

*Full Length Research Paper*

# Synthesis and characterization of styrenated rubber seed oil alkyd

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Rubber seed oil alkyd was post-polymerized with styrene monomer at ratios of 1:2, 1:4, 1:6, 1:8, and 1:10 at 100°C for 3 h (samples i - v) and 6 h (samples A - B), to obtain two sets of styrenated alkyds. The styrenated alkyds and the rubber seed oil alkyd were all characterized and evaluated by standard methods, for their physico-chemical properties, drying schedule and chemical resistance. All the resins showed good properties. However, the styrenated alkyds gave a faster drying time, even in the absence of a drier. Unlike the unstyrenated alkyd which is only resistance to water, brine and acidic media, the styrenated alkyds were also resistant to alkali. The styrenated alkyds prepared over a period of 6 h gave shorter drying time than those prepared in 3 h, irrespective of the alkyd - styrene ratios.

**Key words:** Synthesis copolymerization, coating, classification, modification.

## INTRODUCTION

In the surface coating industries, oil-modified polyesters or alkyds dominates as the most widely used solvent-borne binder (Bognar et al., 1991). These low molecular weight esters which are products of polycondensation reaction of polyol, diacid, and mono-acid (oils or fats) are very flexible and versatile and have been found to be com-compatible with other polymer systems (Anthawale et al., 2000). Also, attempt on waterborne alkyd, which is as a result of current trends in the industry to meet up with environmental regulation and government legislature has been successful according to several report (Aigbodion et al., 2003a, 2003b; Duta et al., 2004; Makarewick, 1996).

Despite the advantages of alkyd such as good adhesion, film flexibility, colour, gloss, broader temperature range application, etc, there are some draw-backs, for instance, its susceptibility to alkali as a result of the splitting of the ester linkages by hydrolysis, this reaction is very typical of esters. In addition, compared to other synthetic resin, alkyd resin is relatively slow-drying. However, it can be modified by several physical (blending)

and chemical (co-polymerisation) processes which will lead to products that could meet up with wide range of applications. This is borne out of the fact that it is very compatible with a variety of other polymers, such as, acrylic, nitrocellulose, phenol, epoxy resin, etc, where the technical features of both polymers are combined to give products with improved properties that meet up with a wide of end utilization (Wang et al., 2002; Aigbodion and Okieimen, 1996).

Rubber seed oil has been reported to be suitable for both alkyd and water-borne alkyd resin Okieimen et al., 2002; Ikhuoria et al., 2005). The oil which is obtained from the seed of rubber tree is presently not exploited industrially in Nigeria where there are large expanse of land of rubber plantation scattered around the length and breadth of the southern part of the country, irrespective of its reported potentials, such as alkyd synthesis, epoxy-dation of the oil, production of metal soaps and biodiesel etc, (Okieimen and Eboaye, 1992; Ikhuoria et al., 2002). These rubber estates are capable of providing about 13,000 ton of rubber seed oil annually (Nwakwo et al., 1986). The oil is unsaturated and comprised mainly of oleic, linoleic and linolenic acids. The function of oils and fats in alkyd is to provide the site for free radical cross-linking, which is the mechanism of drying of oil-modified polyesters (Stevens, 1999). However, alkyds dry within few to several hours, but with certain modification, this

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**Table 1.** Fatty acid composition of rubber seed oil.

Fatty acid	%
<b>Saturated</b>	
C16:0 Palmitic acid	17.51
C18:0 Stearic acid	4.82
Total	22.33
<b>Unsaturated</b>	
C18:1 Oleic acid	25.33
C18:2 Linoleic acid	37.50
C18:3 Linolenic acid	14.21
Total	77.04
Others	0.63

**Table 2.** Preparation of styrenated alkyds.

Styrene:alkyd ratio		Reaction time (h)	Temperature (°C)
1 : 2	I	3	100
1 : 4	II	3	100
1 : 6	III	3	100
1 : 8	IV	3	100
1 :10	V	3	100
1 : 2	A	6	100
1 : 4	B	6	100
1 : 6	C	6	100
1 : 8	D	6	100
1 :10	E	6	100

duration could be reduced, thus further improving its drying properties.

In earlier studies, we have reported the syntheses of chlorinated rubber seed oil alkyd and maleic anhydride modified alkyd, both which offered flame retardancy and water dispersibility respectively (Bentley and Turner, 1998). However, these modification did not improve the drying time neither could it help to mask the ester linkages from undergoing hydrolytic splitting in alkali medium, hence, the need to improve rubber seed oil alkyd in this regards was borne, especially as styrene is known to give rigid polymers (Morrison and Boyd, 1992), that are used for quick drying enamels and primers. This present study seeks to investigate the effect of styrene modification on the properties of rubber seed oil alkyd as it is known that polystyrene is very resistant to the action of alkalis both in alcoholic and non-aqueous media.

## METHODS

Rubber seed oil (RSO) was extracted by solvent method from rubber seed obtained from Rubber research institute of Nigeria, Benin City, Nigeria. The fatty acid composition of the oil is depicted

in Table 1. Analytical grade styrene, phthalic anhydride, glycerol, litharge, xylene, benzoyl peroxide, cobalt and calcium naphthalates (driers) obtained from Sigma-Aldrich were used. The oil was characterized using standard methods.

## Alkyd preparation

Medium oil length RSO alkyd was prepared according to the mono-glyceride method as described in earlier report (Ikhuoria and Aigbodion, 2005, 2006) in a three necked flask fitted with Dean and Stark under reflux and azeotropic condition. The alkyd was thinned with xylene, appropriate amount of driers were added and then applied as thin films on glass panels and air-dried. The alkyd was evaluated for its physico-chemical and coating properties using ASTM methods.

## Styrenation

The styrenated alkyds were prepared by post co-polymerization of the alkyd resin. The alkyds were with-drawn into a 500 ml quick-fit flask and heated in the presence of an initiator, benzoyl peroxide, under reflux at 100°C at ratios 1:2, 1:4, 1:6, 1:8, and 1:10, for 3 h (samples i - v) and 6 h (samples A - B) respectively as shown in Table 2. The polymer was thinned with xylene and applied as thin films on glass panel and air dried without the aid of a drier. The styrenated alkyds obtained were characterized and evaluated for their coating properties, such as, drying and chemical resistance. The reaction scheme is shown in Figures 1 and 2.

## FT-IR Spectroscopic measurement

The infra red spectroscopy of the rubber seed oil (RSO), its alkyds and styrenated alkyds, were recorded using KBr cell on a Nicolet Avatar 330 FT-IR spectrometer.

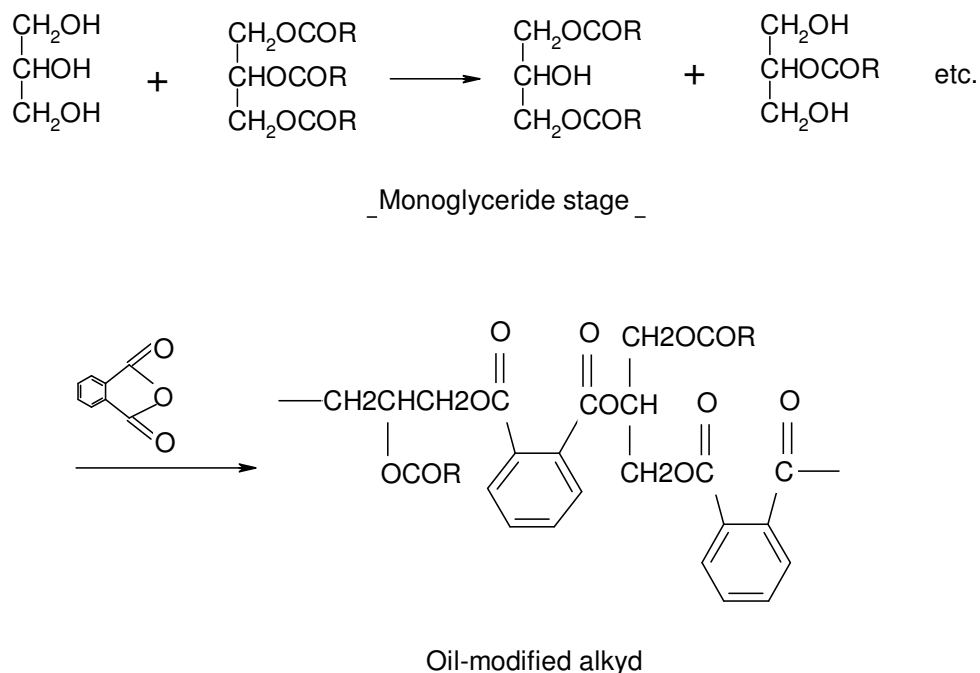
## RESULTS AND DISCUSSION

### Rubber seed oil (RSO)

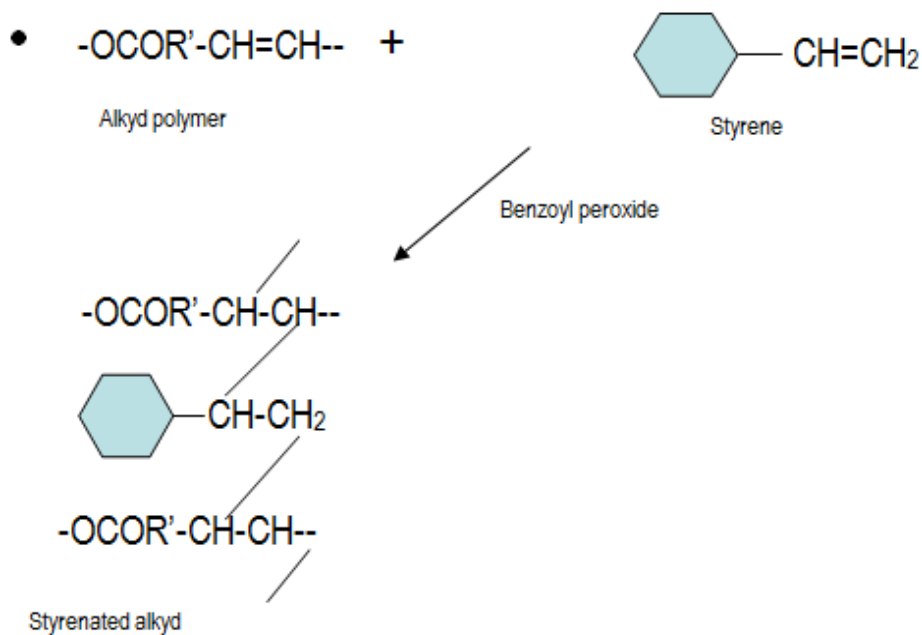
The fatty acid composition of the golden yellow rubber seed oil is depicted in Table 1. The three major unsaturated fatty acids are also revealed, with linoleic fatty acid higher than the others. This high level of unsaturation is also supported by the iodine value of the oil which is 139.95  $\text{gl}_2/100 \text{ g}$  in Table 3. This implies sufficient double bond site to facilitate free radical crosslinking.

### Alkyd resin

Their physico-chemical properties are shown in Table 3 and are quite comparable to those of the alkyd, except their iodine values. The brownish coloured RSO alkyd shows characteristic properties typical of alkyds as reported in our earlier studies ((Athawale et al., 2000; Dutta et al., 2004; Ikhuoria and Aigbodion, 2005) as shown in Table 3. The styrenated alkyds obtained i - v and A - E were viscous and light brown in colour. The iodine value was observed to increase as the level of substitution increased instead of decreasing. This could be due to the



**Figure 1.** Reaction scheme for the synthesis of oil modified alkyd resins.



**Figure 2.** Reaction scheme for styrenated alkyd.

double bonds in the styrene structure. The set with a higher reaction time of 6 hours (A - E) were also observed to have a lower iodine value than those with shorter reaction time of 3 h (i - v). This could be due to the consumption of the double bonds as polymerization progressed.

### Performance characteristics of the resins

The performance characteristics of the alkyd and the styrenated alkyd in terms of drying schedule and chemical resistance are shown in Table 4. The alkyd were set-to-touch at about 30 min, surface dried at 3 h

**Table 3.** Physico-chemical properties of the oil and the resins.

Property	RSO	Alkyd	Styrenated alkyds									
			I	II	III	IV	V	A	B	C	D	E
			LB	LB	LB	LB	LB	LB	LB	LB	LB	LB
SG (30 °C)	0.921	0.931	0.931	0.933	0.932	0.933	0.938	0.932	0.934	0.934	0.933	0.932
AV (mg KOH/g)	22.05	11.89	11.93	11.94	12.01	12.01	12.04	12.01	12.00	12.11	12.18	12.18
IV (g I <sub>2</sub> /100 g)	139.95	142.06	148.05	147.00	149.90	148.21	148.75	136.11	138.06	140.17	141.00	142.10
SV (mg KOH/g)	189.05	202.12	209.08	211.00	210.83	211.07	211.14	205.60	206.11	206.68	211.50	212.71

IV = Iodine value; GY = golden yellow; B = brownish; LB = light brown.

**Table 4.** The performance characteristics of RSO alkyd and the styrenated alkyd samples.

Sample*	Drying schedule			Chemical resistance (Media)			
	Set-to-touch (min)	Surface dry (h)	Dry through (h)	0.1M H <sub>2</sub> SO <sub>4</sub>	0.1 M NaOH	NaCl (5% Solution)	Water (Cold)
Alkyd	30	3	12	1	2	1	1
I	>5	11/2	21/2	1	1	1	1
II	>5	11/2	21/2	1	1	1	1
III	>5	11/2	21/2	1	1	1	1
IV	>5	11/2	21/2	1	1	1	1
V	>5	11/2	21/2	1	1	1	1
A	>5	11/2	21/2	1	1	1	1
B	>5	11/2	21/2	1	1	1	1
C	>5	11/2	21/2	1	1	1	1
D	>5	11/2	21/2	1	1	1	1
E	>5	11/2	21/2	1	1	1	1

\*See Table 2 for the preparation of the samples.

and were completely dried at about 12 h later. Their chemical resistance showed that they are resistant to brine, water and acid, but susceptible to alkali, as they were removed in alkali medium. Their drying schedule of the styrenated alkyd as revealed in Table 4 clearly shows an improvement from that of the pure alkyd, as they were set-to-touch in about 5 min, surface dry in one and a half hours. They were all completely dried in about two and half hours. This drying time was irrespective of the amount of styrene used in the co-polymerization.

The chemical resistance of the styrenated alkyds is similar and also shows an improvement on the pure alkyd. Unlike the unstyrenated alkyd which was only resistant to brine, water and acid, the styrenated alkyds also showed resistance to alkali. This therefore means that styrenation assisted in masking the ester linkages of the polyester from alkali hydrolysis.

### Spectral elucidation

The spectral of rubber seed oil, alkyd, and styrenated alkyd as shown in Figure 3 depicts the characteristic listed in Table 5. The absorption band in the region of

1850 - 1650 cm<sup>-1</sup>, which corresponds to carbonyl group, is of particular interest. From the FT-IR spectral, this region shows typical absorption of carbonyl group, which is sharp and strong, in RSO and alkyd. However, for the styrenated alkyd, the peak is not broad and sharp, but rather, it is almost withdrawn or shortened. This could explain the reason why the styrenated alkyds are not removed in alkali medium, because the polystyrene moiety tend to shield the carbonyl group from hydrolysis of the strongly nucleophilic base, as it is known that the hydroxides attacks the carbonyl carbon to effect cleavage of the bond between the oxygen and the acyl group (Morrison and Boyd, 1992). The styrenated alkyd also has a C - H out of plane bending absorption at 699 nm.

### Conclusion

Oil modified polyester or alkyd resin remains the work-horse of many coating systems, especially in the automotive industry. This is due to some of its short comings such as poor chemical resistance and relatively longer drying time. From the results of this study, post-polymerisation of alkyd with styrene has further improved

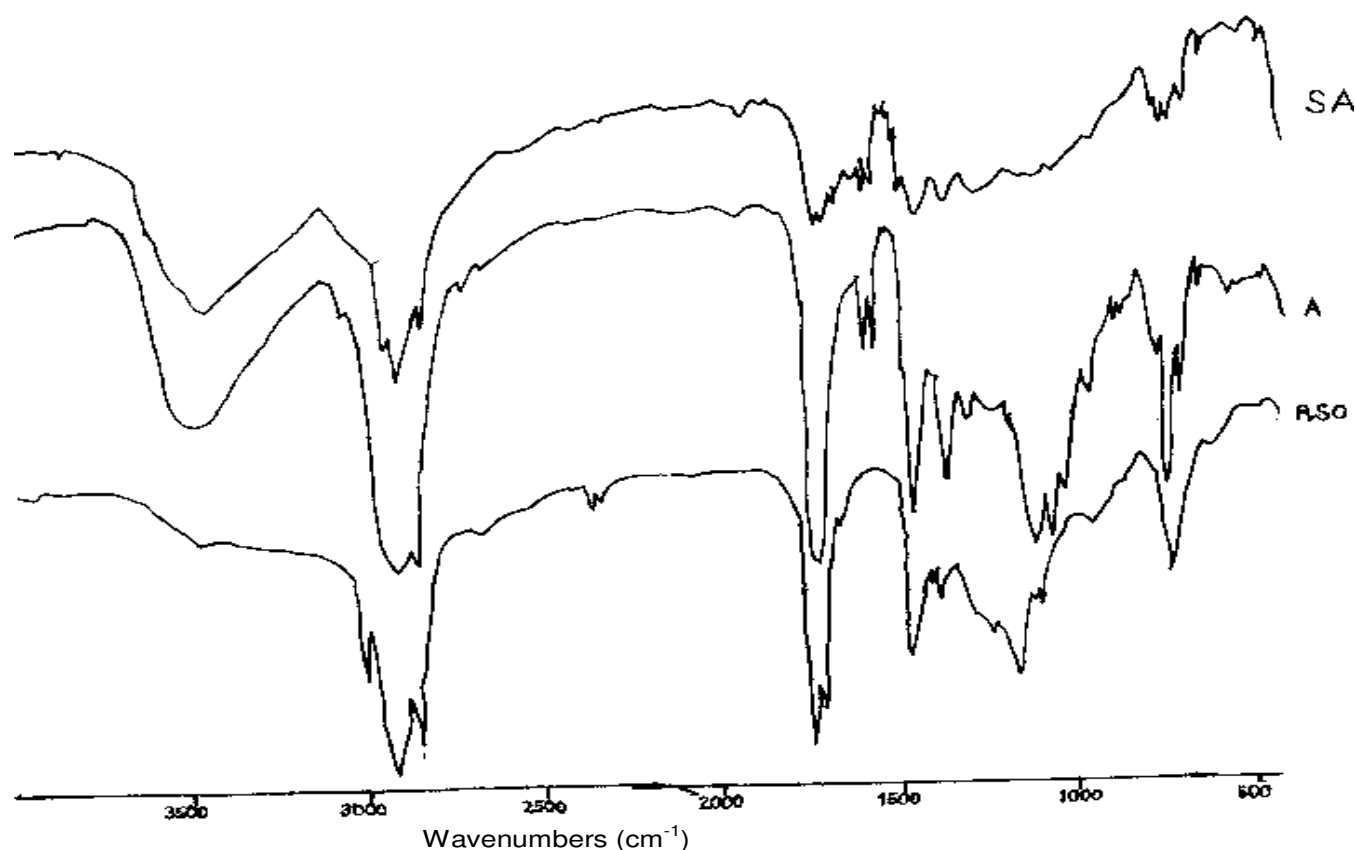


Figure 3. FT-IR of rubber seed oil (RSO), alkyd (A), and styrenated alkyd (SA).

Table 5. FT-IR measurement data.

Assigned group	RSO alkyd	Styrenated alkyd
	Wave numbers (cm <sup>-1</sup> )	Wave numbers (cm <sup>-1</sup> )
OH	3465	3448
-CH <sub>2</sub> -	2923, 2854	2954, 2924, 2854
O-C=O	1727	1735, 1720
Aromatic ring		1491
-CH <sub>2</sub> -	1460	1459
-CH <sub>3</sub>	1377	1377
C-O	1284, 1123	1128
C-H out of plane		699

these properties. The resultant styrenated alkyd, dried much faster than pure alkyd (even in the absence of driers), and possessed better chemical resistance. This study also showed that longer reaction time gave a faster drying resin.

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