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Blends of Epoxidized Alkyd Resins Based on Jatropha Oil and the Epoxidized Oil Cured with Aqueous Citric Acid Solution: A Green Technology Approach

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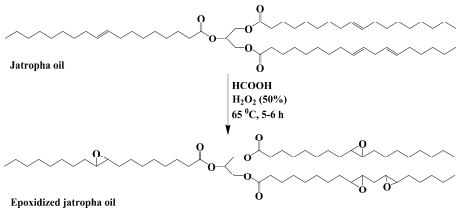
Abstract

➢Alkyd resins were made from jatropha oil using a two-step method that included alcoholysis and polyesterification reactions, using 100% Phthalic Anhydride. To enhance their performance properties, the resins were mixed with different wt% of epoxidized jatropha oil (EJO) and aqueous citric acid, without the need for additional catalysts or solvents. Blending was facilitated via epoxidation of the alkyd resins. The prepared blends were characterized by Fourier transform infrared and NMR (1 H and 13C) spectroscopy studies. It was noted that blending led to significant improvements in properties such as curing time, chemical resistance, scratch hardness, thermal stability, and tensile strength of the alkyd resins. In particular, there was a noticeable increase in tensile strength by 3.18 MPa and thermal stability by 42°C when the blends contained 50% EJO. The results indicate the strong influence of the amount of EJO and citric acid on the performance of the alkyd resins. Additionally, the thermal and mechanical properties of the cured films could be further enhanced through post-curing at 160°C. Overall, the results of this study suggest suitability of these blends in surface coating applications.

Synthesis

➢ **Scheme 1: schematic of Epoxidation of Jatropha Oil**



➢ **Preparation of Alkyd resin from Jatropha Oil:** Jatropha oil based alkyd resins were synthesized by a two-step method. The first step was the alcoholysis process in which monoglyceride of jatropha oil was prepared by reaction of jatropha oil with glycerol in a 1:2 mol ratio at 220 °C using CaO as the catalyst (0.05 wt % with respect to oil). The reaction was continued for 1.5 h, and the formation of the product was confirmed by checking the solubility in methanol at a regular interval of time. The reaction was stopped when the reaction product was completely soluble in methanol at room temperature. In the second step, the esterification reaction was carried out between monoglyceride and phthalic anhydride (0.12 mol) at 225 °C and the reaction was continued until it reached acid value in the range of 10−20.

➢ **Schematic of Epoxidation of Alkyd Resin**

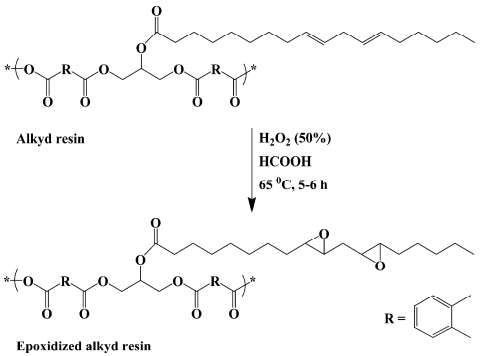
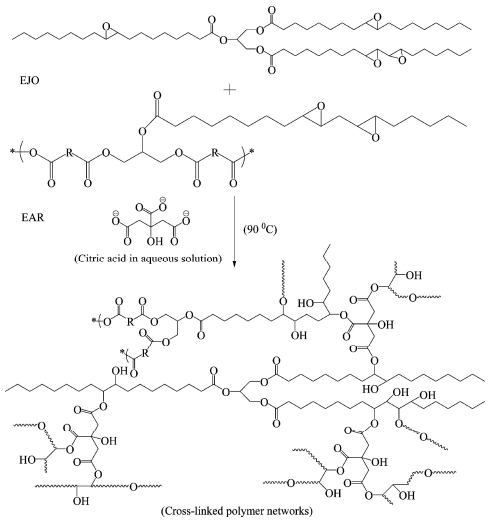


Table 1. Properties of the EJO and EAR

entry	acid value (mg of KOH/g)	hydroxyl value (mg of KOH/g)	iodine value (g I_2/100g)	epoxy equivalent weight (g/eq)	viscosity at 25 °C (Pa·s)	average functionality
JO[a]	2.50	4	105		0.518	
EJO	3.80	37 ± 5	21 ± 2	397 ± 5	0.623	2.40
AR[b]	18.30	18 ± 3	37 ± 2		23.14	
EAR	21.15	26 ± 3	9 ± 2	724 ± 7	23.47	

[a]JO = jatropha oil. [b]AR = alkyd resin.

➢ **Cross-linked polymer networks of EAR and EJO with citric acid**



➢ **Preparation of the Blends**: A concentrated aqueous solution of citric acid was prepared by mixing 3 parts by weight of $C_6H_8O_7 \cdot H_2O$ with 1 part of distilled water, and the mixture was heated to 90 °C. After the citric acid completely dissolved, the solution was poured in a 50 mL round-bottom flask containing the different amounts of EAR and EJO with continuous stirring to generate an emulsion of the said components. In all the cases, the stoichiometric ratio of carboxylic acid equivalents and epoxy equivalents was taken as 1:1. Table 2 summarizes the compositions of the different formulations.

Table 2. Composition (g) of Blends of EAR and ESO[a]

sample particulars[b]	EAR	EJO	$C_6H_8O_7 \cdot H_2O$	water
AJO20	4	0.8	0.796	0.264
AJO30	4	1.2	1.002	0.333
AJO40	4	1.6	1.207	0.401
AJO50	4	2.0	1.412	0.470

[a](epoxy equivalents)/(carboxylic acid equivalents) = 1. [b]The number denotes wt % of EJO with respect to EAR.

Table 3. Performance of the Blends

properties	alkyd	AJO20	AJO30	AJO40	AJO50
curing time (h, at 120 °C)	9.0	8.5	8.0	7.25	6.45
scratch hardness (kg)[a]		2.5	2.7	2.9	3.2
tensile strength (MPa)	0.72	1.63	2.13	2.58	3.18
elongation at break (%)	67	90	102	116	129
gloss (60°)	80	82	83	84	85
adhesion (%)	100	100	100	100	100

[a]Limit of the instrument for scratch hardness was 10.0 kg (highest).

FT-IR and NMR

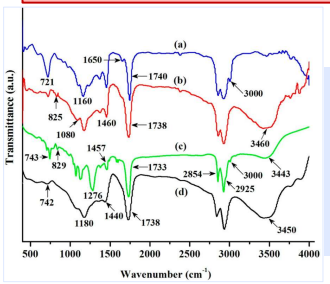


Figure 1:FT-IR spectra of (a) jatropha oil, (b) EJO, (c) EAR, and (d) AJO30

➢Figure 1(a): C=O stretching vibration: 1740 cm−1
C-O-C stretching vibration of ester group: 1160 cm−1
alkene double bond: 1650 cm−1
➢Figure 1(b): the oxirane ring was introduced : 825 cm−1
the formation of by-product hydroxyl group in EJO: 3460 cm−1
➢Figure 1(c): epoxidation of double bonds of alkyd resins: 829 cm−1
C=O stretching vibration: 1733 cm−1
➢Figure 1(d): C=O stretching vibration: 1738 cm−1
C-O-C symmetric bending vibration: 1180 cm−1

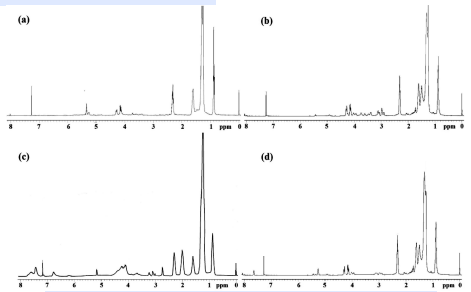


Figure 2: 1 H NMR spectra of (a) jatropha oil (JO), (b) EJO, (c) EAR, and (d) AJO30

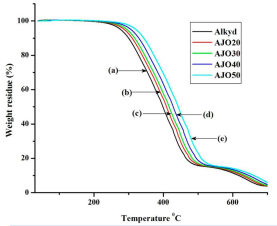


Figure 3. TGA curves of (a) alkyd resin, (b) AJO20, (c) AJO30, (d) AJO40, and (e) AJO50

Table 4. Thermal Degradation Data of the Alkyd Resin and the Blends

entry	sample	T_i (°C)[a]	decomposition temperature (T_d) at different wt losses (°C) 5%	25%	50%	wt residue at 700 °C (%)
1	alkyd resin	280	278	341	398	3.88
2	AJO20	291	287	352	409	3.91
3	AJO30	299	295	359	416	4.15
4	AJO40	310	307	371	428	4.83
5	AJO50	322	321	385	442	5.04

[a]T_i = initial degradation temperature.

Conclusions

➢Jatropha oil based alkyd resins were cured by blending with completely biobased polymer networks of EJO and aqueous citric acid solution. Epoxidation of the alkyd resin facilitated the cross-linking reactions. The curing time, thermal stability, and mechanical properties of the alkyd resins improved significantly upon blending. The curing time of the alkyd resins was reduced to 6.45 h, and the thermal stability and tensile strength were increased by 42 °C and 3.18 MPa, respectively. The technique reported here offers a number of advantages, including environmentally friendly, low cost, easy performance, solvent free/catalyst-free, and biobased content, opening a number of opportunities in the paint industries. Overall, the results of the study suggest a high potential for these blends with high biobased content to be used for surface coatings. This is a green technology approach. Moreover, the thermal and mechanical properties of the films were observed to be improved further on postcuring at 160 °C. The molecular rearrangements produced by thermally activated transesterification reactions of −OH groups generated in the ring opening polymerization reaction with residual −COOH groups resulted in increased crosslinking density of the polymer networks.