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ORIGINAL PAPER

Palm Oleic Acid Based Alkyds: Effect of the Fatty Acid Content on the Polyesterification Kinetics

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Abstract The kinetic behavior of polyesterification of the alkyd resins synthesized using glycerol and phthalic anhydride modified with oleic acid from the palm oil at temperatures between 120 and 240 °C was studied. Three alkyds having oleic acid contents of 28, 40, and 65% were prepared by employing fatty acid method. The extent of the polyesterification reaction and average degree of polymerization were monitored by determining the acid number of the aliquot of the reaction mixture at various intervals of time and by measuring the volume of water evolved. Kinetic studies revealed that initial reaction rates followed a second-order kinetics up to certain limit and thereafter deviations were observed. The extent of reaction varied from 77.4 to 86.3% before deviation for all the three samples and exhibited a considerable degree of conversion. The second-order rate constants calculated from the linear part were found to be of the order of 10^{-5} g (mg KOH)$^{-1}$ min^{-1}. Molecular weight of the alkyd samples was determined by GPC; number average molecular weight of the alkyds ranged from 980 to 2,070.

Keywords Palm oleic acid · Polyesterification · Kinetic studies · Extent of reaction · Molecular weight

Introduction

In view of the increasing environmental cognition, the use of vegetable oils in non-food applications has attracted appreciable interest because of their biodegradability, ability to undergo chemical modifications and renewable nature [1]. Vegetable oils have been used as modifiers of alkyd resin for the purpose of imparting certain properties, such as ability to provide air-dry coatings, film hardness, durability, crosslinking and economical balance, and these include chiefly linseed oil, soybean oil, castor oil and tall oil.

Alkyd resins are used extensively for synthesis of paint [1], adhesive [2], ink [3], varnish [4] and various coating industries [5]. These resins have been prepared by the polycondensation of polyhydric alcohols and polyacids modified with triglyceride oils (using alcoholysis process) or its fatty acids (using fatty acid process). In the alcoholysis process, alkyds are synthesized in a two steps procedure due to insolubility of polyacids in the oils. As for the fatty acid process, fatty acid is used instead of oil and all the reactants are soluble in each other. Thus, all the raw materials are added together at the beginning of the reaction in just a single step [6, 7].

The common problems for alkyd resins are that they are typically used in diluted form in organic solvents and that some of the alkyd resins such as palm oil-based alkyd resins are not able to air dry due to their low iodine value. In order to overcome these problems, the use of alkyd emulsions had been employed by emulsifying the alkyd resins in water [8] and by copolymerizing it with acrylate monomers to enhance their properties [9] or to interesterification with another oil to produce a workable coating resin [10].

Based on our literature search, there are very few reports on the use of palm oil or its derivatives alone in making alkyd resins for coating application. Some of the research groups have modified palm oil-based alkyd resins with other chemicals to form the polymers with improved properties [11–15].

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Since alkyd resin composition and synthesis procedure can have the significant effect on the properties of alkyd resins, it is therefore important to investigate on the kinetic treatment in order to understand the physical characteristic changes during of the reaction. However, the kinetic studies on alkyd resin formation especially by the fatty acid method have not received much attention. Only few studies have been reported on African locustbean and rubber seed oils [16, 17]. Recently Satheesh Kumar and co-workers have investigated kinetics of Jatropha seed oil using alcoholysis [18]. They observed that early stages of reaction followed a second-order law.

The objective of the present work is to study in more detail the kinetic behavior of polyesterification of alkyd resins from palm oleic acid with three different oil lengths by measuring the acid number of the alkyds formed, extent of reaction (P) and average degree of polymerization ($\bar{X}_n$). In this study, the alkyd samples were prepared using different method from those reported in the literature, i.e. fatty acid method. The resulting alkyds were characterized by FTIR spectroscopy and gel permeation chromatography (GPC).

Materials and Methods

Materials

Oleic acid (99.5%) from palm oil and glycerol (99.5%) were purchased from Emery Oleochemicals Sdn. Bhd., Malaysia. Phthalic anhydride, PA, was provided from P.T. Petrowidada Indonesia. Ethanol, toluene, potassium hydroxide and potassium hydrogen phthalate were reagent grade chemicals from Merck.

Preparation of Palm Oleic Acid Based Alkyd Resins

Three alkyd samples having oleic acid contents of 28, 40, and 65% were coded as POl28, POl40 and POl65 respectively. These alkyds were prepared by polyesterification reaction using a pre-weighed PA, oleic acid and glycerol (as per the formulation given in Table 1), and were formulated according to the procedure of Patton [19]. All the ingredients were charged into a 2-L four-neck round bottomed glass reactor equipped with a condenser, thermometer, mechanical agitator and a Dean-Stark decanter for separating the water evolved from the reaction. The mixture was stirred and temperature was raised to 120–180 °C for 1 h. The temperature was subsequently increased and maintained at 220–240 °C. The reactions were completed after the by-product (i.e. water of reaction), was collected to an amount according to that calculated from the reaction stoichiometry. Progress of the polycondensation reaction, during the synthesis of samples, was monitored by periodically checking the acid number of the reaction mixture. Figure 1 depicts one of the plausible mechanisms for this reaction.

Characterization Methods

Infrared Spectroscopy (FTIR)

Infrared spectra of alkyd samples were recorded on a Perkin Elmer FTIR RX1 spectrometer at room temperature, with 4 scans from 4,000 to 400 cm^{-1} and resolution of 4 cm^{-1} using the NaCl pellet technique.

Gel Permeation Chromatography (GPC)

The molecular weight distributions of the samples were determined with the GPC setup consisting of a Water 600 controller, Water 717 Auto sampler and Water 2,414 Refractive Index detector. Tetrahydrofuran (THF) was used as eluent at a flow rate of 1 mL/min. The calibration of the GPC column was performed with monodispersed polystyrene (PS) standards. Sample was dissolved in tetrahydrofuran (THF) at around 2 mg/mL.

Calculation of Extent of Reaction and Average Degree of Polymerization Based on Acid Number

The polyesterification can be experimentally followed by titrating for the unreacted carboxyl groups. Determining the acid number of the reaction mixture was carried out following a procedure adapted from ASTM D1980-87. The Patton gel point, referred to the extent of reaction when gelation might occur [19], was calculated to avoid any gelation during the reaction. In calculating Patton's gel point, the most important parameter is the alkyd constant, K, which is defined as Eq. (1),

$$\mathrm{K} = \frac{\sum \mathrm{m}_0}{\sum \mathrm{e}_\mathrm{A}} \tag{1}$$

where, m_0 is total moles present at the beginning of reaction and e_A is value of acid equivalent. The value of K should be greater than 1.00 so that gelation would not occur at 100% reaction conversion. In this work, the K values were greater than unity for all alkyds and gelation did not occur during the reactions.

The extent of reaction, P, was calculated from end group analysis of aliquots of the reaction mixture withdrawn at various time intervals during the reaction using the following Eq. (2).

Table 1 Ingredients and properties of the alkyd samples

Ingredients/properties	Alkyd samples		
	PO128	PO140	PO165
Oleic acid (%)	28	40	65
PA (%)	44	34	15
Glycerol (%)	28	26	20
Color	Dark viscous brownish	Brownish	Light brownish
Acid value (mg KOH g^{-1})	16	16	8
Molecular weight (M_n)	2,070	1,210	980

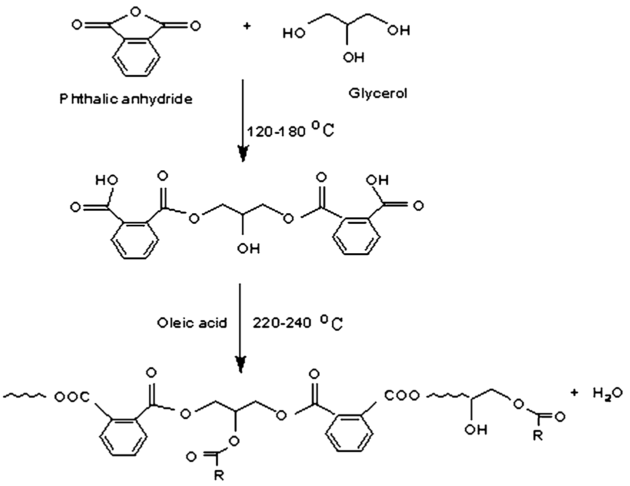

Fig. 1 A plausible reaction mechanism in the polyesterification of the alkyd samples, where R stands for $CH_3–(CH_2)_7–CH=CH–(CH_2)_7–$

$$P = [(AN)_0 - (AN)_t]/(AN)_0 \qquad (2)$$

where $(AN)_0$ = acid number at the zero time, $(AN)_t$ = acid number at the distinct time.

The average degree of polymerization, $\bar{X}_n$, defined as the average number of structural units per polymer chain and was calculated based on P using Eq. (3) at different times of reaction.

$$\bar{X}_n = (1 - P)^{-1} \qquad (3)$$

Results and Discussion

Structural Analysis by FTIR Spectroscopy

FTIR spectra of alkyd samples and oleic acid were recorded to confirm their structures, (Fig. 2). The strong band at 1,730 cm^{-1} is due to the carbonyl group in ester linkages. The weak absorption bands at 1,580 and 1,599 cm^{-1} arising from C=C are due to the aromatic rings in PA. Free hydroxyl groups are expected to be present at 3,486–3,524 cm^{-1} resulting from stoichiometric excess of glycerol in alkyds formulation and these groups are not present in oleic acid. Bands were observed at 3,004–2,854 cm^{-1} for C–H stretching aromatic and aliphatic, 1,458 cm^{-1} for C–H bending, 1,282 and 1,125 cm^{-1} for C–O–C stretching of ester. All these characteristic absorption bands support the structure of alkyd samples formed from palm oleic acid.

Polyesterification Reaction Mechanism and Reducing Acid Number

Changes in the acid number with increasing reaction time for the different alkyd samples are plotted in Fig. 3. As it can be observed the decrease in acid number is faster in the early stages than the later stages during the reaction for all samples. These changes in acid number can be elucidated on the basis of the different reactivity of primary and secondary OH groups of glycerol. Since primary OH group is more reactive than a secondary OH group, indeed rapid decrease in acid number at the initial stages of reaction occurs when primary hydroxyl groups react, followed by secondary OH groups which react in the later stages [20]. The rate of reduction in acid number in later stages is also due to the result of formation of crosslinks or branching between the chains [17] which consequently increases viscosity in the reaction medium.

With reference to Fig. 3, the most rapid decrease in acid number is observed for PO140 and the least for PO165. Therefore, the ratio of glycerol to acid in the alkyd formulation can influence on the rate of reduction acid number. Aigbodion and Okieimen also obtained similar results [16] where that rate of change in acid number for alkyd resin with 50% oil content was higher than that of alkyd resin with 34% oil and that the slowest rate of reduction of acid number was reported for alkyd resin, having 60% oil.

Extent of the Reaction and Average Degree of Polycondensation Reaction

As has been reported earlier [21], poly-functional and mono-functional polyesterification reactions can be expressed as a second-order rate law. Equation (4) below shows the rate law expression.

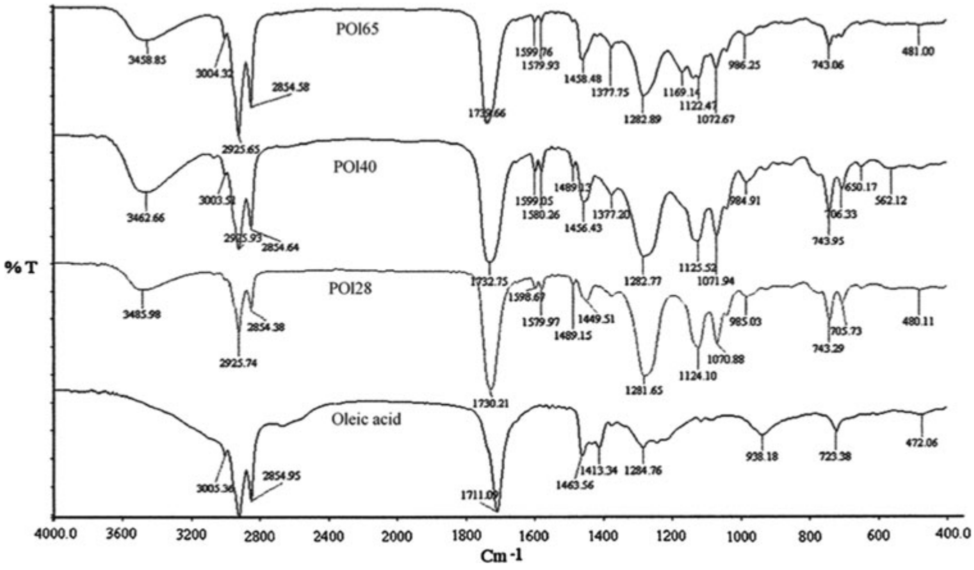

Fig. 2 Infrared spectra of alkyd samples and oleic acid

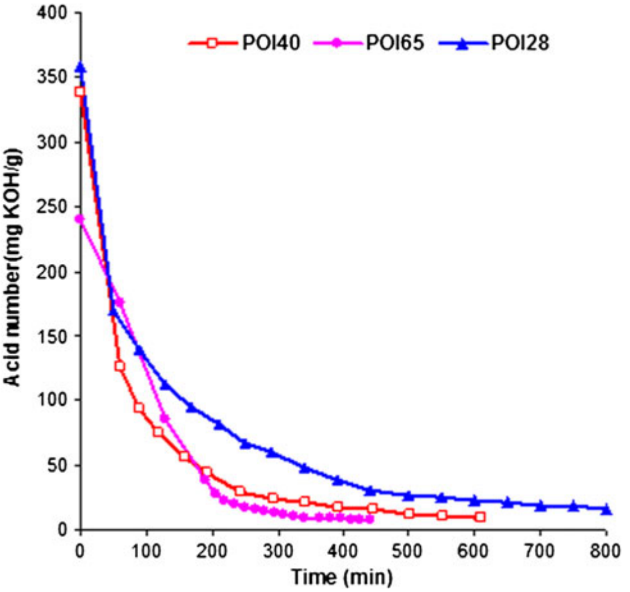

Fig. 3 Plot of changes in acid number versus reaction time for three alkyd samples

$$(1 - \mathrm{P})^{-1} = \mathrm{C}_0 k \, \mathrm{t} + 1 \qquad (4)$$

where k is the rate constant, while t refers to reaction time and C_0 is initial concentration. In this work, the acid number is substituted for C_0. Corresponding to Eq. (4), graphs of $(1-\mathrm{P})^{-1}$ against time of reaction should be linear if k is constant during the reaction. Figure 4 shows that the graphs for the three alkyds during the first stage are linear up to certain limit whereby straight-line plots are obtained and after 190–210 min the graphs deviate from linearity. The first linear part is considered to represent time of formation of linear molecules due to existence of higher content of glycerol and PA in the formulation of the alkyd samples at the initial part while the second part (non linear part) depicts period of formation of complex branching or crosslinking in the alkyd chains. Aigbodion and Okieimen reported similar trend for alkyds modified with rubber seed oil and using African locustbean seed oil in the synthesis of alkyd resins [16, 17].

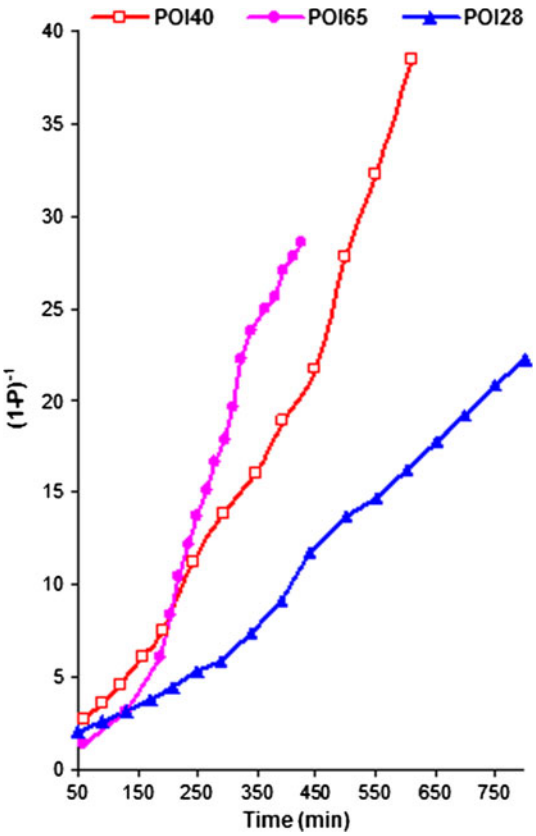

Fig. 4 Graphs of $(1 - \mathrm{P})^{-1}$ against time for the alkyd samples

Table 2 Calculated P, $\bar{X}_n$ and (*k*) at the deviate point from linearity, and extent of reaction at the end of reaction for the three alkyd samples

Samples	Kinetic parameters				
	Time (min)	P %	$\bar{X}_n$	$k \times 10^5$ g (mg KOH)$^{-1}$ min^{-1}	P % at the end of reaction
POl28	210	77.4	4.4	4.1	95.5
POl40	192	86.3	7.3	9.8	97.0
POl65	190	85.9	7.1	18.0	97.0

Table 2 shows the extent of reaction and the average degree of polymerization calculated before the points of deviation from the linear part for all the three samples. The results reveal that the extent of reaction at this region changes from 77 to 86.3% which is higher than the results obtained for reaction between PA and glycerol which varied between 75 and 80% [22]. The results obtained from palm oleic acid based alkyd resins also showed significant extent of reaction at the end of reaction as exhibited in Table 2.

The second-order rate constants, *k*, calculated through the linear part of Fig. 4 are tabulated in Table 2. Sample POl65 shows the largest value of 18.0×10^{-5} g (mg KOH)$^{-1}$ min^{-1}. These results prove that ratio of the reactants used (PA, glycerol and oleic acid) in the reaction affects the polyesterification rate. The high *k* value obtained from POl65 sample of 65% oleic acid content is reflected from the higher conversion compared to the POl28 sample. The lowest *k* and P% were obtained for POl28 which can be attributed to the relatively highest molecular weight and consequently highest viscosity. As the mixture becomes more viscous after reaching a certain conversion level, the motion of the molecular chains would become very slow. As such, POl28 shows the least extent of the reaction and rate constant.

As synthesis procedure can have significant effect on the alkyd resin properties, the composition of the natural oils is also an important contributing factor towards the alkyd resin properties. Table 3 compares the fatty acid distribution and the unsaturation content in palm oil [23], African locustbeen seed oil [16] and Jatropha seed oil [18]. From this table, palm oil and its derivatives typically have low iodine value compared with the African locustbean seed oil and Jatropha oil due to lower content of unsaturated fatty acids.

From Table 4, polycondensation rates for oleic acid based-alkyds demonstrate higher rates and higher yields than those of African locustbean seed oil [16] and Jatropha oil [18].

Traditionally, alkyd resins are prepared in a molecular weight range of 40,000–100,000 with relatively high iodine values in either aliphatic or aromatic solvents. From GPC results, palm oleic acid-based alkyds with different oil lengths prepared in this research have low molecular weight. As such, coatings obtained from palm oleic acid based alkyds are not suitable for making air dry coatings. Similar to other poor air dry alkyds, the alkyds studied in

Table 3 Some fatty acid distribution in palm oil, African locustbeen seed oil and Jatropha seed oil

Fatty acid	Palm oil (%)	African locustbeen seed oil (%)	Jatropha seed oil (%)
Palmitic acid (16:0)	39	31.00	13–14
Stearic acid (18:0)	5	7.70	6–7
Oleic acid (18:1)	45	8.80	41–43
Linoleic acid (18:2)	9	42.50	34–35
Other	2	10.00	1

Table 4 Comparing of time, extent of reaction (P), second-order rate constant (k) and oil/fatty acid content for alkyds from African Locustbean, Jatropha seed oil and Oleic acid

Oil/fatty acid	Time (min)[a]	P %[a]	$k \times 10^5$ g (mg KOH)$^{-1}$ min^{-1}	Oil/fatty acid content (%)
African locustbean	60–120	57.9–63.5	(6.0–12.5)	27–60
Jatropha seed oil	60–120	49.3–62.5	(2.1–3.4)	40–80
Oleic acid	190–210	77.4–86.3	(4.1–18.0)	28–65

[a] Measured at the point of deviation from linearity

this work need to be modified either by blending or copolymerization with other fast drying to reduce production cost and to provide crosslinking, good gloss and flexibility.

Conclusion

Palm oleic acid based alkyds, a plant based and environmentally friendly alkyds, were successfully synthesized by using the one-step fatty acid process.

The polyesterification kinetics of palm oleic acid based-alkyd resins with three different oil lengths revealed that irrespective of oil length, the alkyd samples follow second-order law at the initial stage of polyesterification time with rate constant of order of 10^{-5} g (mg KOH)$^{-1}$min^{-1}. This discloses that a linear type of polymer was formed in this stage. Branched polymeric chains were formed after 210, 192 and 190 min for POl28, POl40 and POl65 respectively. The decrease in acid number was faster for POl40 at the initial stage of reaction as well as the extent of reaction and value of the average degree of polymerization at the point of deviation from the linearity. POl28 sample, having relatively the highest molecular weight and consequently highest viscosity, shows the least extent of reaction at the point of deviation and lowest second-order rate constant for the linear part.

Palm oleic acid based alkyds investigated as non-drying alkyds are recommended for blending or copolymerization with other fast drying to produce a workable coating resin.

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