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PREPARATION AND CHARACTERIZATION OF RUBBER SEED OIL ALKYDS

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SUMMARY

Preparation of rubber seed oil alkyds were carried out to furnish more information on process control and quality of the finished alkyds. Six samples of alkyds formulated to contain 20% (I), 30% (II), 35% (III), 40% (IV), 50% (V) and 60% (VI) oil content were prepared from phthalic anhydride, glycerol and rubber seed oil using the monoglyceride method. Acid values were determined for in-process samples withdrawn at various stages of the reaction. The extent of reaction and degrees of polymerization were calculated from end-group analysis. The results suggest that end-group analysis could be used to monitor progress of reaction. The reaction occurred in two phases due to the different reactives of primary and secondary hydroxyls or glycerol with carboxyl groups. Essentially, linear chain molecules are formed in phase one while crosslinking of the chains occur in phase two. Characteristics such as colour, acid value, iodine value, saponification value and percent non-volatile matter of the final alkyds depend on the rate and extent of esterification as deduced from acid value. The level of unsaturation in the final alkyds depends on the amount of oil used.

Keywords: rubber seed oil, alkyds, extent of reaction, Degree of polymerization

INTRODUCTION

In many of the ultimate coating applications of alkyds, it is required that the alkyds be capable of forming hard and durable film after application on the substrate. Such alkyds have been found to be composed of fairly large molecules (Flory, 1949).

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Despite the potential of rubber seed oil in the preparation of oil–modified alkyds, relevant information about their preparation (such as rate of esterification at various stages of reaction and growth in molecular chains) are relatively inadequate in Nigeria. Knowledge of the events/reactions occurring at different stages of alkyd preparation allows effective control of processes of reaction in order to get alkyds of desired quality. However, estimation of extent of polyesterification and degree of polymerization (which is a measure of the sizes of molecules)could be done empirically through endgroup analysis like determination of acid value of the in process samples (Bobalek and Chiang, 1994; and Bobalek et al, 1994). similarly, Kienle et al (1939) also reported the study of polycondensation reaction by determining acid value of reaction mixture at different stages of reaction and calculating extent of reaction thereof.

Thus this work is to estimate the extent of polyesterification reaction occurring and degree of polymerization at different stages of reaction through the measurement of acid value of the reaction mixture.

MATERIALS AND METHODS

Laboratory grade phthalic anhydride and glycerol from BDH were used in the preparation of the alkyds without further purification. The phthalic anhydride had an anhydride content of 99.0% and the glycerol had a purity of 98.5%. rubber seed oil was extracted by mechanical screw press.

Preparation of alkyds

Six kinds of alkyds (Table 1) formulated to have oil content of 20% (I), 30% (II), 35% (III), 40% (IV), 50% (V) and 60% (VI) were prepared from phthalic anhydride, glycerol and rubber seed oil according to an earlier method (Aigbodion, 1991). In the present study, the condensate was drained into a Dean and Stark apparatus where the water of esterification was withdrawn and the cooking solvent (Xylene) was returned through an overflow point into the reaction flask. In each preparation, the monoglyceride was first prepared by reacting the glycerol with rubber seed oil (Payne, 1954). The monoglyceride was then cooled to a temperature of about 140 degrees centigrade before adding the phthalic anhydride. The point of adding the phthalic anhydride was taken as zero reaction time. The temperature was quickly raised to about 230°C and maintained at a range between 230 - 250°C throughout the reaction. Sampling was carried out at 30 min. intervals to determine acid value of the reaction mixture.

Table 1. *Composition of alkyds*

Ingredients	I	II	III	IV	V	VI
Rubber Seed Oil (%)	20	30	35	40	50	60
Mole ratio of phthalic anhydride to glycerol	1.00:1.44	1.00:1.32	1.00:1.32	1.00:1.29	1.00:1.25	1.00:1.10

Properties such as colour, acid value, iodine value, saponification value and percent non-volatile matter of the final alkyds were determined using standard techniques (ASTH D-1).

Calculation of percent esterification and degree of polymerization

The extent of esterification (P) with respect to acid value was calculated as follows: $P = C_o - C_t / C_o$ where C_o is the acid value at zero reaction and C_t is acid value after t reaction time; and Degree of Polymerization, $DP = 1/(1 - P)$ (Bobalek and Chiang, 1964 and Bobalek *et al*, 1964).

RESULTS AND DISCUSSION

Changes of acid value with time during reaction for each sample are shown in figures 1 and 2. These plots show that preparation of rubber seed oil alkyds by the monoglyceride process occur in two stages; that is, two different reactions take place. At the early stages of the reaction, changes in acid value were rapid. Thereafter, it became slow down to a certain extent of reaction when the decrease became sharp again.

A consideration of the likely events that occurred during the reaction is relevant in order to understand the observed trend above. In esterification reaction the rate of changes in acid value depends on the following factors; different reactivities of primary and secondary hydroxyls of glycerol with carboxyls of phthalic anhydride, proportions of hydroxyls and carboxyls, changes in temperature and removal of water of condensation (Goldsmith, 1948). It is well known that primary hydroxyls of glycerol are more reactive than the secondary hydroxyls. This has been shown for fatty acids which form unstable secondary glycerides easily converted into primary glycerides as long as primary hydroxyls are available (Nagata, 1964). Goldsmith (1948) has reported that reaction between primary hydroxyls of glycerol and carboxyl of phthalic anhydride is extremely rapid at 160°C and that this is completed at a temperature of about 200°C; and that the reaction involving secondary hydroxyl of glycerol and carboxyl of phthalic anhydride occurs at temperature between 230 and 250°C. However in this present study, immediately after the addition of phthalic anhydride to the monoglyceride the temperature was raised to 230°C.

From the foregoing therefore, it is evident that the first region of these plots represents the period when the primary hydroxyls of glycerol reacted with carboxyls of phthalic anhydride. This could only result in the formation of linear chains. Since monoglycerides are essentially alpha-substituted, there is correspondingly reduced supply of primary hydroxyls for esterification. Thus the relatively small primary hydroxyls available were readily esterified immediately hence the initial sharp decrease in acid value. After this stage, the reaction slackens until the temperature is reached when the secondary hydroxyls begin to react.

Table 2 shows extents of reaction and degrees of polymerization at various stages of reaction. Time intervals in the course of reaction during which primary hydroxyls reacted (figures 1 and 2), the extents of reaction range from 33.90% for sample V and to 51.7% for sample III. The corresponding degrees of polymerization are rather low and range from 1.51 for sample V and to 2.07 for sample III. However during the second phase of the reaction which represents the period when secondary hydroxyls reacted degrees of polymerization increased considerably even up to 33.69 for sample IV. Nagata (1969) has reported high esterification and remarkable growth in alkyd chains at temperatures above 200°C. At this second stage therefore crosslinking of the chains is thought to occur.

Characteristics of the finished alkyds are given in Table 3. The dark colour of these alkyds is due to the dark colour of the oil used. The acid values obtained are low enough since esterification cannot be 10% complete. The levels of unsaturation of the alkyds are somewhat lower than that of the oil (iodine value = 131.01). However, unsaturation in these alkyds can be said to be proportional to the quantity of oil used in the formulation. The saponification value represent ester linkages present in the alkyds. Percent non-volatile matter which represent film-forming component of the alkyds are comparable to those round earlier for alkyds modified with rubber seed oil (Aigbodion, 1991).

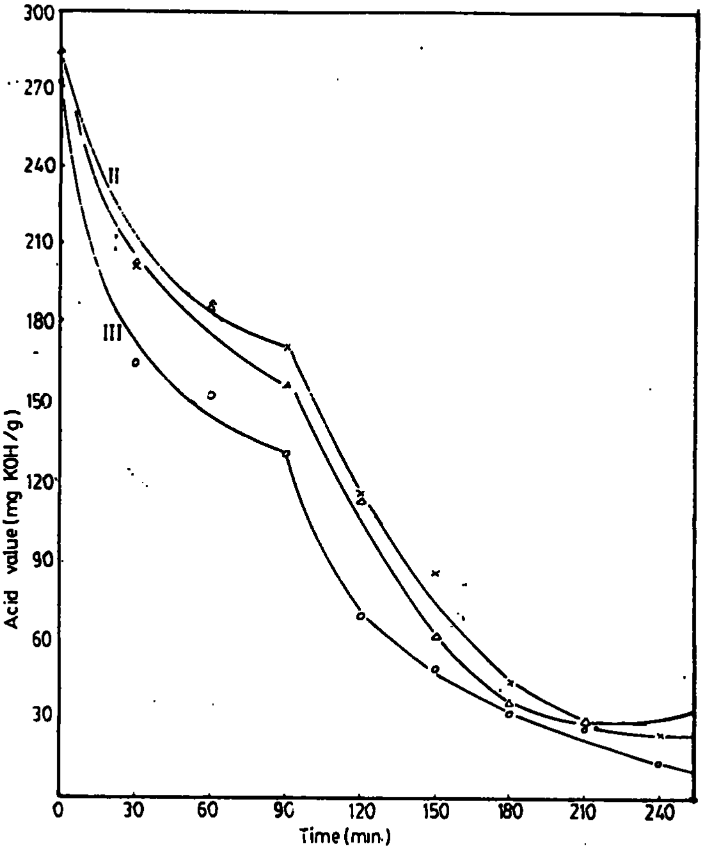

Fig. 1 Changes in acid value with time for samples I,II,III

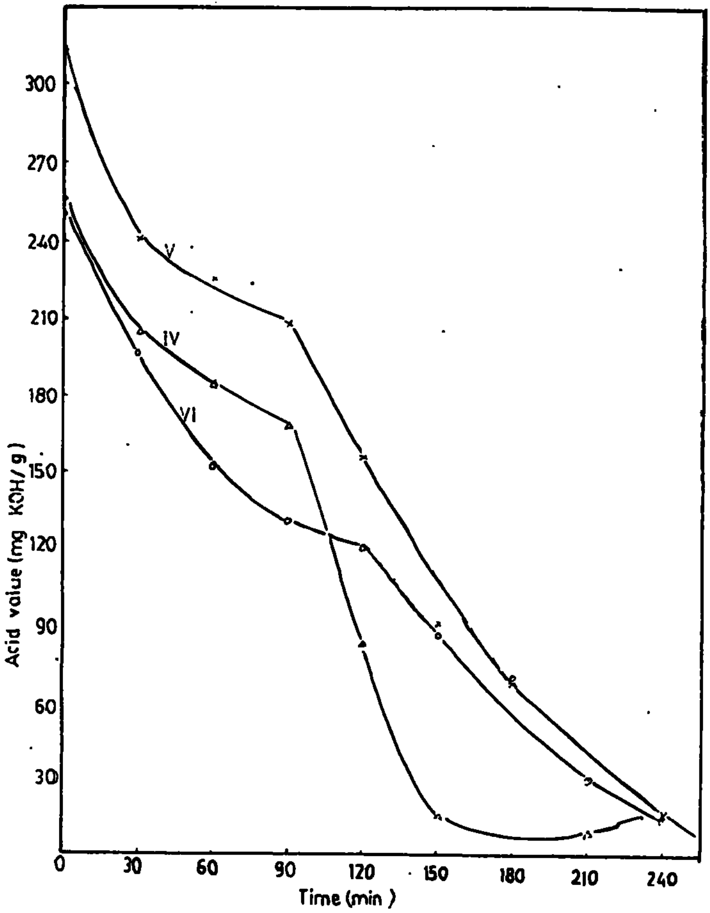

Fig. 2 Changes in acid value with time for samples IV,V and VI

Table 2. *Percent esterification (%P and degrees of polymerization (DP) in bracket at various times of reaction*

Time (Mins)	I	II	III	IV	V	VI
	%P DP	%P DP	%P DP	%P DP	%P DP	%P DP
30	25.45(1.40)	28.04 (1.39)	39.36 (1.65)	20.54 (1.26)	23.12 (1.30)	33.45 (1.50)
60	33.95(1.51)	32.60 (1.48)	43.87 (1.78)	28.75 (1.40)	28.36 (1.40)	39.19 (1.64)
90	45.08(1.82)	38.93 (1.64)	51.71 (2.07)	34.97 (1.54)	33.90 (1.51)	48.01 (1.92)
120	60.38(2.52)	58.37 (2.40)	74.83 (3.97)	79.81 (4.95)	50.46 (2.02)	51.80 (2.07)
150	78.77(4.71)	69.47 (3.28)	82.18 (5.61)	95.01(20.04)	71.20 (3.47)	65.84 (2.95
180	87.42(7.95)	84.90 (6.62)	88.44 (8.65)	-	78.64 (4.68)	72.36 (3.62)
210	89.86(9.86)	-	90.72(10.78)	97.03(33.67)	-	88.70 (8.85)
240	-	91.97(12.45)	95.73(23.40)	-	95.22(20.92)	94.65(18.69)

Note: (-) no sampling carried out

Table 3. *Some characteristics of final alkyds*

Characteristics	I	II	III	IV	V	VI
Colour	Dark	Dark	Dark	Dark	Dark	Dark
Acid value (mg KOH/g)	11.57	9.70	5.88	5.27	4.67	7.21
Iodine value (Wijs)	23.69	29.61	38.07	60.91	80.37	83.75
Saponification value	1006.32	846.33	981.93	818.27	1206.37	843.61
Non-volatile matter (%)	60.21	67.45	65.81	70.69	74.03	67.33

CONCLUSION

Essentially, the preparation of rubber seed oil alkyds by the monoglyceride process occurred in two stages. Nature of the reaction occurring depends on the proportion of ingredients used and could be understood through the measurement of acid value of the reaction mixture. Extent of reaction of the final alkyds quite exceeded the critical value of 88.80% found by Bobalek et al (1964) when drying properties of the alkyds become optimum. Thus adequate development of the estimated 13,929 tonnes of rubber seed oil that can be produced annually in Nigeria (Nwankwo *et al*, 1986) would contribute immensely to the nation's requirement of vegetable oil.

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