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Research Paper :

Polymerised salicornia oil based alkyd resins and its comparision with polymerised Karanja Oil Based Resins

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ABSTRACT

Salicornia and Karanja oils are widely available in India. With the aim to develop value added products from local resources, Salicornia and Karanja oils were polymerized thermally and thermocatalytically using various percentage of benzoyl peroxide (BPO) as a free radical catalyst. During polymerization the free fatty acid content increases as revealed by increasing acid value and unsaturation decreases as indicated by decreasing iodine value. Alkyd resins were prepared from thermally polymerized, thermocatalyticlly polymerized and unpolymerized oils. The mechanical and chemical properties of air-dried and baked films of alkyd resins were studied and compared. The study indicates that the film properties of the alkyds prepared from the catalytically polymerized oils are better than those of the alkyds from the thermally polymerized and unpolymerised oils.It was also observed that the Salicornia oil based alkyds have better properties than Karanja oil based alkyds . Karanja oil based alkyds were not suitable for coating due to its nondrying nature.

Key words : Polymerised salicornia oil, Polymerised karanja oil, Iodine value, Alkyd resins, Thermal and thermocatalytical polymerization

Among the oldest coatings, binders are "drying oils". The drying oils have been used as raw materials for decorative and protective coatings due to their ability to polymerize or dry after they have been applied to surface to form tough, adherent,impervious and abrasion resistance films (1). The film properties of the resins based on drying oils such as linseed oil and soyabean oil are generally satisfactory. However, the rising cost of traditional oils on one hand and the ready cheap availability of nontraditional oils have attracted the attention of researchers (2,3,4). Since the oils by themselves can not meet the desired film properties, a number of ways for oil modification have been proposed (5,6) *viz*., introduction of functional groups like ester (7), amide (8), oxarine (9), urethane (10), esteramide (11) etc. The synthesis of low molecular weight polymers like alkyds, polyepoxies, polyurethane and polyesteramide was carried out by the incorporation of such functional groups in oils (12-15). One of the methods of modifying the oils is polymerization. The thermal and catalytic polymerization of oil is widely reported in literature (16-22).

In the present study, thermal and thermocatalytic polymerization of Salicornia (*Salicornia brachiata*) and Karanja (*Pongomia pinnata*) oils were conducted . The polymerized oils were used to prepare alkyd resins.

MATERIALS AND METHODS

Karanja oil was procured from SPRERI (Sardar Patel Renewable Energy Research Institute, Vallabh Vidyanagar). Salicornia oil was procured from CSMCRI (Central Salt and Marine Chemicals Research Institute, Bhavnagar).All other chemicals used for the study were of laboratory grade .Characteristics of the oils have been shown in Table 1.

Table 1 : Characteristics of oils

Sr. No.	Characteristics	Salicornia	Karanja
1.	Acid Value	9.80	7.8
2.	Saponification Value	230	185
3.	Iodine Value	128.0	81.0
4.	Hydroxyl Value	9.0	6.0
5.	SpecificGravity	0.92	0.919
6.	Refractive Index	1.4642	1.4690

Polymerization of oil:

Oil was placed in a round bottom flask.In thermocatalytic polymerization benzoyl peroxide (% 0.5, 1.0, 1.5 to 2.0) was added as a catalyst. The temperature was raised to 230^{0}C. The samples for checking viscosity and R.I. were taken out after every 1 hr. The Polymerization was carried out for 4 h in all the cases.

Similar procedure was repeated for thermal polymerization but catalyst was not added. Viscosity and refractive index of polymerized oils were determined by gardner bubble viscometer and Abbe's refractometer, respectively. The results of polymerization are shown in Tables 1, 2 and 3.

Preparation of Alkyd Resins:

Oil was heated to 100^0C in a round bottom flask and glycerol was added along with litharge and calcium octoate. The temperature was raised to 220^0 C ± 2^0 C and maintained until the sample gave the clear methanol solubility test. After cooling to 100^0C, phthalicanhydride and maleic anhydride were added in respective batches along with xylene (8 % of total charge as a solvent).It was added to the flask to which Dean and Stark moisture trap was attached.

The temperature was raised to 160^0 C ± 2^0 C and was held at the value for one hour to remove the water of the reaction. After removing xylene, temperature was raised to 240^0 C and kept constant until the acid value came down.

The heating was stopped and the temperature was lowered to 120^0 C. The charge Was thinned with xylene to 60% nonvolatiles .The charge weight of materials for the preparation of alkyds are shown in Table 3.

RESULTS AND DISCUSSION

The results of polymerisation of Salicornia and Karanja oils are reported in Tables 2.1 and 2.2, respectively. It shows that as the time of polymerization increases the viscosity, acid value and R.I.value of the resin increases. The increase in values may be due to the decrease in unsaturation (23) *i.e.* increase in molecular weight. The decrease in iodine value also indicates that amount of unsaturation decreases as time of polymerization increases.

A comparison of viscosities of thermally polymerized and catalytically polymerized oils indicates that as the catalyst content increases the viscosity increases, *i.e.*the molecular weight increases. The degree of reduction in unsaturation depends on amount of unsaturation present in the pure oil.

The characteristics of alkyd resins derived from the catalytically and thermally polymerized oils (Table 3) indicate that the viscosity of resins prepared from thermally polymerized oils is less than the catalytically polymerized oils. It was also observed that the viscosity of resins increases with increase in per cent catalyst content .The rise in catalyst concentration raises the viscosity of the oil due to rise in the molecular weight on account of polymerization (24).

The color of the resins is observed to be darker than their corresponding oil. This may be because of the

Table 2.1 Characteristic of polymerized salicornia oil

Type of polymerization	Catalyst benzoylperoxide (%)	Time of polymerization (hour)	Iodine value	Acid value (mg KOH/gm)	Viscosity	R. I. Value
Thermal	-	1	135	9.8	A	1.4320
polymerization	-	2	134	12.1	A	1.4400
	-	3	132	16.2	B	1.4420
	-	4	130	18.3	B	1.4500
Catalytic	0.5	1	133	11.3	A	1.4670
polymerization	0.5	2	130	16.0	B	1.4978
	0.5	3	128	18.0	B	1.5150
	0.5	4	125	21.3	C	1.5209
	1.0	1	129	13.0	B	1.4980
	1.0	2	126	17.3	C	1.5149
	1.0	3	122	20.0	C	1.5206
	1.0	4	119	25.3	D	1.5213
	1.5	1	124	15.2	C	1.5150
	1.5	2	121	18.5	C	1.5210
	1.5	3	118	22.0	D	1.5215
	1.5	4	117	26.3	E	1.5220
	2.0	1	121	27.0	C	1.5210
	2.0	2	120	29.0	D	1.5217
	2.0	3	119	30.2	D	1.5223
	2.0	4	117	31.0	E	1.5231

Table 2.2 : Characteristics of polymerised Karanja oil

Type of polymerization	Catalyst benzoylperoxide (%)	Time of polymerization (h)	Iodine value	Acid value (mg KOH/g)	Viscosity	R. I. Value
Thermal	-	1	80.1	8.0	A	1.4690
Polymerisation	-	2	79.5	8.3	A	1.4704
	-	3	79.3	8.5	B	1.4786
	-	4	78.0	9.0	B	1.4850
Catalytic	0.5	1	79.3	8.25	A	1.4977
Polymerisation	0.5	2	78.7	8.50	B	1.5135
	0.5	3	78.1	8.76	B	1.5197
	0.5	4	77.8	9.18	C	1.5245
	1.0	1	78.9	8.53	A	1.5280
	1.0	2	77.0	9.14	B	1.5200
	1.0	3	76.2	9.40	C	1.5250
	1.0	4	75.0	10.23	C	1.5295
	1.5	1	76.5	8.80	B	1.5240
	1.5	2	75.1	9.15	C	1.5290
	1.5	3	74.6	9.56	C	1.5345
	1.5	4	73.0	10.44	D	1.5423
	2.0	1	74.2	8.93	B	1.5257
	2.0	2	73.5	9.34	C	1.5298
	2.0	3	71.0	9.98	D	1.5314
	2.0	4	69.2	10.87	D	1.5365

Table 3 : Charge weight for 100 g of Alkyd resin

Alkyd code	Oil (g)	Glycerine (g)	Phthalic anhydride (g)	Maleic anhydride (g)
SA	50	17	33	-
PSA	50	17	33	-
CPSA	50	17	33	-
KA	43	19	37.5	0.5
PKA	43	19	37.5	0.5
CPKA	43	19	37.5	0.5

Table 4 : Characteristic of Alkyd resiens

Resin code	Color Gardner	Viscosity	Acid value	Catalyst (%)
SA	12	C	11.8	-
PSA	13	C	13.2	-
CPSA 1	13	D	14.7	0.5
CPSA 2	14	D	15.3	1.0
CPSA 3	14	E	15.8	1.5
CPSA 4	14	E	16.1	2.0
KA	17	B	20.1	-
PKA	17	B	22.3	-
CPKA 1	18	B	23.5	0.5
CPKA 2	18	C	25.1	1.0
CPKA 3	18	C	26.8	1.5
CPKA 4	18	C	28.7	2.0

(% of Catalyst, 0.5% =1, 1%=2, 1.5%=3, 2.0%=4)

unsaturation part of fatty acid is believed to be attacked by oxygen during processing of resin. The color of the resin also depends on the color of the pure oil. The Salicornia oil based alkyds have lighter color than the others due to lighter color of the pure oil.

Films and their evaluation:

The films of all the resins synthesized were applied and cured separately for air drying and baking .The alkyd resins based on Karanja oil show very slow rate of drying, even after 24 hrs exposure at ambient temperature and 15 mines at 150^{0}C ,there was no surface drying and hence more time was given for drying of resins based on Karanja.The comparison of mechanical and chemical properties of both the types of films is reported in Tables 5 and 6.

In general, for both the Salicornia oil and Karanja oil based alkyd air dried films, the scratch hardness and impact resistance of the alkyds prepared from catalytically polymerized oil are better than those of the thermally polymerized and unpolymerized oil. The impact resistance

Table 5 : Air-dried film properties of Alkyd resins

Resin code	Scratch hardness (gms passes)	Impact resistance (lb inches)	Water resistance (7 – days)	Acid resistance	Alkali resistance
SA	1800	75	B,E	B,F	C
PSA	1800	100	B,E	B,F	C
CPSA 1	2000	125	B	B	B,F
CPSA 2	2200	175	A	B	B,F
CPSA 3	2400	225	A	B	B
CPSA 4	2600	250	A	B	B
KA	600	75	D,E	C,F	C
PKA	800	75	D	C,F	C
CPKA 1	800	100	D	C,E	C
CPKA 2	800	100	C,E	D,E	D
CPKA 3	1000	100	C	D,E	D
CPKA 4	800	100	C	D,E	D

A-Not affected, B-Slight swelling and blistering, C-Swelling and Blistering, D-severe Swelling and blistering, E-Loss of adhesion , F-Loss of gloss

Table 6 : Baked film properties of Alkyd resins

Resin code	Scratch hardness (gms passes)	Impact resistance (lb inches)	Water resistance (7 – days)	Acid resistance	Alkali resistance
SA	1800	150	B	C	B,F
PSA	2000	175	B	B,F	B,F
CPSA 1	2200	200	B	B	B
CPSA 2	2400	250	A	B	B
CPSA 3	1800	275	A	B	B
CPSA 4	1600	175	A	B	B
KA	800	75	C	D,E	D,F
PKA	800	100	C	C,E	D
CPKA 1	1000	100	C	C,E	D
CPKA 2	1200	125	C	C,F	C,E
CPKA 3	1200	125	B,F	C,F	C
CPKA 4	1200	125	B	C,F	C

A-Not affected, B-Slight swelling and blistering, C-Swelling and blistering ,D-Severe Swelling and blistering, E-Loss of adhesion , F-Loss of gloss

and scratch hardness increase with increase in catalyst loading *i.e.* benzoyl peroxide from 0.5 to 2.0%. This might be due to increase in initial molecular weight of the oil (23), which is reflected in the resulting alkyd. The same result has been obtained for baked film properties of both alkyds. But the comparison of mechanical properties of the baked films of Salicornia based alkyd indicates that as the catalyst content increases the values of scratch hardness and impact resistance increases but after some time it decreases. This might be due to highly cross linked molecular structure formed in case of baking systems compared to their corresponding air dried films which increase brittleness of the film after baking (25).

The mechanical properties of the alkyds prepared from thermally polymerized oil are nearly the same as those of the alkyds prepared from unpolymerized oil. This can be attributed to the fact that no significant polymerization occurred in the former sample.

Scratch hardness and impact resistance values of the baked systems have been found to have higher values than their corresponding air-dried counter parts. This can be attributed to the highly cross linked molecular structure formed in case of baking systems compared to their corresponding air dried films. This cross-linked structure enables them to have higher resistance to scratch and impact (25).

The chemical resistance of the various films of alkyds, both air dried and baked have been studied by immersion method, for a specific length of time.

Among all the prepared resins from both the oils, the chemical resistance tests *viz.*, acid, alkali, water and xylene show that the alkyds prepared from thermocatalytically polymerized oil have better resistance than those from thermally polymerised and unpolymerized oil.

The similarity in results of thermally polymerized and unpolymerised oil alkyds supports the fact that no significant polymerization occurred in the formal sample (22).

It was also observed that as the amount of catalyst increases in polymerization the chemical resistance value of the resin films increases. This might be due to increase in molecular weight of the based oils.

However, the method of curing also has a significant effect on these properties of resins.

It was observed that chemical resistance properties of the baked films have better values than their air dried counter parts. Higher crosslink density in the baked films is mainly responsible for superior chemical resistance (25). Further, the baked films have higher number of C-C linkages formed during curing. These are very much resistant to degradation by chemicals and hence these films show improved performance.

The comparison of the chemical resistance properties of the films based on alkyds and Salicornia oil based alkyds indicates that Salicornia oil based alkyds have better values this might be due to presence of higher amount of unsaturation in later which leads higher cross link density *i.e.* better chemical resistance. Karanja oil based resin is notsuitable for coating industries.

Conclusion:

The present study reveals that the catalytically polymerized oil based alkyd resins have better chemical properties than the thermally polymerized and unpolymerized oil based alkyds. The study also indicates that as the amount of catalyst increases rate of polymerization increases which results in better chemical resistance.

The study suggests that between the two nontraditional oils, Salicornia oil has better properties than the Karanja oil. Karanja oil is not suitable for coating application due to its non drying nature. The overall study suggests that non traditional Salicornia oil, which is available in large quantity in INDIA, can be polymerized and Alkyd resins prepared from them can provide a good option for surface coating applications.

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