

## Kinetic Studies on Polyesterification of Unsaturated Oils and Diacids in the Alcoholysis Process

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**Abstract:** Polyesterification of unsaturated oils-coconut, soybean and palm kernel oils with glycerol and phthalic anhydride was investigated at 280°C. The oil content for the three resin samples was 60% each. The kinetic behaviour of the polyesterification and the resulting alkyd resins, were studied as a function of conversion and the reaction time. The relationship between the degree of polymerization,  $\bar{X}_n$  and reaction time show that the formation of long oil alkyds of coconut, soybean and palm kernel oils follows a second order kinetics with slight deviation from linearity at the onset of the reaction. This deviation suggests the occurrence of chain branching at relatively short intervals along the polymer chain.

**Key words:** Kinetics, unsaturated oils, polyesterification, alcoholysis, phthalic anhydride

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### INTRODUCTION

The research of this kind has initially been focused on the properties modification of alkyd resins produced by polyesterification of unsaturated or drying oils with diacids and glycerol. The significance of the kinetic studies of alkyd resin formation cannot be overemphasized, as such knowledge is useful in classification of polymerization reactions and polymers and studying the conditions necessary for synthesis of high molecular weight alkyds. The determination of the correct reaction order is of great importance, since the calculation of activation energies must be related to correct order of reaction and in addition to its direct contribution to alkyd fundamentals, knowledge of activation energies is of value in the design and control of alkyd processes (Igwe and Ogbobe, 2001).

Alkyd resin is an important component of surface coatings. It is widely used in the coatings and paints industry and they have become indispensable raw materials that are used for the production of industrial and household finishes (Ogunniyi and Odetoye, 2007). It contributes to properties such as coating flexibility, strength and durability, adhesion and gloss. Alkyd resin is a product of polyesterification reaction of unsaturated oils like soybean, linseed oils etc with diacids and glycerol. There have been several other attempts to define alkyd resins over the years. One of such definitions is that of Bobalek *et al.* (1964), which define alkyd resins as the reaction product of polyhydric alcohol and poly-functional acids modified by fatty acid or their triglyceride. Lanson (1985) define alkyd resins as

unsaturated polyesters, in which the unsaturation is located at chain ends instead of within the polymer chain. Igwe and Ogbobe (2001) describe it as oil-modified polyesters. Ikhuoria *et al.* (2004) define alkyd resins as products of polycondensation reaction between polybasic acids and polyhydric alcohol modified with fatty acid or drying oil.

With the exception of few studies in the field, kinetic studies on alkyd resin formation have not received adequate attention. Aigbodion and Okieimen (1996) studied the kinetics of the preparation of rubber seed oil alkyds and found that the initial reaction rates followed second order kinetics with deviation at the later stage of reaction. The measurement also shows that the rate constant was in the order of  $10^{-5} \text{g (mg KOH)}^{-1} \text{min}^{-1}$ . Kinetic studies on the preparation of rubber seed oil alkyds has been widely studied Aigbodion and Okieimen (1996), Aigbodion and Pillai (2001) and Okieimen and Aigbodion (1997). Igwe and Ogbobe (2001) carried out similar study, using melon seed, rubber seed oils and linseed and soybean oils. The studies showed that the polyesterification reactions did not follow a second order equation during the early part of the reactions. However, a second order kinetics was obtained after 150 min of conversion of monomers to products at the later stages of the reaction during, which time the degrees of polymerizations ( $\bar{X}_n$ ) > 5.

The objective of this present research is to study the kinetics of synthesis of alkyd resins from coconut, palm kernel and soybean oils through measuring the acid values of the alkyds formed, average degree of polymerization ( $\bar{X}_n$ ) and extent of reaction ( $P_n$ ).

## MATERIALS AND METHODS

The reagents used were of analytical grade and the coconut oil was obtained by solvent extraction using n-hexane. Palm kernel oil and soybean oil were obtained in a refined form and used without further purifications. Distilled water was used throughout the analytical procedures.

Three samples of alkyd resins of coconut, palm kernel and soybean oils were prepared using 152.00 g of the oils (soybean, coconut and palm kernel oils), 34.75 g of glycerol, 3.35 g of litharge (PbO) and 60.00 g of phthalic anhydride based on the methods described by Ikhuoria and Aigbodion (2006). Determining the acid values of aliquots of the reactions mixture at 20 min intervals monitored the extent of reaction. 2.0 g of aliquots of the reaction mixture were dissolved in a neutralized methanol/propanol mixture of 1:1 ratio. The resulting mixture was then titrated to a phenolphthalein end point with a 0.1 M methanolic potassium hydroxide at room temperature. The acid value of the prepared alkyd resins were then calculated using the expression (ASTM, 1994)

$$\text{Acid Value (AV)} = \frac{MV \times 56.1}{W} \quad (1)$$

Where:

M = Concentration of KOH<sub>(aq)</sub>

V = Volume of KOH<sub>(aq)</sub> used

W = Weight of oil in (g) used and 56.1 is the molecular weight of KOH

The extent of reaction, P<sub>n</sub> and the number average degree of polymerization  $\bar{X}_n$  were calculated from end group analysis of aliquots of the reaction mixture withdrawn at 20 min interval using the following relationships:

$$P_n = \frac{(AV)_n - (AV)_m}{(AV)_n} \quad (2)$$

Where:

(AV)<sub>n</sub> = The acid value at the initial time (n)

(AV)<sub>m</sub> = The acid value at the later time (m)

$$\bar{X}_n = \frac{1}{1 - P_n} \quad (3)$$

where, P<sub>n</sub> is the extent of reaction of phthalic anhydride (Odian, 2004; Fried, 2003).

## RESULTS AND DISCUSSION

The rate of a step polymerization is conveniently expressed in terms of the concentrations of the reacting

Table 1: Acid values of the resins in MgKOH/g

| Time (min) | Coconut oil resin | Soybean oil resin | Palm kernel oil resin |
|------------|-------------------|-------------------|-----------------------|
| 20         | 0.0849            | 0.0923            | 0.0923                |
| 40         | 0.0738            | 0.0849            | 0.0812                |
| 60         | 0.0591            | 0.0738            | 0.0812                |
| 80         | 0.0369            | 0.0627            | 0.0701                |
| 100        | 0.0369            | 0.0517            | 0.0406                |
| 120        | 0.0332            | 0.0369            | 0.0295                |
| 140        | 0.0295            | 0.0369            | 0.0258                |
| 160        | 0.0221            | 0.0258            | 0.0185                |
| 180        | 0.0185            | 0.0185            | 0.0148                |

functional groups. Thus, the polyesterification can be experimentally followed by titrating for the unreacted carboxyl groups with a base (Odian, 2004). Table 1 shows the fall in acid value during the polyesterification reaction of alkyds formation at various time intervals.

The decrease in acid values with time in Table 1 follows the usual polyesterification reaction where polymerization rate is synonymous with the rate of formation of products, i.e., the monomer vanish gradually, while the polymer is form by step wise means. An expression for the reaction rate can be obtained following the general procedures for handling a reaction scheme with the characteristics described (Moore and Pearson, 1981) as:

$$\text{Rate} = \frac{dx}{dt} = K(a - x)(b - x) \quad (6)$$

Where:

a and b = Initial concentrations of each reactive groups

x = The decrease in concentration of each component at time t

K = The rate constant of the reaction

Table 1 shows, different rates of decrease of acid value for the three oils alkyd resins. This is because coconut, soybean and palm kernel oils contain different fatty acid substituents, capable of yielding varied alcoholysis products. Also, observed in Table 1 is a rapid decrease in acid value in the first 80 min of reaction for coconut oil resin; 120 min of reaction for soybean oil resin and 100 min of reaction for palm kernel oil resin. This may be attributable to the reaction of the dibasic acid (phthalic anhydride) with the primary hydroxyl groups of the monoglyceride to form linear polyesters. Below 80 min, 100 and 120 min of reaction for coconut, palm kernel and soybean oil resins respectively, the plots show no reasonable decrease in acid values for the three oils resins. This may suggest that, at this period of reaction, the secondary hydroxyls come into play. Molecules of phthalic anhydride react with the secondary hydroxyls and connect the short chains forming a complex branched or network structures. When approximately, 80% esterification has taken place, the resin becomes infusible.

The molecular weight of a polymer is of prime concern from the practical viewpoint, for unless a polymer

Table 2: Extent of reaction ( $P_n$ ) of phthalic anhydride

| Time (min) | Coconut oil resin | Soybean oil resin | Palm kernel oil resin |
|------------|-------------------|-------------------|-----------------------|
| 20         | 0.0849 (8.5)      | 0.0923 (9.2)      | 0.0923 (9.2)          |
| 40         | 0.1307 (13.0)     | 0.0802 (8.0)      | 0.1203 (12.0)         |
| 60         | 0.3039 (30.4)     | 0.2004 (20.0)     | 0.2004 (20.0)         |
| 80         | 0.5654 (56.5)     | 0.3207 (32.1)     | 0.2405 (24.1)         |
| 100        | 0.5654 (56.5)     | 0.4399 (44.0)     | 0.5601 (56.0)         |
| 120        | 0.6090 (60.9)     | 0.6002 (60.0)     | 0.6804 (68.0)         |
| 140        | 0.6525 (65.2)     | 0.6002 (60.0)     | 0.7205 (72.0)         |
| 160        | 0.7397 (73.9)     | 0.7205 (72.0)     | 0.7996 (80.0)         |
| 180        | 0.7821 (78.2)     | 0.7996 (80.0)     | 0.8397 (84.0)         |

Values in brackets are percentage

is of sufficiently high molecular weight (approximately, >5000-10,000) it will not have the desirable strength characteristics (O dian, 2004). It is therefore, important to consider the change in polymer molecular weight with reaction time. The extent or fraction of reaction  $P_n$ , which is defined as the fraction of the hydroxyl or carboxyl functional groups that has reacted at time  $t$  was evaluated using Eq. 2.  $P_n$  is also, referred to as the extent or fraction of conversion. Table 2 shows, the  $P_n$  values at various time intervals for the three oil alkyd resins. Knowing the extent of reaction  $P_n$  of phthalic anhydride create an insight on the level of free acid in the finished product, which is of significant importance on the application of alkyd resin.

The number-average degree of polymerization  $\bar{X}_n$ , which is defined as the average number of structural units per polymer chain was determined base on  $P_n$  values at different time intervals using Eq. 3. The  $\bar{X}_n$  values for the coconut, soybean and palm kernel alkyds are shown in Table 3. Figure 1 shows, a plot of average degree of polymerization  $\bar{X}_n$  versus time of reaction in minutes.

Equation 3 indicates that a plot of  $1/(1-P_n)$  versus time of reaction should be linear. This behaviour has been generally observed in polyesterifications (O dian, 2004). Figure 1, a plot of number average degree of polymerization  $\bar{X}_n$  versus time is a non-linear function of time at times less than about 140 min of reaction, i.e., below 70% conversion (Table 2) for the three oil alkyd resins. This is an indication that the polymerization reaction did not follow a second order kinetics during the early stage of the reactions.

Igwe and Ogbobe (2001) made similar observations in the study of alkyd resin formation from melon seed, linseed and rubber seed oils. On the contrary Aigbodion and Okieimen (1996) observed deviation from second order kinetics in the study of preparation of rubber seed oil alkyds at the latter stage of reactions.

The deviation from second order kinetics at the early stage of polyesterification reaction under the investigation suggests the occurrence of chain branching at relatively short intervals along the polymer chain. Nonetheless, a second order kinetics was observed at

Table 3: Degree of polymerization reaction ( $\bar{X}_n$ )

| Time (min) | Coconut oil resin | Soybean oil resin | Palm kernel oil resin |
|------------|-------------------|-------------------|-----------------------|
| 20         | 1.0928            | 1.1017            | 1.1017                |
| 40         | 1.1504            | 1.1368            | 1.0892                |
| 60         | 1.4366            | 1.2506            | 1.2506                |
| 80         | 2.3010            | 1.3167            | 1.4721                |
| 100        | 2.3010            | 2.2732            | 1.7854                |
| 120        | 2.5575            | 3.1289            | 2.5013                |
| 140        | 2.8777            | 3.5778            | 2.5013                |
| 160        | 3.8417            | 4.9900            | 3.5778                |
| 180        | 4.5893            | 6.2380            | 4.9900                |

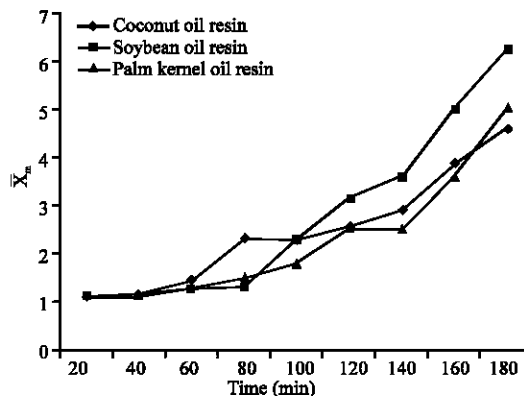


Fig. 1: Plot of degree of polymerization versus time of reaction (min)

>70% conversion. At this period of reaction a straight-line plot was obtained (Fig. 1). This period of reaction is of considerable importance to the alkyd chemists in calculating the activation energies of the resin. Knowledge of the activation energy is of importance in the design and control of alkyd processes.

## CONCLUSION

The kinetics of coconut, soybean and palm kernel long oil alkyd resins has been studied. The results show that the three-alkyd samples did not follow second order kinetics at the early stage of reaction but rather show second order kinetics at the latter stage of reaction.

The decrease in acid values of the alkyds has been found to be rapid in the first 130 min of polyesterification reactions. This shows that a linear type polymer was commonly formed in the first 130 min of reaction.

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