Kinetic Studies in the Synthesis of Alkyd Resin Using Crude *Azadirachta indica* and Soybean Seed Oils as Modifiers

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ABSTRACT

Medium oil alkyds of 50% oil length, modified with crude neem and soybean seed oils were synthesized using the alcoholysis method with phthalic anhydride and glycerol. Lead oxide (II) and xylene were used as catalyst and azeotropic solvent, respectively. The kinetics of the reaction was monitored by the determination of the acid value of aliquots of the reaction mixtures at 30-min intervals. The initial rate of reaction followed the second order kinetics and thereafter deviations were observed. It was observed that the initial rate of decrease in acid value was more rapid for the soybean medium alkyd than for the neem medium oil alkyd. The second order rate constant for soybean medium oil alkyd was 11.3×10^{-4} g (mg KOH)$^{-1}$ min^{-1} and that of the neem seed was 2.0×10^{-4} g (mg KOH)$^{-1}$ min^{-1} . The gel time for the neem medium oil alkyd was found to be two and a half times slower than that of soybean medium oil alkyd; thus giving preference for the synthesis of the soybean medium oil alkyd over that of neem medium oil alkyd.

INTRODUCTION

Alkyd resins are a complex network of polyesters, prepared through the reaction of fatty acids (vegetable oils such as soy oil, linseed oil, tall oil and castor), polyols (i.e., glycerol, pentaerythritol, trimethylopropane, ethylene glycol), and a dibasic acid or anhydride, such as phthalic anhydride, maleic anhydride, or iso-phthalic acid (Sypros 2002). Their main difference with other polyester resins is that they contain unsaturated fatty acid side groups.

Apart from the resins, alkyd paints contain a suitable solvent (xylene or mineral spirits), a set of driers, such as various metal naphthenates (especially those of Co, Pb, Mn, Zr, or Ca), and pigments as well as other additives, which improve performance (Weiss 1987). In the presence of atmospheric oxygen, alkyd paints dry (or more accurately harden) through a complex free radical cross-linking reaction of the side-chain fatty acid double bonds (Hofland 1995). The role of the drier is to catalyse the decomposition of the hydroperoxides, initially formed by the addition of oxygen to the double bond, into free radicals. The rapidity of the drying process as well as the hardness of the final coating depends on the amount of oil fatty acids incorporated into the alkyd resins (the oil length) and their degree of unsaturation. Long-oil alkyds contain 60% fatty acid by weight, medium-oil, 40-60%; and short-oil, less than 40%. Alkyd resins that contain only saturated fatty acids are used mainly as plasticizers or in oven-dried coatings (Prane 1986).

Oil-modified alkyd resins constitute a major group of resins used as binders in the coatings industry and is estimated that alkyd resins contribute about 70% to the conventional binders being used in the surface coating (Bajpai and Seth 2000). In spite of the level of development in alkyd resins technology, most modern alkyd resins are still been modified with naturally occurring fats and oils, which could be from some seed plants or from animal sources. Alkyd resins produced this way are referred to as oil-modified alkyd resins. Usually, the natural oil in the oil modified alkyds reacts with atmospheric oxygen in what is termed oxidative drying of the oil component leading to the formation of a network of polymers cross-linked through the C=C bond. The film formed through oxidative drying of the oil shows improvement in properties like drying time, hardness or water resistance (Akintayo 2004).

Alkyd resin synthesis is a polycondensation reaction and the most widely used method is alcoholysis wherein the triglyceride is first reacted with the polyol at a reaction temperature of between 230-250°C to generate the monoglyceride. This is then reacted with phthalic anhydride and water is removed in the process. The aim of this work was to carry out preliminary kinetic studies in the synthesis of alkyd resins using crude neem seed oil (a lesser known oil) and crude soybean oil as modifiers. We have been interested in unconventional seeds and seed oils for possible nutritional or industrial applications (Oderinde and Ajayi 2000; Ajayi *et al.* 2004).

MATERIALS AND METHODS

Sample collection and extraction

The seeds of neem and soybean were purchased from local markets in Ibadan, Oyo State, Nigeria. The seeds were shelled by cracking to remove the kernels inside. The kernels were then ground to powder in a Hammer mill and stored in an air-tight sample bottle in a refrigerator (4°C) until needed for analysis. Oils were exhaustively extracted from the seeds with a Soxhlet extractor using hexane (BDH) (Ajayi 2008). The solvent was removed completely and the oils obtained were used for this study.

Alcoholysis

The alcoholysis method of Orthmer (1963) was followed in the preparation of medium (50% oil length) oil alkyds using crude neem and soybean oils, glycerol and phthalic acid; PbO [lead (II) oxide] was used as catalyst. Using the recipe in **Table 1**, the medium oil alkyd preparation was carried out in a three-necked round bottom flask on a magnetic hot plate with plastic-coated magnetic stirrer inserted to ensure thorough mixing during the

Research Note

Table 1 Recipe for alkyd preparation.

Material	Medium oil alkyd (g)
Oil	37.5
Glycerol	16.5
Phthalic anhydride	21.0
Catalyst (PbO)	0.03
Oil length (%)	50

Table 2 Variation of acid values and values of AVo/AVt[a] with time for medium alkyd for crude soybean and neem oils.[b]

Time (mins)	Variation of acid value (mg KOH/g oil)		Value of *AVo/AVt*	
	Soy bean	Neem	Soy bean	Neem
0	157.08 c	210.94 d	1.00 e	1.00 e
30	43.68 c	93.13 d	3.60 e	2.26 f
60	13.46 c	87.52 d	11.67 e	2.4 f
90	5.61 c	69.56 d	28.00 e	3.03 f
120	3.65 c	44.88 d	42.86 e	4.70 f
150	1.12 cc	31.42 d	140.0 e	6.71 f
180	-	24.68	-	8.55
210	-	10.10	-	20.88
240	-	5.61	-	37.60

[a]AV_o = Initial acid value; AV_t = Acid value at time (t),
[b]Values in the same horizontal row sharing different letters are significantly different at the 5% level

polymerization reaction. The first outlet was fitted to a nitrogen gas cylinder to provide an inert atmosphere for the reaction. The other two outlets were fitted with a water-cooled condenser and thermometer, respectively. 10% xylene (based on the total weight of recipe used) was used as the azeotropic solvent (Ikuoria *et al.* 2004). Two stages were involved in the preparation:

i) Alcoholysis or monoglyceride: The oil was reacted with the glycerol at a temperature of 240°C. Alcoholysis was deemed completed when one part of the mixture was soluble in three parts of methanol. At this point, the reaction mixture was cooled to 140°C.

ii) The second stage involves the addition of phthalic anhydride and the temperature was raised and maintained at 240°C. The progress of the polymerization reaction was monitored by removal of aliquots of the reaction mixture at an interval of 30 min. The acid value was determined using the method described by Pearson (1976).

Statistical analysis

Results are expressed as the means of three separate contents. The data were statistically analyzed by the student's *t*-test at $P \leq 0.05$.

RESULTS AND DISCUSSION

Table 2 shows the results of variation of acid value (AV) and values of AV_0/AV_t with time for the medium oil alkyds of crude neem and soybean oils. The information in **Table 2** was used to plot **Figs. 1-3**.

Rate of alkyd synthesis

The acid value determination is a measure of unreacted carboxylic group in the resin during the reaction; as a result, changes in the acid value are a useful means for monitoring the rate of alkyd formation. By using Carothers' principle (Kienle 1949; Akintayo 1995) to determine the rate constant K, it can be deduced that the number of moles of -COOH = acid value (AV) $\times 10^{-3}$.

By introducing a function p called extent of reaction which is determined experimentally by calculating the unreacted free carboxylic group (-COOH) by titration; then the extent of reaction at time

$$t = P = \frac{AVo - AVt}{AVo} \tag{1}$$

or

$$\frac{AVt}{AVo} = 1 - P \tag{2}$$

The degree of polymerization

$$DP = \frac{\text{No. of molecules originally present}}{\text{No. of molecules finally present}}$$

$$\frac{AVo}{AVt} = (1 - P)^{-1} \tag{3}$$

The rate equation for the case under study can be expressed as

$$AVo.Kt = \frac{AVo}{AVt} - \text{constant} \tag{4}$$

and

$$\frac{AVo}{AVt} = AVo.Kt + \text{constant} \tag{5}$$

Hence a plot of AV_o/AV_t against time should give a straight line $AV_o.K$ from which K can be calculated.

Fig. 1 shows that as the reaction progresses, the acid value also decreases. From the graph there was a sharp decrease in acid value at the initial stage, which was then followed by a period of gradual decrease in acid value. This observed pattern in variation of acid value with time could be explained in terms of the reactivity of the primary and the secondary hydroxyls of the glycerol with the phthalic anhydride. It was noted that the primary hydroxyl group reacted faster than the secondary hydroxyl group; this suggests that the rapid decrease in acid value at the initial stage of the reaction corresponds to the time when the primary OH group reacted; while the later stage represents the period when the secondary OH group reacted. Akintayo (2004) reported that the period when there was change in acid value during polycondensation reaction was less rapid, possibly indicating the beginning of formation of a three-dimensional network of polymer as a result of the cross-
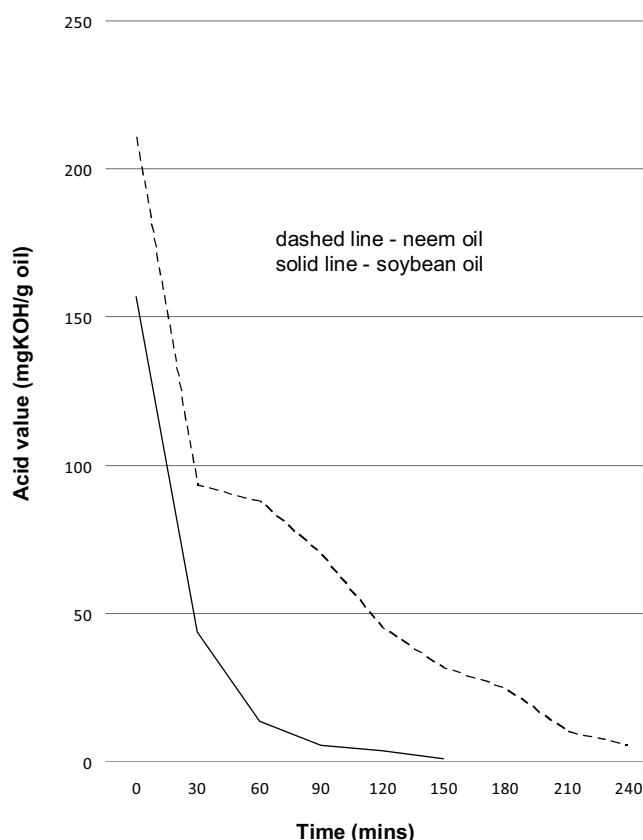

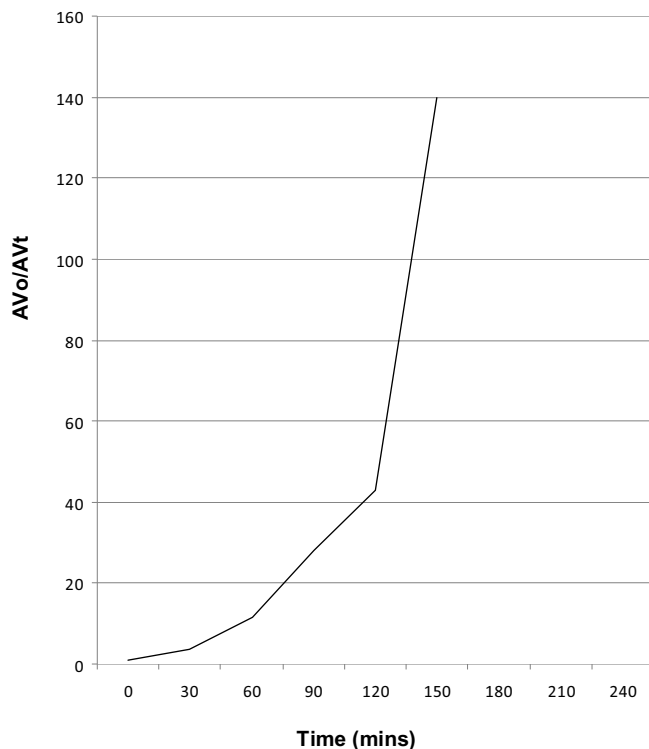**Fig. 1 Variation of acid value with time for crude medium oil alkyd of soybean and neem oil.**

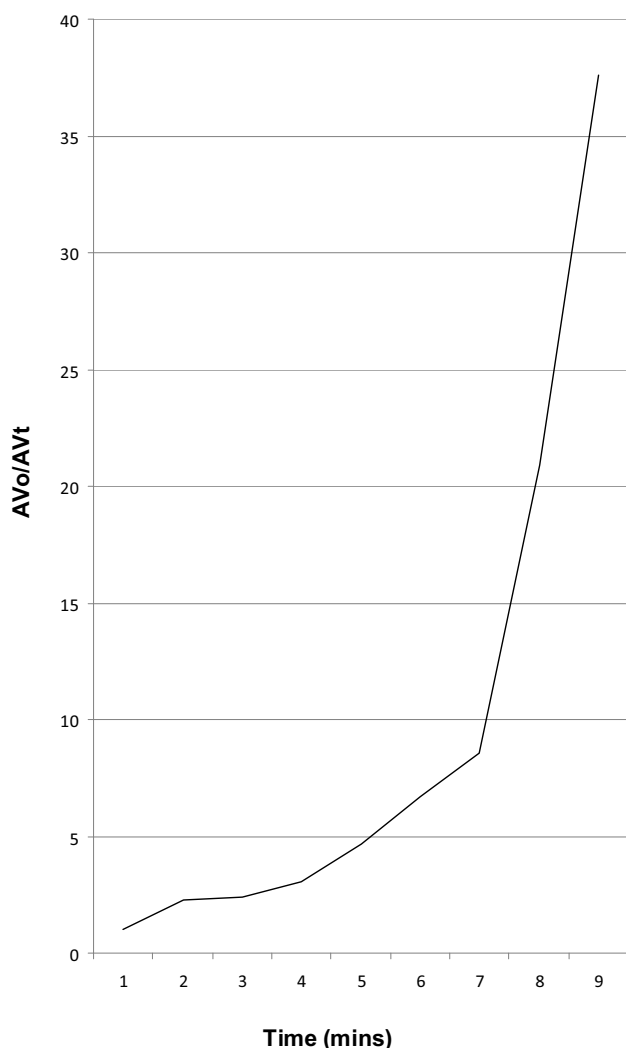**Fig. 2 AVo/AVt for medium oil alklyds for crude soybean oil.**

Fig. 3 AVo/AVt for medium oil alklyds for crude neem oil.

Table 3 Values* of rate constant k, gel time and extent of reaction at gelation for medium oil alkyd modified with crude soybean and crude neem seed oil.

	Rate constant k g (mg KOH)$^{-1}$ min^{-1} x 10^{-4}	Gel Time (min)	Extent of reaction (%)
Soybean oil	11.3 a	60 a	97.8 a
Neem oil	1.8 b	150 b	85.1 b

*Values in the same horizontal row sharing different letters are significantly different at the 5% level

linkage of the alkyd chain during the reaction which involves the secondary hydroxyl group moiety. There was probably cross-linking of the alkyd chains resulting in the formation of a large molecular weight polymer which could have resulted in increased viscosity of the reaction medium. In this study, it was observed that the decrease in acid value was more rapid for soybean oil alkyd than for neem oil alkyd.

Figs. 2 and **3** showed an initial straight line portion after which there was deviation from linearity. The first linear portion was considered to represent the time of formation of linear molecules while the second non-linear probably represented the period of cross-linking of the alkyd chains. This trend has also been observed for rubber seed oil (Ikuoria *et al.* 2004), *Albizia benth* oil (Akintayo and Adebowale 2004), and melon seed oil (Ibemesi 1993). The observation for soybean oil alkyd has further confirmed similar work on soybean oil by Akintayo (1995). The values of the second order rate constant K calculated from linear portion of **Figs. 2** and **3** are 11.3×10^{-4} and 1.8×10^{-4} g (mg (K0H)$^{-1}$ min^{-1} for medium oil alkyd of soybean oil and neem seed oil, respectively (**Table 3**). From this result, it may be suggested that the rate of alkyd production could possibly be dependent on the differences in the constituent fatty acids of the two oils instead of the ratio of reactants used in the formation as noted by Akintayo and Adebowale (2004) since the two alkyds have the same formulation. Other factors that could have affected the rate constant in polyesterification reactions include the proportion of the reactants, speed of agitation of the reaction mixture, changes in temperature and removal of water of esterification.

CONCLUDING REMARKS

In this study, crude soybean and neem oils have been used in the preparation of medium oil alkyd and based on the results from the kinetic study; one could suggest a preference for the medium oil alkyd of soybean oil than the one for neem oil since it gives better alkyd yield within shorter time as indicated by the gel time of 60 min for soybean oil alkyd; while that of neem seed oil is 150 min.

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