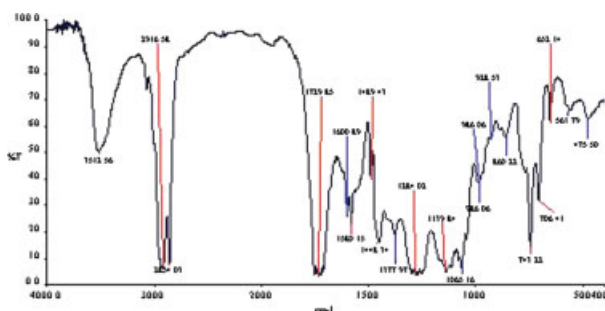


Figure 2 FTIR spectrum of alkyd resin from rapeseed oil. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE III
Comparison of Physical Properties of Alkyd resin and Varnish

Sr. No	Properties	Specified value in IS 10026	Alkyd resin prepared from Jatropa oil	Alkyd resin prepared from Rapeseed oil	Commercial alkyd resin (SyntolacI-60) ^a
A	Alkyd Resin				
1	Density		1.26	1.01	1.14
2	Viscosity		1,66,000 cps	1250 cps	41,600 cps
3	Nonvolatile matter		92.71%	70%	98.96%
B	Varnish based on Alkyd resin				
1	Density		1.075	0.94	1.08
2	Viscosity		50 cps	50 cps	200 cps
3	Nonvolatile matter		50%	50%	50%
4	Drying time in thin film		4 h 130 °C	3 h at 120 °C	3 h at 120 °C
5	Flash point, °C	Nontacky 23 °C min	25 °C	36 °C	25 °C
6	Ability to cure in considerable thickness		S.2,U.2, I.5, I.4.2	S.2,U.2, I.5, I.4.2 wrinkled, nontacky, soft rubber like few bubbles	S.2,U.2, I.5, I.4.2
7	Check for resoftening	Not worse than w ₂	w.2	w.2 no change and few bubbles	w.2 no change and few bubbles
8	Reaction with copper	Shall not react	Does not react	Does not react	Does not react
9	Flexibility	No crack	No crack observed	No crack observed	No crack observed
10	Effect of varnish on Enameled wires	Pencil hardness not softer than H	Passed test	Passed test	Passed test
11	Résistance of transformer oil. After 48 h at 100 °C (A) Visual examination	No evidence of attack	No softening, blistering, wrinkling, disintegration or separation of varnish film Slightly yellow color of oil	No softening, blistering, wrinkling, disintegration or separation of varnish film Slightly yellow color of oil	No softening, blistering, wrinkling, disintegration or separation of varnish film Slightly yellow color of oil
	(B) Acidity of oil (before and after aging)	0.4 KOH /g max	(b) Acidity: Nil (before and after)	(b) Before: 0.012 mg KOH/g, after: 0.03 mg KOH/g	(b) Acidity: Nil (before and after)
	(C) Sludge value of oil (Before and after aging)	0.1 % max	(c) Nil (before and after)	(c) Before: 0.01 % After: 0.015 %	(c) Nil (before and after)
12	Effect of heat aging on flexibility (100 h at 110 °C)	No visible change or detachment of film	No crack observed	No crack observed	No crack observed

^a Commercial alkyd resin SyntolacI-60 is procured from Synthad chemical Pvt Ltd, Vallabh Vidyanagar, Gujarat.

TABLE IV
Comparison of Electrical Properties of Varnish

Sr. no	Properties	Specified value in IS 10026	Alkyd resin prepared from Jatropha oil	Alkyd resin prepared from Rapeseed oil	Commercial alkyd resin (Syntolacl-60) ^a
1.	Volume resistivity	$1 \times 10^{12} \Omega \text{ cm (min)}$	$1 \times 10^{12} \Omega \text{ cm}$	$1 \times 10^{15} \Omega \text{ cm}$	$4.03 \times 10^{13} \Omega \text{ cm}$
2.	Thermal rating	–	130°C (Class B)	120°C	130°C
3.	Dielectric constant	–	2.22	1.73	3.2
4.	Dissipation factor	–	0.0098	0.0225	0.0088
5.	Electric strength	50 kV/mm (Min)	66 kV/mm	100 kV/mm	42 kV/mm

^aSupplied by Synthad Chemical Pvt., Ltd., Vallabh Vidyanagar, Gujarat.

Jatropha and Rapeseed oil with syntholacl-60 commercial resin as available in market are shown in Tables III and IV. It is observed that most of electrical properties such as break down strength; surface resistivity, dielectric constant, dissipation factor etc. are matching. The Electrical properties such as volume resistivity, Dielectric constant, Dissipation factor and Electric strength of alkyd resin prepared from Rapeseed oil, are better than all other resins.

A market survey on cost of commercial alkyd resins available in Indian market was carried out and compared with the cost of alkyd resins prepared from jatropha and rapeseed oil. It was observed that these resins are cheaper by 18–25% in cost.

CONCLUSION

1. Electrical grade varnishes have been synthesized from Jatropha oil and Rapeseed oil. The varnishes meet all the requirement of relevant Indian Standard for class "B" baking type insulating varnish.
2. The adhesion strength of Jatropha-based varnish is found poor. It can be improved by incorporating suitable additives.
3. The varnishes made are suitable for low tension application.

References

1. Gast, L. E.; Schneider, W. J.; Cown, J. C. *J Am Oil Chem Soc* 1966, 43, 418.
2. Patel, P.; Shah, T.; Suthar, B. *J Polym Mater* 1989, 6, 193.
3. Rokicki, G.; et al. *J Macromol Sci Pure Appl Chem A* 1996, 33, 509.
4. Trevino, A. S.; Trumbo, D. L. *Prog Org Coat* 2002, 44, 49.
5. Ikhuoria, E. U.; Aigbodiain, A. I. *J Appl Polym Sci* 2006, 101, 3073.
6. Azam, M.; et al. *Chinese J Chem* 2007, 25, 705.
7. Mannari, V. M.; Raval, D. A. *Res Ind* 1995, 40, 38.
8. Raval, D. A.; Roy, T. K.; Mannvari, V. M. *Int Sci Ind Res* 1996, 55, 263.
9. Roy, T. K.; Mannari, V. M.; Raval, D. A. *Int Sci Ind Res* 1997, 56, 159.
10. Zafar, F.; Sharmin, E.; Ashraf, S. M.; Ahmed, S. *Prog Org Coat* 2004, 51, 250.
11. Nayak, P.; Mishra, D. K.; Parida, D.; Sahoo, K. C.; Nanda, M.; Lonka, S.; Nayak, P. L. *J Appl Polym Sci* 1997, 63, 67.
12. Raymond, M. P.; Bui, V. T. *J Appl Polym Sci* 1998, 700, 1409.
13. Teng, G.; Soucek, M. D. *J Am Oil Chem Soc* 2000, 77, 381.
14. Wold, C. R.; Ni, H.; Soucek, M. D. *Chem Mater* 2001, 13, 3032.
15. Economy, J. *J Macromol Sci Chem A* 1984, 21, 1705.
16. Ahamad, S.; et al. *J Appl Polym Sci* 1999, 72, 1679.
17. Tiwari, S.; et al. *J Appl Polym Sci* 2003, 87, 110.
18. Zafar, F.; Sharmin, E.; Ashraf, S. M.; Ahamad, S. *J Appl Polym Sci* 2004, 92, 2538.
19. Indian Standard 10026, 1999.
20. Vagish, S.; Krishna Moorthy, P. A. *J Appl Polym Sci* 1993, 50, 367.