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The effects of polybasic acid type on kinetics of the preparation of cottonseed oil based alkyd resins

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Abstract: *The kinetics of the alcoholysis-polycondensation of cottonseed oil (COSO), glycerol (GL), phthalic anhydride (PA), Maleic anhydride (MA) and Succinic acid (SA) leading to the formation of alkyd resins were investigated. Three grades of alkyd samples formulated to have oil content of 50% were prepared with COSO, GL, PA (I), MA (II) and SA (III) respectively. The extent of polycondensation was monitored by measuring the volume of water of esterification evolved, determining the pH and acid value of aliquots of the reaction mixture at various intervals of time. The extent of reaction (P_n) and number-average degree of polymerization ($\overline{X_n}$) were calculated from end-group analysis of aliquots of reaction mixture withdrawn at various intervals of time. The rate of water evolution for COSO MA and COSO SA alkyds respectively were in the order of 10^{-1} cm^3/min, while that of COSO PA alkyd was in the order of 10^{-2} cm^3/min. The pH of the in-process samples increases with decreased in acid values. The initial reaction rates followed second order kinetics and thereafter deviations were observed. The $\overline{X_n}$ calculated in the region of deviation from second order kinetics suggests the occurrence of chain branching at relatively short intervals along the polymer chain. The second order rate constants for all the alkyd samples were of the order 10^{-4} $g(mgKOH)^{-1}min^{-1}$.*

Keywords: *Alkyd resin; Alcoholysis; Coatings, Kinetics, Polybasic acids; Polycondensation*

I. Introduction

In the last decade, the depletion of crude oil and increasing oil price have pushed scientists to turn to eco – friendly and cost – effective materials while investigating renewable natural materials as an alternative source of monomers in the manufacturing of polymer [1 and 2]. Also, the consumer and industrial interests in the development of eco – friendly materials have catapulted the environmentally benign agricultural resources as feedstocks of the polymer industry [3]. The fatty acid esters derived from the triglyceride vegetable oils are an attractive source of raw materials for polymer synthesis [4] because of their environmentally benign properties. One of the most widely used types of organic coatings is alkyd resin, which is produced by the reaction of polybasic acid with polyhydric alcohol modified with triglyceride vegetable oils. Alkyd resin has acquired a good reputation because of their economy, ease of application and availability of raw materials [5, 6 and 7]. In addition, they are largely biologically degradable polymers because of the oil and glycerol parts [8], and they are eco – friendly compared to petroleum – based polymers that constitute environmental pollution and degradation. Other unique properties of alkyd resins that make it an indispensable raw material in surface coating industry include gloss and gloss retention, good adhesion and hardness properties, film flexibility and durability [9, 10, 11 and 12].

Although kinetic studies of products such as alkyd resin is difficult to investigate due to apparent failure in applying the theory of polycondensation due to complications resulting from innumerable side reactions[13 and 14], many researchers have investigated the kinetics of alkyd resins by determining the acid value of aliquots of the reaction mixture withdrawn at various time intervals. Kinetic studies of alkyd resin prepared from phthalic anhydride and glycerol modified with triglyceride vegetable oils have been reported [12, 13, 14, 15 and 16].

In our previous studies [17], alkyd resins have been produced from polybasic acids (maleic anhydride and succinic acid) other than phthalic anhydride, which is used conventionally and pH of aliquots of the reaction mixture withdrawn at regular time intervals during preparation of alkyd resin have been successfully determined [18]. It was therefore thought that kinetics of this products from different polybasic acids be studied using amount of water of polycondensation evolved, end – group analysis and pH of the aliquots of the reaction mixture withdrawn at various time intervals. Hence, this research is aimed at using end-group analysis, amount of water of esterification and pH to study the effects of polybasic acid type on rates of polyesterification and the beginning of cross-linking (time of gelation) during preparation of cottonseed oil alkyd resins using phthalic anhydride, maleic anhydride and succinic acid as polybasic acids.

II. Experimental

2.1 Materials

Cottonseed oil was purchased at Sabongari market, Kano and used in alkyd synthesis without further purification. Technical grade polybasic acids- phthalic anhydride (BDH, England), maleic anhydride (BDH, England) and succinic acid (BDH, England), glycerol and xylene were obtained from commercial sources and used in the preparation of alkyd resins without further purification.

2.2. Preparation of alkyd resins

Three grades of alkyd samples formulated to have oil content of 50% were prepared with GL, COSO, PA (I), MA (II) and SA (III) respectively using the recipe and the monoglyceride method according to the procedure described in our previous studies [17 and 18]. Xylene was used as the refluxing solvent and each alkyd sample was processed to acid value below 10 mgKOH/g.

Aliquots of the reaction mixture were withdrawn at 20 min intervals and the acid value determined by titrimetric method [19], the pH of the mixture was determined using a pH meter model pH-016. The volume of water of esterification evolved was measured at the same time.

2.3 Theory of end-group analysis, extent of conversion and average degree of polymerization of alkyd resins

However, the rate of a step polymerization is conveniently expressed in terms of the concentrations of the reacting functional groups [20]. Thus, the polyesterification can be experimentally followed by titrating for the unreacted carboxyl groups with a base, i.e., monitoring the acid value. Considering a simple esterification reaction below (“Equation 1”), the rate of polymerization, R, can then be expressed as the rate of disappearance of carboxyl groups, – d [COOH]/dt (“Equation 2”).

$$\sim COOH + \sim OH \rightleftharpoons COO\sim + H_2O \qquad 1$$

$$R = \frac{-d[COOH]}{dt} = K[COOH]\,[OH] \qquad 2$$

For most polymerizations the concentrations of the two functional groups are very nearly stoichiometric [20 and 21], and “Equation 2” can be written as

$$-\frac{d[A]}{dt} = K[A]^2 \qquad 3$$

$$-\frac{d[A]}{[A]^2} = Kdt \qquad 4$$

where [A] is the concentration of – OH groups or - COOH groups. However, “Equations 2 and 3” show that synthesis of alkyd resins follows second – order reaction, with K as the second order rate constant. By integrating “Equation 4”, we have a second order rate constant.

$$-\int \frac{d[A]}{[A]^2} = K\int dt \qquad 5$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_o} = Kt \qquad 6$$

where $[A]_o$ is the initial concentration at t = 0 and $[A]_t$ is the concentration after time, t, of hydroxyl or carboxyl groups respectively. It is convenient at this point to express “Equation 6” in terms of the extent or fraction of reaction (P_n) defined as the fraction of the hydroxyl or carboxyl functional groups that have reacted at time t [20 and 21]. However, “Equation 7” gives P_n, which is also referred to as the extent or fraction of conversion.

$$P_n = \frac{[A]_0 - [A]_t}{[A]_o} \qquad 7$$

This implies

$$[A]_t = [A]_0 - [A]_0 P_n = [A]_o\,(1 - P_n) \qquad 8$$

Substituting for $[A]_t$ in “Equation 6” and rearrangement, we have

$$\frac{1}{(1-P_n)} = [A]_o\,Kt + 1 \qquad 9$$

Hence, “Equation 9” is a second – order rate equation with K as second order rate constant. In addition, “Equation 9” indicates that a plot of $\frac{1}{(1-P_n)}$ versus t should be linear. This behaviour has been generally observed in polyesterification [20]. Several authors have plotted this graph during kinetic studies of rubber seed, coconut, soybean, castor, palm kernel, melon seed and cottonseed oils alkyds preparation [12, 13, 14, 15, 18, 22 and 23] and observed deviations from linearity (second order) either at the early stage of the reactions or towards the end of the reactions.

The deviation from second order kinetics of polyesterification reaction was attributed to occurrence of chain branching at relatively short intervals along the polymer chain [12]. In addition, Onukwli and Igbokwe [22] attributed this to the periods of reaction of the primary – OH and the secondary – OH leading to the formation of linear and three-dimensional molecules respectively.

Odian [20] and Fried [21] define ($\overline{X}_n$) as the average number of structural units per polymer chain.

$$\overline{X}_n = \frac{1}{(1-P_n)} \qquad 10$$

This “Equation 10” relating the degree of polymerization to the extent of reaction was originally set forth by Carothers and is often referred to as Carothers equation [20].

The extent of the reaction and number-average degree of polymerization were calculated from the end-group analysis of aliquots of the reaction mixture withdrawn at various intervals of time using the relationships in “Equations 7 and 10” respectively. The values of $\overline{X}_n$ for COSO alkyd samples (I), (II) and (III), as well as acid values, pH and water of esterification obtained were plotted with reaction time. Also, rates of polymerization of alkyd resins were calculated using “Equation 9” (end-group analysis) and based on the amount of water of polycondensation evolved at each stage of reaction.

III. Results and discussion

3.1Kinetic studies of the preparation of COSO alkyd resins based on water of esterification

The use of variations in the volume of water of esterification evolved with time to study the rate of polycondensation has been reported in our previous studies [18]. Table 1 and Fig. 1 respectively show the variation and rate curve of the volume of water evolved with reaction time during COSO alkyds preparation with PA, MA and SA respectively. It can be seen that at the early stages of reaction, the volume of water evolved was high, and then decreased at longer periods of reaction. This observation may be because of high initial esterification reaction, which could lead to depletion in the available functional groups reacting. Aigbodion and Okieimen [13] and Isaac and Ekpa [18] made similar observations during the kinetics of the preparation of rubber seed, melon seed and cottonseed oils alkyds resin respectively. The variations in the volume of water of esterification evolved during the polyesterification reaction can also be attributed to limitation in inter-contact between the reacting functional groups due to increased viscosity (of the reaction medium) as the reaction progressed. The volume of water evolved also increases in the order: SA alkyd sample (III), MA alkyd sample (II), and PA alkyd sample (I) (Table 1 and Fig. 1). The amount of water of esterification was lowest in PA cottonseed oil alkyd resin and highest with succinic acid cottonseed oil alkyd resin, while that of MA cottonseed oil alkyd resin was intermediate (Fig. 1).

It is expected that the theoretical (calculated) water of esterification should be greater than that evolved during the polycondensation reaction; this is because polycondensation hardly gets to completion before termination. However, as observed in Fig. 2, the amount (grams) of water evolved in sample (III) is higher than those of samples (II) and (I) respectively. It is also observed that the amount of water evolved in sample (III) is greater than the theoretical water of esterification. On the other hand, the theoretical water for samples (I) and (II) was greater than the water evolved. The observed excess water of esterification in SA alkyd sample (III) may be because succinic acid was used instead of succinic anhydride.

Aigbodion and Okieimen [13] attributed increased volume of water evolved during polyesterification reaction to factors such as rate of agitation of reaction mixture, and the contribution by glycerol and xylene. It is also evident from Fig. 2 that MA alkyd sample (II) produced highest amount (gram) of water evolved.

The amount of water of condensation calculated was also observed to follow the trend: sample (II) greater than sample (III) and sample (I). This may be due to differences in the molar mass of the polybasic acids (PA – 148 g/mol, SA – 118.09 g/mol and MA – 98 g/mol) which were used in the calculation of theoretical water of these resins.

3.2 Rate of polymerization reaction based on the volume of water evolved

The rates of water evolution calculated from the linear portions of the plots in Fig. 1 are given in Table 2. The rate of evolution of water of esterification in samples (II) and (III) are faster than that of sample (I). This observation may be due to the difference in structure of maleic anhydride and succinic acid, which contain aliphatic carbon chains compared to phthalic anhydride with benzene ring in its structure. The slight difference at the initial rate of water evolution between samples (II) and (III) (Table 2) could be due to the double bond present in maleic anhydride chain, which could lead to isomerization to trans form. The rate of water evolution for samples (II) and (III) were in the order of 10^{-1} cm^3/min, while that of sample (I) was in the order of 10^{-2} cm^3/min. This implies that the rate of water evolution was fastest in samples (II) and (III) compared to sample (I).

3.3 Variation of pH and acid values with time during COSO alkyds synthesis

Variations of acid values of alkyd resins with time have been widely used to study the kinetics of alkyd resin synthesis [12, 13, 14, 15, 16, 18, 22 and 23]. The pH is another parameter that has not been widely explored and exploited. In our previous work [18], pH of COSO and melon seed oil alkyds were determined. Similar procedure was employed in this research to determine the pH of alkyd samples (I) – (III). The successful use of pH values in the kinetic studies of COSO alkyds synthesis, which is more reliable than the used of acid value, since the determination of pH values is by instrumental method has been one of the major contributions of this research in the area of surface coating research.

It is observed that the pH of the alkyd samples increases rapidly at the early stages of reaction as the acid value also decreased in like manner (Figs 3 and 4). This was followed with a period of a more gradual increase in pH as the acid value also decreased gradually. This variation may be due to decrease in concentration of H^+ as the primary and secondary hydroxyl of glycerol reacts with PA, MA and SA respectively, and cottonseed oil. Mechanism of alkyd resin synthesis reveals intermediate reactions leading to alkyd formation to include polyesterification reactions between polybasic acid and hydroxyl groups of polyhydric alcohol to form half – esters; esterification reactions of the hydroxyls of polyol with the carboxyls of fatty acid, polybasic acid half – ester or polybasic acid [18]. The two reactions above resulted in a decrease in the concentration of hydrogen ions of the reaction mixture, thereby increasing the pH. The initial increase in pH of the reaction mixture may be due to initial increase in rate of reaction as the temperature is gradually increased. Two linear portions were observed in Figs 3 and 4. At the point of deviation from linearity (about 80 min of reaction) there seem to be no difference in the pH and acid values of the three alkyd samples. Variation in pH and acid values were observed at the first linear portions of Figs 3 and 4 such that pH of sample (I) was greater than that of sample (III) and sample (II). The acid values increases in the order: sample (II), sample (III), and sample (I). This may be attributed to the fact that the alkyd samples were prepared using the same oil length and the differences in the pH and acid values indicate the differences in the acid strength of the three polybasic basic acids used.

The initial marked decrease in the acid value of the reaction mixture observed in Fig. 4 is also rationalized based on the different reactivities of α- and β -OH groups of glycerol. Goldsmith [24] reported that α-OH groups of glycerol react much faster than do their β -OH counterparts. Thus, the initial rapid decrease in the acid value observed correspond to the time when α-OH groups reacted. A similar high rate of conversion during the early stages of the reaction between glycerol and phthalic anhydride has been reported [14, 18, 22 and 23]. The initial marked decrease in acid value of the samples at early stages of reaction can also be explained based on the temperature of the reaction. For instance, Aigbodion and Okieimen [13] suggested that at a temperature of about 160 ^{0}C primary hydroxyls of glycerol react rapidly with phthalic anhydride, while secondary hydroxyl react at temperatures above 230 ^{0}C. Thus, the initial marked decreased in acid value found for all the samples may be assumed to be because of increase in the rate of esterification accompanying the rapid increase of temperature to 230 ^{0}C. An increase rate of esterification reaction at temperatures above 200 ^{0}C has been reported [25].

Summarily, the acid values of the in – process samples of alkyds sample (I) – (III) decreases with time; the acid value decreases as the pH increases and pH increases with time. There was no variation in pH and acid values in the second linear portions of Figs 3 and 4.

3.4. Extent of reaction of polybasic acids and number– average degree of polymerization of PA, MA and SA cottonseed oil alkyd samples

The application properties of alkyd resins are governed mainly by composition of the alkyd samples, but variations in the process of synthesis also have significant effects [13 and 26]. In alkyd synthesis, it is usually observed that there is a time region during the course of reaction when there is a sharp drop in acid value of the reaction mixture. Kinetic treatment of data obtained from end-group analysis could afford a better understanding of events such as changes in the physical characteristics of the reaction medium occurring during alkyd preparation.

However, in polyesterification reactions it is generally assumed that the reactivity of the functional group does not depend on the size of molecule to which it is attached [13]. It is observed from the result that P_n and $\overline{X}_n$ for the alkyd samples increases in a stepwise manner with reaction time. This implies, polyesterification reaction of triglyceride oils with polybasic acids is a stepwise reaction.

For polycondensation reactions, it was proposed that plots of $\overline{X}_n$ against time should be linear throughout the reaction [18]. This is also confirmed from Equation 9. However, in Fig. 5, which shows the plots of the degree of polymerization of PA, MA and SA cottonseed oil alkyd resins respectively, two distinct portions are obvious. The first portion is the initial linear portion, which corresponds to a period when the primary hydroxyl groups of glycerol reacted and the second curved portion, which corresponds to the period when the secondary hydroxyl groups of glycerol reacted. This region of deviation from linearity in these plots is considered to mark changes in the physical characteristics of the reaction medium, most probably the period marking the beginning of the formation of relatively large molecular species and the cross – linking of the alkyd chains. The three alkyd samples show similar behavior in terms of degree of polymerization and extend of reaction of polybasic acids. This may be because the alkyds were prepared using the same oil length (50% medium oil).

The alkyd samples did not show linearity at the early stages of reaction up to 60 min of reaction (Fig. 5). Linearity started at 60 min of reaction for samples (I), (II), and (III) corresponding to 65.04%, 47.33% and 60.14% (Table 3) conversion respectively. The value of second order rate constant, K_2, calculated at the onset of linear portions of Fig. 5 are given as 1.4×10^{-4} $g(mgKOH)^{-1}min^{-1}$, 6.2×10^{-4} $g(mgKOH)^{-1}min^{-1}$ and 1.1×10^{-4} $g(mgKOH)^{-1}min^{-1}$ (Table 4) respectively. Deviations from linearity were observed at 120 min for sample (I) and 140 min for samples (II) and (III) (Fig. 5) respectively. The values of P_n at the point of deviations were given as 78.91% (sample I), 85.74% (sample II) and 84.24% (sample III) (Table 3). The corresponding values of K_2 were 1.5×10^{-4} $g(mgKOH)^{-1}min^{-1}$ (sample I), 1.9×10^{-4} $g(mgKOH)^{-1}min^{-1}$ (sample II) and 1.7×10^{-4} $g(mgKOH)^{-1}min^{-1}$ (sample III) (Table 4). Many authors [13, 14, 18, 22 and 23] have reported similar observations for alkyds prepared from other oils.

It is well known that the rate constant in esterification reactions is dependent on the proportion of the reactants, speed of agitation of the reaction mixture, changes in temperature and removal of water of esterification [13]. For a second order reaction, K_2 will also depend on the initial concentration of the reactants (acid value). The initial acid values of samples (I) and (III) are about the same magnitude, but the rate of decrease in acid value is fastest for sample (I) hence it relatively larger K_2 values. Those of samples (II) and (III) were about the same and there was no significant difference in their K_2 values.

It is obvious from the above results that the initial reaction rates in the preparation of cottonseed oil alkyds resins with PA, MA and SA follow second order kinetics with rate constants of the order 10^{-4} $g(mgKOH)^{-1}min^{-1}$. The rate of polymerization of COSO PA is faster than that of COSO MA and COSO SA alkyd resins respectively. The $\overline{X}_n$ calculated in the regions of deviation from second order kinetics suggests the occurrence of chain branching at relatively short intervals along the polymer chain.

IV. Conclusion

The results from this research revealed that the initial reaction rates in the preparation of alkyd resins using cottonseed oil as triglyceride oil and phthalic anhydride, maleic anhydride and succinic acid respectively as the polybasic acids follow second order kinetics with rate constants of the order 10^{-4} $g(mgKOH)^{-1}min^{-1}$. The plot of the degree of polymerization of these alkyd samples shows no linearity at the early stage of reaction.

The average degree of polymerization calculated in the region of deviation from second order kinetics suggests the occurrence of chain branching at relatively short intervals along the polymer chain. The pH of aliquots of the reaction mixture of cottonseed oil PA, MA and SA based alkyds determined at 20 min intervals increases as the acid value decreased.

The volume of water of esterification evolved increases in the order: SA alkyd sample (III), MA alkyd sample (II), PA alkyd sample (I). The amount of water of esterification evolved was lowest in PA cottonseed oil alkyd resin and highest with SA cottonseed oil alkyd resin, while that of MA cottonseed oil alkyd resin was intermediate. On the other hand, water of esterification evovled for SA cottonseed oil alkyd resin was greater than water of esterification calculated. The rate of evolution of water of polycondensation was highest in MA and SA COSO alkyd samples respectively. Based on end-group analysis, PA cottonseed oils alkyd attained the highest degree of polymerization at the shortest time compared to MA and SA cottonseed oil alkyds counterparts. The rate of polymerization of MA and SA cottonseed oil alkyd resins was the same.

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Table 1 Water evolved at various stages of reaction during cottonseed oil alkyd resins synthesis

	Water evolved (cm^3)		
Time (min)	**Sample (I)**	**Sample (II)**	**Sample (III)**
0	1.50	2.40	2.80
40	3.00	5.00	5.00
60	3.70	6.20	6.20
80	5.00	6.90	7.00
100	5.80	7.30	8.40
120	6.00	7.50	9.20
140	6.15	7.60	9.80
160	6.25	7.75	9.90
180	6.35	7.80	10.00

Sample (I) – 50% COSO PA alkyd resin; Sample (II) – 50% COSO MA alkyd resin; Sample (III) – 50% COSO SA alkyd resin.

Table 2 Rate of reactions during the synthesis of cottonseed oil alkyd resins (water evolution rate)

	Rate of reaction (cm^3/min)		
S/No	**Sample (I)**	**Sample (II)**	**Sample (III)**
1	7.5×10^{-2}	1.2×10^{-1}	1.4×10^{-1}
2	7.5×10^{-2}	1.3×10^{-1}	1.3×10^{-1}
3	6.2×10^{-2}	1.0×10^{-1}	1.0×10^{-1}

Sample (I) – 50% COSO PA alkyd resin; Sample (II) – 50% COSO MA alkyd resin; Sample (III) – 50% COSO SA alkyd resin.

Table 3 Extent of reaction (P_n) of polybasic acids during PA, MA and SA cottonseed oil alkyd resins synthesis

	P_n (%)		
Time (min)	**Sample (I)**	**Sample (III)**	**Sample (III)**
0	-	-	-
20	23.04	17.12	13.69
40	40.22	26.36	28.35
60	65.04	47.33	60.14
80	69.34	69.50	71.11
100	76.82	76.86	74.87
120	78.91	81.90	81.13
140	85.01	85.74	84.24
160	90.66	89.82	89.59
180	94.71	94.73	94.01

Sample (I) – 50% COSO PA alkyd resin; Sample (II) – 50% COSO MA alkyd resin; Sample (III) – 50% COSO SA alkyd resin.

Table 4 Second order rate constant K_2 at various time intervals during PA, MA and SA cottonseed oil alkyd synthesis

	Rate Constant (K_2) $g(mgKOH)^{-1}min^{-1}$		
Time (min)	**Sample (I)**	**Sample (II)**	**Sample (III)**
20	7.0×10^{-5}	4.4×10^{-5}	3.6×10^{-5}
40	7.8×10^{-5}	3.7×10^{-5}	4.5×10^{-5}
60	1.4×10^{-4}	1.2×10^{-4}	1.1×10^{-4}
80	1.3×10^{-4}	1.2×10^{-4}	1.4×10^{-4}
100	1.5×10^{-4}	1.4×10^{-4}	1.3×10^{-4}
120	1.5×10^{-4}	1.6×10^{-4}	1.6×10^{-4}
140	1.9×10^{-4}	1.9×10^{-4}	1.7×10^{-4}
160	2.8×10^{-4}	2.3×10^{-4}	2.4×10^{-4}
180	4.6×10^{-4}	4.2×10^{-4}	3.9×10^{-4}

Sample (I) – 50% COSO PA alkyd resin; Sample (II) – 50% COSO MA alkyd resin; Sample (III) – 50% COSO SA alkyd resin.

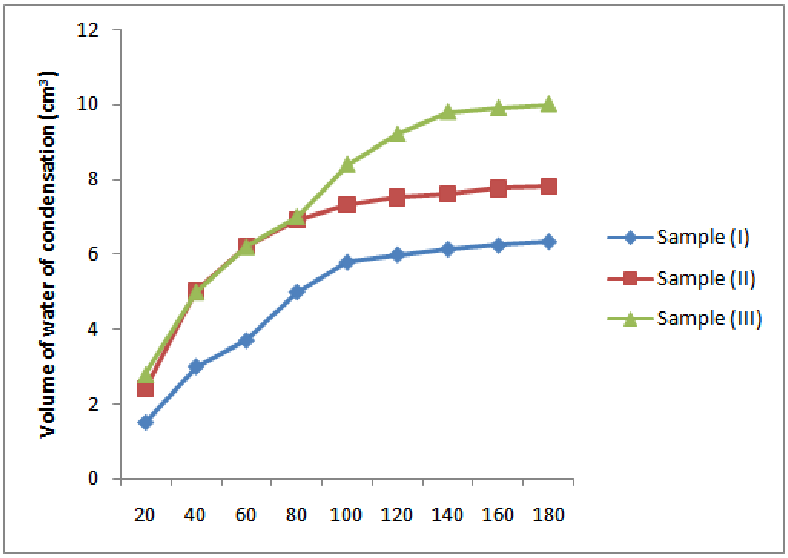

Figure 1 Plot of water evolution versus time for cottonseed oil alkyd sample I, II and III prepared from different polybasic acids.

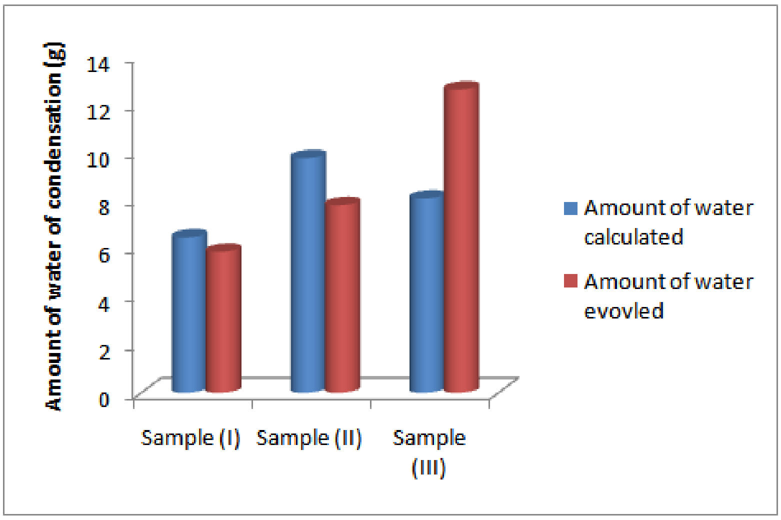

Figure 2 Chart of water of condensation calculated and amount evolved for sample I, II and III

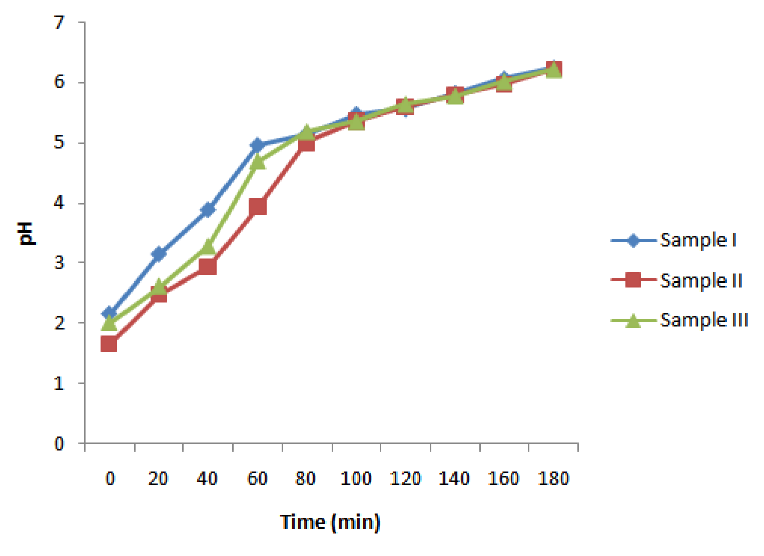

Figure 3 Plot of pH against time for cottonseed oil alkyd sample I, II and III.

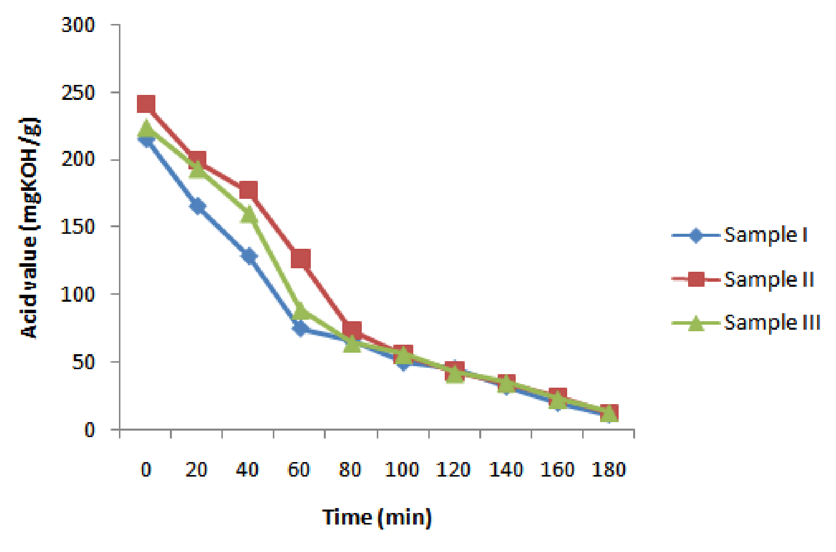

Figure 4 Plot of acid value (mgKOH/g) with reaction time for cottonseed oil alkyd sample I, II and III.

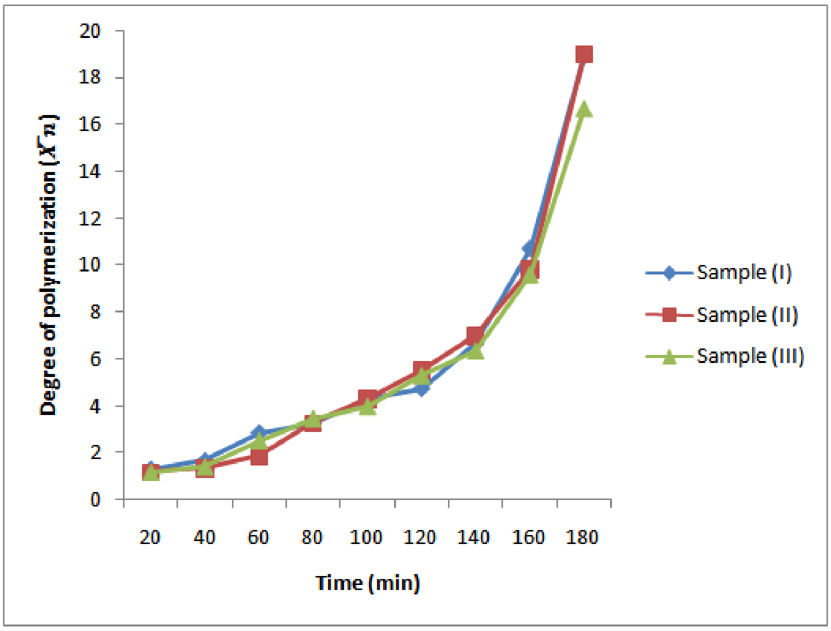

Figure 5 Plot of degree of polymerization versus reaction time for cottonseed oil alkyd sample I, II and III prepared from different polybasic acids.

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