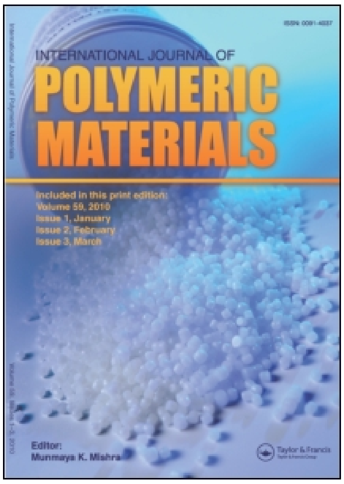

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Alkyd Resins from Polymerised Rubberseed Oil

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Rubberseed oil (RSO) was thermally polymerised at different temperatures. It was also polymerised at the same temperature using various percentage of benzoyl peroxide (BPO) and Azobisisobutyronitrile (AIBN) as free radical catalysts. During polymerisation, the free fatty acid content increased as revealed by increasing acid value and unsaturation decreased as indicated by decreasing iodine value. The FFA, unsaturation, viscosity and refractive index of the polymerised oil samples were determined.

Alkyd resins were prepared from as it is and polymerised rubberseed oil samples. The physical properties and air dried and baked film properties of these alkyd resins were studied and compared.

INTRODUCTION

Among various synthetic resin binders used in surface coatings, alkyds are the most widely used resins due to their versatility of applications and favorable cost-performance balance for most applications [1]. Alkyds offer various types of modification with variety of types of compounds to suit the end product requirements.

Vegetable oils, the important ingredient of alkyds, besides controlling many important film properties, significantly control cost. Many vegetable oils such as soyabean, safflower, sunflower, *etc.*, used in the

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preparation of alkyds are edible and therefore, besides being costlier, face increasing restriction for their use in industrial products. These factors have necessitated to explore potential non-traditional oils for surface coating applications.

Rubberseed oil is commercially available in South Indian states and mainly find low value applications such as in soap making. The exploration of this oil has revealed a suitable alternative fatty acid composition, from the point of view of its utility for surface coating applications.

Thermal polymerisation offers a well known method for modification of oil to improve their properties for use in coating compositions. Polymerisation of oils is known to be catalysed by free radical initiators like hexaphenylethane, hex-*p*-biphenylethane, di-*t*-butyl peroxide [2], benzoyl peroxide [3], *t*-butyl peroxide and other peroxides [4] and metals like lead, aluminium, barium, copper and selenium *etc.* [5, 6].

In the present work, raw rubberseed oil, after suitable refining has been polymerised by heating it separately with BPO and AIBN as a catalyst in varying proportions and without catalyst at the same temperature *i.e.*, at 60, 90 and 230°C.

The various polymerised rubberseed oil samples have been used in the synthesis of medium oil alkyd resins by following monoglyceride process using calcium octoate as a catalyst. The various physical properties of these alkyd resins have been studied and compared.

MATERIALS AND METHODS

Raw rubberseed oil was procured from Kottayam, Kerala state, India and was purified prior to its use. Its characteristics are shown in Table I. The other chemicals used *viz.* glycerol, phthalic anhydride, BPO, AIBN, calcium octotate, xylene, methanol and phosphoric acid were of laboratory reagent grade.

EXPERIMENTAL

Rubberseed oil was refined by the reported method [7].

TABLE I Characteristics of RSO

Sr. No.	*Characteristic properties*	
1	Acid value (mg · KOH/gm)	9.00
2	Saponification value (mg · KOH/gm)	193.00
3	Iodine value	138.00
4	Hydroxyl value	20.00
5	Specific value (15°C)	0.925
6	Refractive index	1.4670
7	Colour [$y = 5\,\mathrm{R}$ (Lovibond)]	11.00

POLYMERISATION OF RUBBERSEED OIL

Refined rubberseed oil (RSO) was heated at different temperatures *viz.* 60, 90 and 230°C using (w/w) of the oil 0.5, 1.0, 1.5 and 2.0 percent of AIBN and BPO separately and respectively as catalyst and without using the catalysts. The temperatures were controlled within ± 2°C. The polymerised oil was taken out after 1, 2, 3 and 4 hours, cooled and was fractionated by shaking one part of the polymerised oil and two parts of *n*-hexane at room temperature for 15 minutes and allowing it to settle for 30 minutes. The two layers were separated. The hexane soluble layer which contains the polymerised oil was decanted off completely from the extract.

Viscosity and refractive index of hexane extracted fraction were determined by Gardner bubble viscometer and Abbe's refractometer respectively. The other properties were determined as per AOCS methods [8].

The characteristics of polymerised rubber seed oil [RSO (P)] are shown in Tables IIA and IIB.

PREPARATION OF ALKYDS [9]

The alkyds from polymerised and as it is oil were prepared in the following way.

Since no major change in the characteristics of the oil was found after polymerizing at 60°C and 90°C using AIBN and BPO as catalysts respectively as compare to polymerization conducted at 230°C, using separately both the catalysts and without using catalysts, the alkyd

TABLE IIA Characteristics of polymerised rubberseed oil

Catalyst	*Concentration of catalyst (%)*	*Time of polymerisation (hour)*	*Iodine value*	*Acid value (mg of KOH/gm)*	*Viscosity (gardner)*	*R.I. at 25°C*	*Temperature °C*
BPO	0.5	1.0	122	11.8	D	1.4978	230
		2.0	119	14.1	D-E	1.5148	
		3.0	115	18.2	E	1.5207	
		4.0	110	20.2	F	1.5248	
	1.0	1.0	116	14.2	D-E	1.5141	
		2.0	113	17.0	D-E	1.5197	
		3.0	109	20.1	E-F	1.5250	
		4.0	106	24.8	F	1.5298	
	1.5	1.0	112	15.0	D-E	1.5204	
		2.0	108	18.3	D-E	1.5255	
		3.0	105	21.8	F	1.5301	
		4.0	103	27.7	F-G	1.5344	
	2.0	1.0	108	16.2	E	1.5244	
		2.0	106	19.8	E-F	1.5300	
		3.0	102	23.4	E-F	1.5354	
		4.0	99	29.2	G	1.5402	
AIBN	0.5	1.0	120	10.3	D	1.4975	230
		2.0	118	13.2	D-E	1.5145	
		3.0	115	17.3	E	1.5201	
		4.0	110	19.4	F	1.5244	
	1.0	1.0	115	13.3	D-E	1.5139	
		2.0	112	16.5	D-E	1.5197	
		3.0	109	19.3	E-F	1.5247	
		4.0	106	14.2	F	1.5296	
	1.5	1.0	110	14.5	D-E	1.5202	
		2.0	107	17.5	D-E	1.5255	
		3.0	105	20.3	F	1.5301	
		4.0	102	26.3	F-G	1.5342	
	2.0	1.0	108	15.3	E	1.5222	
		2.0	105	18.5	E-F	1.5299	
		3.0	101	22.3	E-F	1.5351	
		4.0	98	28.4	G	1.5400	
–	–	1.0	137	9.00	B-C	1.4670	230
		2.0	137	9.00	C	1.4700	
		3.0	136	9.50	C-D	1.4700	
		4.0	134	10.00	C-D	1.4750	

was prepared from the oil which was polymerized at 230°C. The laboratory setup consists of a 500 ml, 3 necked flask, equipped with a glass stirrer, a thermometer, a sampling tube and a Dean-Stark moisture trap.

TABLE IIB Characteristics of polymerised rubberseed oil

Catalyst	*Concentration of catalyst* (%)	*Time of polymerisation* (*hour*)	*Iodine value*	*Acid value* (*mg of KOH/gm*)	*Viscosity* (*gardner*)	*R.I. at 25°C*	*Temperature °C*
BPO	0.5	1.0	135	9.08	B	1.4673	90
		2.0	133	9.18	B-C	1.4690	90
		3.0	130	10.00	C	1.4800	90
		4.0	129	10.08	C-D	1.4890	90
	1.0	1.0	133	9.25	B-C	1.4705	90
		2.0	130	9.50	C	1.4785	90
		3.0	127	10.18	C-D	1.4810	90
		4.0	122	10.25	D	1.4900	90
	1.5	1.0	130	9.38	B-C	1.4780	90
		2.0	125	9.60	C	1.4809	90
		3.0	123	10.20	C-D	1.4910	90
		4.0	119	10.30	D-E	1.5011	90
	2.0	1.0	127	9.50	C	1.4880	90
		2.0	124	9.75	C-D	1.4910	90
		3.0	120	10.30	D	1.5018	90
		4.0	118	10.48	D-E	1.5105	90
AIBN	0.5	1.0	132	9.06	B	1.4670	60
		2.0	130	9.15	B-C	1.4687	60
		3.0	127	9.78	C	1.4795	60
		4.0	124	10.00	C-D	1.4882	60
	1.0	1.0	130	9.15	B-C	1.4700	60
		2.0	127	9.38	C	1.4779	60
		3.0	123	9.88	C-D	1.4806	60
		4.0	120	10.06	D	1.4896	60
	1.5	1.0	129	9.25	B-C	1.4776	60
		2.0	126	9.50	C	1.4803	60
		3.0	123	9.98	C-D	1.4906	60
		4.0	118	10.18	D-E	1.5006	60
	2.0	1.0	126	9.40	C	1.4876	60
		2.0	123	9.70	C-D	1.4900	60
		3.0	120	10.00	D	1.5006	60
		4.0	117	10.35	D-E	1.5100	60
—	--	1.0	138	9.00	B	1.4670	60/90
		2.0	138	9.00	B	1.4670	60/90
		3.0	138	9.00	B	1.4673	60/90
		4.0	138	9.00	B-C	1.4680	60/90

The oil and glycerol were heated to 230°C under constant stirring using litharge and calcium octoate (3% Ca) as a catalyst. The temperature was raised to 250°C until a 1:3 (v/v) methanol dilution test gave a miscible solution. This indicates the formation of monoglyceride. The heating was stopped and temperature was lowered to 120°C. The dibasic acid (phthalic anhydride) along with xylene (8% of total charge) was added slowly with the constant stirring and the temperature was raised to 160°C and held for 1 hr to remove the water, using azeotropic distillation. After removing xylene, temperature was raised to 240°C and kept constant until the desired acid value was reached (< 15). The heating was then stopped and temperature was lowered to 120°C. The charge was thinned with xylene to 60 percent non-volatiles. Charge weight of alkyds is shown in Table III and their characteristics are shown in Table IV.

FILM PREPARATION

Air-dried and baked (150°C for 15 min.) film properties of various alkyds were studied. Driers were added to the samples (Pb-0.5%, Co-

TABLE III Formula for 100 gm of alkyd resin

Alkyd code	*Oil length*	*Temp.°C*	*Thermally polymerised RSO (gm)*	*RSO (gm)*	*Glycerine (gm)*	*Phthalic anhydride (gm)*	*Yield %*
RSO (P)	50	240	50	–	17	33	95
RSO	50	240	–	50	17	33	95
RSO (pwc)	50	240	50	–	17	33	95

pwc: Polymerised without catalyst.

TABLE IV Characteristic of alkyd resin*

Resin code	*Colour (gardner)*	*Acid value (mg · KOH/gm)*	*Catalyst*	*Catalyst percentage*	*Time of polymerisation*
RSO (P)-I	15	11.2	RSO	0.5	4 hr
RSO (P)-II	15–16	13.6	RSO	1.0	4 hr
RSO (P)-III	16	14.9	RSO	1.5	4 hr
RSO (P)-IV	16	15.0	RSO	2.0	4 hr
RSO (P)-V	15	10.0	AIBN	0.5	4 hr
RSO (P)-VI	15–16	12.5	AIBN	1.0	4 hr
RSO (P)-VII	16	12.3	AIBN	1.5	4 hr
RSO (P)-VIII	16	15	AIBN	2.0	4 hr
RSO	14	8.1	–	–	–
RSO (pwc)	15	10.08	–	–	4 hr

*RSO (P) = Polymerised rubber seed oil; RSO = unpolymerised rubber seed oil; RSO (pwc) = RSO polymerised without catalyst.

0.05% and Mn-0.05%) and viscosity of the composition was adjusted suitably by adding xylene. The coating compositions were applied on 6" × 2" mild steel panels and tin panels as specified in the Indian Standard (IS) specification [10] to cast films having dry film thickness of approximately 30 microns.

Mechanical properties such as flexibility and scratch hardness of the films have been determined as per IS specification [10]. The chemical resistance properties [11] *viz.* acid resistance and alkali resistance of the films were studied by immersion of coated panel in 2% by wt. of solution of HCl and NaOH respectively.

RESULTS AND DISCUSSION

The film properties of various alkyds are listed in Tables V and VI.

In general, the results of the characteristics of the polymerised oil and alkyds derived from polymerised oil reveal that for both the catalysts, as the concentration (amount) of the catalyst increases, due to thermal polymerisation, the free fatty acid content in the oil increases but the unsaturation decreases [12]. This is reflected by increase in acid value and decrease in iodine value. Viscosity and

TABLE V Air dried film properties of alkyd resins*

Resin code	*Drying time*		*Scratch*	*Impact*	*Chemical*
	Dry to touch hr · min	*Tack free hr · min*	*hardness kg (passes)*	*resistance lbs inch*	*resistance (unaffected) NaOH (2%) (passes) hr · min*
RSO (P)-I	1.40	8.30	0.8	250	0.45
RSO (P)-II	1.25	7.30	0.9	275	0.50
RSO (P)-III	1.10	6.45	1.0	300	1.00
RSO (P)-IV	1.00	6.00	1.1	300	1.10
RSO (P)-V	1.35	8.15	0.7	250	0.45
RSO (P)-VI	1.20	7.20	0.8	275	0.50
RSO (P)-VII	1.05	6.30	0.85	300	0.55
RSO (P)-VIII	0.50	5.50	0.90	300	1.10
RSO	2.00	ONT	0.7	225	0.35
RSO (pwc)	1.50	ONT	0.7	225	0.40

* The test panels were cured at ambient temperature. The test panels pass the test of HCl (2%), water and xylene for 200 hr. immersion.

TABLE VI Baked film properties of alkyd resin*

Resin code	*Scratch hardness kg (passes)*	*Impact resistance lbs inch*	*Chemical resistance (unaffected) NaOH (%) (passes) hr·min*
RSO (P)-I	1.00	250	1.00
RSO (P)-II	1.10	275	1.10
RSO (P)-III	1.20	300	1.25
RSO (P)-IV	1.30	300	1.45
RSO (P)-V	0.50	250	1.00
RSO (P)-VI	1.00	275	1.10
RSO (P)-VII	1.10	300	1.25
RSO (P)-VIII	1.20	300	1.45
RSO	0.90	250	0.50
RSO (pwc)	0.90	250	0.50

* Baked at 150°C for 15 min. The test panels pass the test of HCl (2%), water and xylene for 200 hr. immersion.

refractive index also show the increasing trend with increase in the time of polymerisation and with increase in the concentration of the catalyst. It is known that with increase in viscosity, the molecular weight increases [13]. The same trend is observed in case of RSO also. The rise in catalyst concentration raises the viscosity of the RSO due to rise in the molecular weight on account of polymerisation [13]. From the results it was revealed that the acid value, iodine value, viscosity and refractive index differs for the oil which was polymerised at 230°C without using catalyst as compared to the oil polymerised using both the catalysts separately at the same temperature. Since, the temperature for catalytic and thermocatalytic polymerisation has been kept the same, in the formal case, thermal polymerisation where as in the latter case, thermocatalytic polymerisation occurs. Naturally the rate of polymerisation in the latter case will be faster. This is substantiated by the difference in values of IV, RI, Viscosity *etc.*, for the samples polymerised thermally and thermocatalytically.

DRYING TIME

In general the drying time of the films from RSO (P) is less than that of alkyd from unpolymerised RSO. The drying time of the alkyd from RSO (P) decreases with increase in catalyst loading. This might be due to increase in initial molecular weight of the oil. With increase in molecular weight, fewer cross links are required to form a coherent film[14] or to reach the dry stage[15]. Drying time for the alkyd prepared from RSO polymerised at 230°C without catalyst is found to be higher than that for the RSO polymerised with both the catalysts. This might be due to difference in molecular weight, which is reflected from the viscosities of the samples.

MECHANICAL PROPERTIES

In general, for both air dried and baked films, the scratch hardness and impact resistance of the alkyds prepared from polymerised oil are better than those from the unpolymerised oil. The impact resistance and scratch hardness increase with increase in catalyst loading [*i.e.*, from 0.5% to 2% BPO and AIBN]. This might be due to increase in initial molecular weight of the oil which is reflected in the resulting alkyd. No significant difference was observed whether BPO or AIBN was used as a catalyst.

The mechanical properties of the alkyds prepared from thermally polymerised RSO are nearly the same as those of the alkyd prepared from unpolymerised RSO. This can be attributed to the fact that no significant polymerisation occurred for the former sample.

CHEMICAL RESISTANCE

The alkali resistance of the alkyds prepared from polymerised oil is better than that of the alkyd prepared from the unpolymerised oil. The alkali resistance for air dried and baked films increases with increase in catalyst loading. This might be due to increase in cross link density of the film[16] resulting from enhanced molecular weight with increase in catalyst loading.

For the alkyd prepared from thermally polymerised RSO, same trend was observed for chemical resistance test which as was observed for mechanical properties.

The chemical resistance tests *viz.* acid, water and xylene show that the alkyds from RSO(P) have better resistance than the one from RSO.

Similar trend with no significant difference was observed while using different free radical catalyst *viz.* BPO and AIBN as a catalyst.

CONCLUSION

The non-traditional oil (RSO) which is employed in present study can be polymerised successfully by using different free radical initiator catalyst and can be used in alkyd preparations for surface coating applications. The free radical initiator used in varying proportions have certain impact on the physical properties of the oil. The film properties of the alkyds prepared from the polymerised oil are better than those of the alkyd from the unpolymerised oil.

From the study, it can be finally concluded that the thermocatalytic polymerisation is more effective than the thermal polymerisation of the oil *i.e.*, the polymerisation carried out using catalyst has the good overall performance properties.

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References

[1] Solomon, D. H. (1977). The Chemistry of Organic Film Formers, R. E. Krieger Pub. Co., New York, p. 78.
[2] Jedlinski, Z. and Uniniski, T. (1951). *Proc. Zensl. Chem.*, **13**, 401.
[3] Barloski, L. and Farbe, V. (1955). *Lack*, **61**, 368.
[4] General Mills Inc., *Netherlands Appl.*, **6**, 441, 299 (1965).
[5] Skellon, J. H. (1950). *J. Chem. Soc.*, 2020.
[6] Lokhande, A. R., Dighe, A. K., Toliwal, S. D. and Raval, D. A. (1993). Research and Industry, **38**, 57–60.
[7] Hui, Y. H. (Ed.) (1996). Baileys Industrial Oil and Fat Products, John Willey and Sons Inc., New York, 5th Edition, **3**, 244–245.
[8] Officials and Tentative Methods of The American Oil Chemists Society, 2nd Ed., Chicago, III (The Gevvend Press, Publishers Champaigh, Illionis) (1960).
[9] Pane, H. F. (1964). Organic Coating Technology, John Willey and Sons Inc., New York, p. 269.

[10] IS 197 (1969). Methods of Sampling and Testing for Varnishes and Lacquers (First revision, 1981) (Bureau of Indian Standards, New Delhi).
[11] Lambourne, R. (Ed.) (1981). Paint and Surface Coatings, Theory and Practice (Ellis Horwood Ltd., Chichester) Chap. 16, pp. 605–619.
[12] Solomon, D. H. (1977). The Chemistry of Organic Film Formers, R. E. Krieger Pub. Co., New York, pp. 60–66.
[13] Wicks, Z. W. Jr., Jones, F. N. and Pappas, S. P. (1992). Organic Coatings: Science and Technology, Vol. 1, John Wiley and Sons Inc., New York, p. 14.
[14] Oldring, P. K. T. (Ed.) (1987). A Manual for Resins for Surface Coatings, Vol. 1, Sita Technology, England, p. 57.
[15] Solomon, D. H. (1977). The Chemistry of Organic Film Formers, R. E. Krieger Pub. Co., New York, p. 65.
[16] Oil and Colour Chemists' Assoc. Australia (Ed.) Surface Coatings, (1983). Vol. 1, Raw Materials and their usage, Chap. 2, pp. 105–108.