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Opinion Article

Enhancing the quality of alkyd resins using methyl esters of rubber seed oil

Esther U Ikhuoria[aΦ], Aireguamen I Aigbodion[b] and Felix E Okieimen[a]

[a]*Industrial Agriculture Products Research Laboratory, Department of Chemistry, University of Benin, Benin City, Nigeria.*
[b]*End-use Division, Rubber Research Institute of Nigeria, Benin City, Nigeria*

Abstract

Purpose: *Alkyd resins constitute a very high proportion of conventional binders used in surface coatings. In order to enhance the quality of these alkyd resins methyl esters of rubber seed oil (MERSO) were used in the preparation of the resins.*
Methods: *MERSO were obtained by in-situ alcoholysis of rubber seed. Alkyd resins having oil lengths of 45, 50 and 55% were prepared with MERSO, phthalic anhydride and glycerol using alcoholysis method. Lead (II) oxide and xylene were used as catalyst and refluxing solvent, respectively. The physico-chemical characteristics of the MERSO and the resins obtained were compared with the corresponding value of rubber seed oil (RSO) and its alkyd resins. Chemical resistance of the alkyd resins was also determined.*
Results: *The acid value of the finished alkyd resins depends on the rate and extent of esterification. Iodine value of the alkyd shows that the level of unsaturation depends on the oil length of the resins. The free fatty acid (FFA) value (1.99%) of the MERSO was much lower than that of the RSO (9.54%). This supports the choice of methyl ester as a preferred alternative to the use of the raw RSO in alkyd resin preparation. All the alkyd samples were fairly resistant to brine, acid and water but poorly resistant to alkali. However, the MERSO alkyds were observed to have a better resistance than the RSO alkyd resins. The scratch/gouge pencil hardness shows that the hardness of the alkyd films decreases with the oil length.*

Key words: *Alkyd resins, rubber seed oil, methyl ester.*

ΦTo whom correspondence should be addressed: *E-mail*: esyikhuoria@yahoo.com

Introduction

Alkyd resins are products of poly-condensation reaction between polybasic acid and polyhydric alcohol modified with fatty acid or drying oil. Oil modified alkyd resins constitute a major group of resins used as binders in surface coatings. It is estimated that alkyd resins contribute about 70% to the conventional binders used in surface coatings today[1]. The popularity of alkyd resins as vehicle for coatings is largely due to their unique properties such as film hardness, durability gloss and gloss retention, resistance to abrasion, etc. impacted on them through modification with drying oils[2]. The oils that are mostly employed for alkyd resin synthesis are linseed, soybean, castor and tall oils[3,4,5]. These oils are largely imported to Nigeria for the formulation of coatings for metal cans used in packing of beverages, drugs, food, etc. However, drying oils are available locally, which have remained untapped. These include rubber seed oil, soybean oil, walnut oil and tobacco oil[6]. Rubber seed is obtained in high yield as a by-product of *Hevea brasiliensis* cultivated primarily for its latex. [7,8,] It is reported to be abundant in Nigeria and is found to contain 42% oil[9]. However, research has shown it to be a rich source of oil that is comparable in quality to dry oils commonly used in surface coatings[10,11,12].

The industrial value of vegetable oil generally depends of its constituent fatty acids and the ease with which it can be modified or combined with other chemicals[13]. Several physical and chemical modifications of the oils to enhance their initial quality have been evolved over the years[14]. Examples of such modification techniques include acrylation[15], catalytic and thermocatalytic polymerization[16] interesterification[17], phosph-orrylation and expoxidation[18]. Chemical transformation of vegetable oil to fatty acid alkyl esters called *transesterification* or *alcoholysis* is one of the methods of modifying the quality of vegetable oils.

Raw vegetable oils are composed of glycerol, esters of fatty acids and various amounts of solubilised impurities such as pigments, vitamins, sterols, phospholipids etc, which may compromise the quality of the finished alkyd resins. Esters of vegetable oils would preclude some of the undesirable effects. This study reports on the in-situ alcoholysis of rubber seed oil (RSO), preparation and characterisation of alkyd resins the RSO and the methyl esters of rubber seed oil (MERSO) aimed at enhancing alkyl resins.

Materials and Methods

Materials

Rubber seeds were collected from the Rubber Research Institute of Nigeria, Iyanomon, Benin City. Laboratory grade phthalic anhydride (PA), glycerol (GLY) and xylene were obtained from BDH, England.

Preparation of rubber seed oil (RSO)

Rubber seeds were air dried in the oven at 50 °C for 72 hr and shelled to obtain the kernels which were then blended to obtain rubber seed meal. Rubber seed oil (RSO) was then extracted from the meal with n-hexane using a soxhlet apparatus.

Preparation of methyl rubber seed oil (MERSO)

The methyl esters of RSO (MERSO) were prepared using the *in-situ* alcoholysis method[4]. In this method, the rubber seed meal was macerated with methanol for 30 min and the slurry obtained was magnetically stirred under reflux for 3 hr at room temperature (30 °C). At the end of the reaction, the mixture was filtered under vacuum, and the residue washed with 200 ml methanol and air-dried overnight at room temperature. The residue obtained was re-extracted in a soxhlet apparatus with n-hexane to obtain the oil fraction remaining in

the residue. The percentage of the dissolved oil in methanol was calculated.

To the filtrate obtained from the *in-situ* alcoholysis was added 100 ml of water and the solution re-extracted with 50 ml n-hexane three times. The combined extracts were washed with water, dried over sodium sulphate and evaporated to give the esterified product. The ester content of the esterified RSO was determined by column chromatography[19].

Preparation of alkyd resins

Six different alkyds were prepared with RSO, MERSO, glycerol, phthalic anhydride using lead (II) oxide as catalyst using the formula in Table 1. The preparation was carried out in a three necked round bottom flask fitted with a motorised stirrer, a Dean-stark trap fitted with water-cooled condenser and a nitrogen inlet tube at a temperature of 230 – 250 ºC. Xylene was employed as the azeotropic solvent[13]. Two stages were involved.

Stage I (*Alcoholysis):* At this stage, the monoglyceride was first prepared by reacting the glycerol with the methyl esters of rubber seed oil (MERSO) at a temperature of 230 to 250 ºC. Alcoholysis was completed when the solubility test in methanol was positive; one part of the reaction mass being soluble in three parts of methanol. The reaction mixture was cooled to 140 ºC.

Stage 2: This stage began with the addition of phthalic anhydride. The temperature was quickly raised to about 230 ºC and maintained at a range of 230 – 250 ºC. Condensed water of condensation was drained into a Dean-Stark trap. The reaction was monitored by periodic determination of the acid value of the mixture until acid value dropped to 10.

Physico-chemical characterisation of alkyd resin

The physico-chemical properties of the alkyd resin samples (colour, specific gravity, refractive index, acid value, free fatty acid, saponification value, iodine value and non volatile matter) were determined according to ASTM standard methods[20,21,22,23].

Performance characteristics of the alkyd resin

The alkyd films were oven-baked at 100 ºC for 1 hr and the resistance of the alkyd films in different service media was determined using a standard method[24]. Pencil hardness of the dried films was also determined [25].

Results and Discussion

The results of the alcoholysis of RSO under various pretreatment conditions are shown in

Table 1: Recipe of the alkyds prepared with crude rubber seed oil (I – III) and its methyl ester derivatives (IV – VI)

	Alkyds					
Recipe	I	II	III	IV	V	VI
Rubber seed oil (RSO) (g)	136.18	151.13	164.87	-	-	-
Phthalic anhydride (PA) (g)	101.04	91.28	83.31	84.46	77.06	69.33
Glycerol (GLY) (g)	62.78	57.60	51.82	52.58	47.95	43.13
Methyl ester (ME) (g)	-	-	-	112.73	124.92	137.60
Oil length (%)	45	50	55	45	50	55
Alkyd constant	1.00	1.00	1.00	1.00	1.00	1.01

Table 2. Methyl esters yield from the maceration process was higher than the other pretreatment conditions. Thus the *in-situ* alcoholysis involving maceration process was generally applied in the production of the methyl esters used in the preparation of the alkyds.

Table 2: Alcoholysis of rubber seed oil

Pretreatment	Ester content (%)	FFA %
-	30.34	0.997
Conditioning	32.90	1.423
Maceration	46.93	1.918

Table 3 shows the physico-chemical properties of RSO and its methyl esters (MERSO) derivative. The acid value of the MERSO is observed to be much lower than that of the crude RSO. This shows that in-situ alcoholysis of RSO in the production of the methyl esters causes less hydrolysis compared to extraction with n-hexane. Since methyl esters of very low free fatty-acid (FFA) is obtained by in-situ alcoholysis, this technique is considered a better method of obtaining rubber seed oil (RSO) derivative suitable in alkyd production as oil of high FFA is undesirable in alkyd formulation. Their saponification values of MERSO and RSO are similar but the iodine value of the MERSO is relatively lower than that of the RSO. This indicates lower level of unsaturation for the MERSO than the RSO.

Table 3: Physico-chemical properties of rubber seed oil and the methyl ester of rubber seed oil (RSO)

Properties	Crude RSO	Methyl esters of RSO
Colour	Light brown	Yellow
Specific gravity	0.93	0.924
Refractive Index	1.4777	1.4648
Acid value	19.18	3.81
Free fatty acid (as oleic)	9.54	1.92
Iodine value	136.2	120.52
Saponification value	181.14	183.04

The physico-chemical properties of the finished alkyds from RSO and its methyl esters are shown in Table 4. All the alkyd samples were processed to acid value below 15. The saponification values of the finished alkyd were found to be higher than that of crude RSO as they are essentially polyesters. All the alkyd resins produced had colour intensity that increased with increasing oil length of the resins. The iodine value of the RSO alkyds (I – III) and the methyl ester alkyds (IV – VI) were observed to have the same trend. These values increased with increase in the oil length of the resins indicating that the level of unsaturation increases as the quantity of the oil and methyl ester used in the resins increases. The hardness of the alkyd films,

Table 4: Physico-chemical properties of the finished alkyds prepared with crude rubber seed oil (RSO) (I – III) and the methyl ester of rubber seed oil (IV – VI)

	Alkyds					
Properties	I	II	III	IV	V	VI
Colour	Brown	Brown	Dark brown	Brown	Brown	Dark brown
Specific Gravity	0.945	0.938	0.933	0.943	0.940	0.938
Acid value	2.41	1.11	0.74	12.70	13.80	14.45
Saponification value	354.10	326.29	322.60	291.95	293.02	299.07
Iodine value	65.64	72.21	83.30	66.30	71.69	80.24
Refractive index	1.4777	1.4762	1.4768	1.5050	1.5018	1.5002
Solid Content (%)	62	60	64	52	56	51
Scratch	3H	3H	HB	HB	B	2B
Gouge	4H	4H	H	H	HB	B

Table 5: Chemical resistance of the alkyd resin films

Alkyd samples	Media			
	Distilled water	0.9M NaCl	0.1M H_2SO_4	0.1M KOH
I	3	1	2	4
II	2	1	2	4
III	3	1	2	4
IV	2	1	1	3
V	2	1	1	2
VI	2	1	1	2

1= No effect, 2 = whitening of film, 3 = shrinkage of film, 4 = shortening of film

as indicated by the pencil hardness, ranged from 3H/4H (Scratch/gouge hardness) for samples I and II to HB/H for sample III for the alkyds modified with RSO. This indicates that the hardness of the film decreases with the oil length. For the alkyd samples modified with the MERSO, scratch/gouge pencil hardness are HB/H, B/HB and B/2B for samples IV, V and VI, respectively. This trend also indicates decrease in hardness as the oil length increases.

The chemical resistance of the alkyd resins to various solvent media are shown in Table 5. From the results, it can be seen that all the alkyd samples (I – VI) are unaffected by the salt medium. The RSO alkyd samples (I – III) have the same resistance to acid, base and salt, despite the difference in the oil length of the alkyds. However, sample II was less susceptible to water than other RSO alkyds. MERSO alkyds (IV – VI) have the same resistance to water, salt and acid, but sample IV is less resistant to basic solution than samples V and VI. In general, all the MERSO alkyds (IV – VI) have better resistance to the various solvent media than the RSO alkyd samples (I – III).

Conclusion

Raw rubber seed oil (RSO) and its methyl esters (MERSO) derivative have been used in the preparation of alkyd resins. MERSO seems to be more promising in the production of alkyd resins than the raw rubber seed oil as indicated by its physico-chemical properties and those of the finished alkyds including their chemical resistance. The high chemical resistance exhibited by these alkyd resins shows that they are promising in formulating coatings like nitrocellulose lacquers for metal cans used in packaging foods, beverages and drugs. Further studies are on-going on the possibility of blending these alkyd resins with other film formers like phenol-formaldehyde resin to enhance their performance as binders.

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