

Production and Characterization of Castor Oil-Modified Alkyd Resins

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Abstract: The reaction of the polyesterification of glycerol, phthalic anhydride and dehydrated castor oil leading to the formation of alkyd resins was studied. Alkyd resins of 40% (I), 50% (II), 60% (III), 40% (IV), 50% (V), 60% (VI), 40% (VII), 50% (VIII) and 60% (IX) were prepared with three different catalysts-lead (II) oxide, lithium hydroxide and calcium carbonate. The extent of reaction (PA) and average degree of polymerization (DP) were determined from end-group analysis of aliquots of the reaction mixture at various time intervals. Results on the degree of polymerization indicated formation of appreciably high molecular weight resins, soluble in xylene (3:2 dilution), with qualities varying with oil length. The untreated and dehydrated castor oil had acid and saponification values of 2.89 and 182.0 and 5.9 and 189.40, respectively. The variation of drying time with the catalyst used showed that the shorter alkyd resins (40%) dried faster than the medium (50%) and long alkyds (60%). In addition, the reaction completion time for the 40% oil alkyds was shorter than for medium and long alkyds.

Key words: Alkyds, saponification, polymerization, castor oil, resin

INTRODUCTION

Oil-modified alkyd resins and water-borne alkyds have been a major group of resins used in the surface coating industry as vehicle and binder. The popularity of alkyds as vehicles for coating are largely due to their film hardness, durability, gloss and gloss retention, abrasion resistance and other characteristics imparted on them through modification of the drying oil (Majumdar *et al.*, 1998). Large quantities of oil are also needed for the production of alkyds. In the past linseed oil, which was largely imported was the most widely used vegetable oil in alkyd resin production, resulting in the attendant high cost of production. Other vegetable oils used have included rubber seed oil, tung oil and soyabean oil.

Castor oil has been valued as non-drying oil and its lubricating and hydraulic properties. However, it has been reported that its modification by severe dehydration resulted in an oil with excellent drying properties for use in the production of alkyd resins (Spyros, 2004). Dehydrated castor oil is known for its non-yellowing film formation, outstanding colour retention and high degree of unsaturation, flexibility and adhesion in protective coating (Ogunbiyi *et al.*, 1996). Thus its high conjugated, linoleic properties, which aids rapid cross-linking at elevated temperatures make it ideal for use as a close substitute for linseed oil.

In Nigeria, the demand for alkyd resins has increased over the years even though technical information on local production is scanty. In this reaserch therefore, the effect of reaction conditions and catalyst concentration on different oil lengths of castor oil (dehydrated)-based resin as well as that of acid value, average molecular weight and degree of polymerisation on the drying times of the resins produced are examined. Comparison is also made with commercially available alkyd resins.

MATERIALS AND METHODS

Extraction and refining of oil from castor oil seed: Castor seeds were purchased from the Ogbete main market, Enugu. These were dehulled to obtain the embryo. The embryos were sun dried for one week followed by oven drying at temperatures between 70 and 80°C to reduce the moisture content. The dried seeds were milled. The oil was extracted by the solvent method using a Soxhlet extractor.

Crude castor oil obtained was refined to remove undesired impurities by degumming, bleaching and alkali refining.

Dehydration of castor seed oil: Refined castor seed oil was mixed with 0.5 g H₂SO₄ in a conical flask and heated to 250-300°C in an inert atmosphere of nitrogen. The

temperature was maintained for about one h and a vacuum of 4-6 mm Hg applied. At the end of this period, the source of heat was removed and the dehydrated oil allowed to cool.

Characterisation of castor oil: The physicochemical properties (relative density, moisture content, melting point, free fatty acids content, iodine value, peroxide value saponification value and viscosity of the oil were determined using the American Oil Chemists Society methods (AOCS, 1996).

Production of alkyd resin: Nine grades of alkyd resin were prepared with glycerol, phthalic anhydride and castor oil using the formulations shown in Table 1 (Aigbodion and Pillai, 2001). The reactions were carried out in a 1000 mL round bottom flask equipped with a variable speed motorised stirrer, nitrogen gas inlet tube, a Dean and Stark trap attached to water cooled condenser and thermometer. Heating was achieved with a heating mantle.

The measured quantity of dehydrated castor oil was poured into the flask and heated to about 120°C to expel moisture. The measured quantity of glycerol was added at this temperature before increasing the temperature to 200°C. After about 30 min, a small quantity of the aliquot was taken to check for solubility in methanol, which indicated formation of the monoglyceride and the end of the first stage of the production.

At the beginning of the second phase, the temperature was lowered to about 180°C and the measured quantity of phthalic anhydride was added, followed by addition of 300 mL xylene into the reaction mixture to remove the water of esterification by forming an azeotrope. The temperature was gradually increased to 240-250°C and maintained at this temperature for about 3 h. Aliquots were withdrawn from the reaction mixture at intervals of 30 min to check for drop in acid value. The reaction was discontinued when the acid value attained the value of about 10 mg KOH g⁻¹ and the alkyd resin allowed to cool.

Table 1: Formulations used for the production of the alkyd resins

Sample I, IV, VII	Dehydrated castor oil-120 g
40% Oil length	
Phthalic anhydride	-120.63 g
Glycerol	-59.37 g
Total	-300 g
Sample II, V, VII	Dehydrated castor oil-150 g
50% Oil length	
Phthalic anhydride	-102.96 g
Glycerol	-47.04 g
Total	-300 g
Sample III, VIII, IX	Dehydrated castor oil-180 g
60% Oil length	
Phthalic anhydride	-89.82 g
Glycerol	-30.18 g
Total	-300 g

Characterisation of dehydrated castor oil based alkyd resin:

The physicochemical properties (relative density, iodine value, saponification value and viscosity of the alkyd resins were determined using similar methods as for the oil characterization above. Drying test was conducted using the ASTM standardized test (ASTM, 1994), for resins produced with catalysts CaCO₃, LiOH, PbO and oil lengths of 40, 50 and 60%. The test was performed for surface dry (set-to-touch) and tack-free conditions.

RESULTS AND DISCUSSION

Properties of the alkyd resin: Table 2 and 3 show the properties of the castor oil and of the alkyd resin produced using modified castor oil. It was seen that the resins produced had relatively low acid values which is an advantage since higher values would contribute to corrosion. The saponification values were also within acceptable limits (Patton, 1962).

It was further observed that the iodine values increased with oil length irrespective of the catalyst used. This was due to the increase in the level of unsaturation with oil length which in turn enhanced the drying performance of the alkyd resin.

Variation of acid value with reaction time: The variation of acid value of the resins with processing time is shown in Fig. 1. It was observed that there was an initial sharp decrease which slowed down at later stages in the reaction. There was also an abrupt drop in the acid value. This was attributed to the different reactivities of primary-OH and secondary-OH groups of the glycerol with

Table 2: Physicochemical properties of castor oil

Property	Value
Saponification value (mg KOH g ⁻¹)	182.0 mg
Specific gravity (30°C)	0.9299
Average molecular weight	307.6
Percentage oil yield	44.69
Free fatty acids	1.45
Moisture content	8.77% (shelled seed) 11.25% (Deshelled seed)
Acid value (mg KOH g ⁻¹)	2.89
Iodine value (g I ₂ 100g ⁻¹)	82.80
Peroxide value	6.7

Table 3: Alkyd resin characterisation

Sample	Saponification value	Acid value	Iodine value	Colour
I	350.11	1.02	24.65	Dark brown
II	369.35	6.10	36.33	Dark brown
III	286.97	8.09	41.99	Dark brown
IV	353.50	6.87	28.72	Dark brown
V	345.68	9.22	35.43	Dark brown
VI	384.37	10.86	36.00	Dark brown
VII	328.36	8.59	25.35	Dark brown
VIII	362.89	7.27	300.50	Dark brown
IX	334.36	8.35	27.59	Dark brown

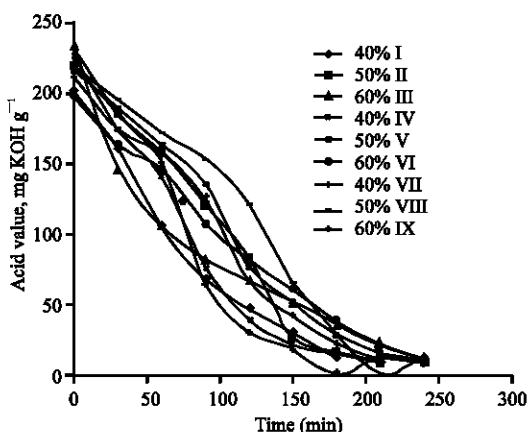


Fig. 1: Variation of acid value with time

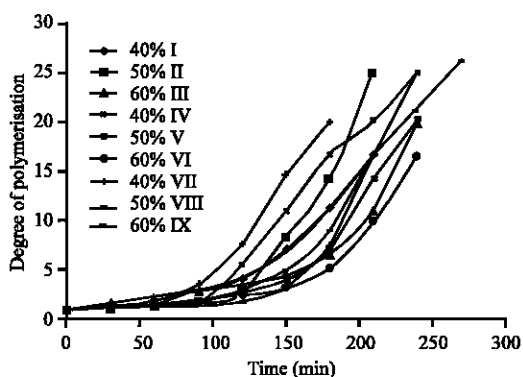


Fig. 2: Variation of degree of polymerisation with time

carboxyl group of the phthalic anhydride as reported in literature (Aigbodion and Okieimien, 1991). Thus during the initial rapid decrease in the acid value for all the samples corresponded to the reaction of the primary-OH of the monoglyceride while the other portion of the plot where reaction was slow corresponded to the reaction of the secondary-OH. It was also seen that the acid value of all the samples decreased with increase in oil length. This was due to the high amounts of di- and triglyceride present in the reaction mixture of the long oil alkyds thereby diluting the mixture and the concentration of the acid anhydride. It was also seen that the reaction was fastest with the 40% oil length, following from possible steric effects. From Fig. 1, it was evident that the reaction using PbO as catalyst proceeded with a fastest rate, followed by reactions with LiOH and CaCO₃ in that order. This variation in the reaction rate was attributed to the rate of adsorption on the active site on the surface of the catalyst. It has been reported that strong adsorption of a reacting species during heterogeneous catalysis led to retardation of the reaction (Paton, 1962).

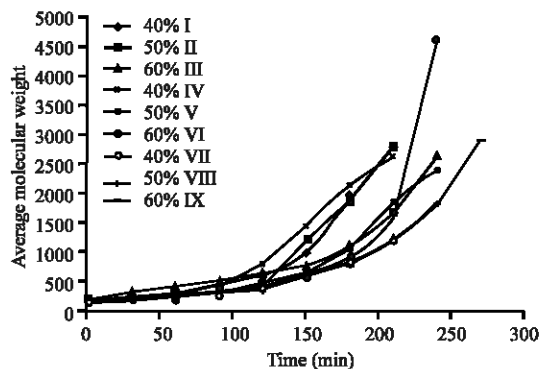


Fig. 3: Variation of average molecular weight with time

Variation of the degree of polymerization with time: The variation of the Degree of Polymerization (DP) with time is shown in Fig. 2. These plots show a linear behaviour up to a certain point followed by a deviation from linearity. This is contrary to literature position proposing a linear plot of DP against time even though the result observed in Fig. 2 has also corroborated other research reports (Sabin *et al.*, 1997). The reason for this trend was attributed to the periods of reaction of the primary-OH and the secondary-OH leading to the formation of linear and three dimensional molecules, respectively (Aigbodion and Pillai, 2001). It was also seen from these plots that the 40% oil length attained the highest degree of polymerization at the shortest time.

Variation of average molecular weight with time: The variation of the average molecular weight with reaction time for the in-process samples is depicted in Fig. 3. It was adduced that there was no reasonable increase in the molecular size of the reaction mixture at the earliest stages of the reaction. However, there was appreciable increase as the reaction progressed. The low molecular weight observed at the beginning of the reaction was attributed to the low rate of polymerization. Increase in the polymerization rate resulted in the corresponding increase in weight. This trend continued until the gelation point, at which structural changes began to occur in the polymer size of the molecules in solution. This observation is in agreement with literature reports. It was also seen from Fig. 3 that the molecular weight of the in-process samples decreased with an increase in the oil lengths as also reported in literature (Aigbodion and Pilai, 2001). It has also been suggested that an increase in oil length increases the amount of fatty acid available for reaction, which in turn results in a higher chance of termination of chain growth, resulting in lower molecular weight polymers (Nagata, 1969). The variation of the extent of reaction with time is shown in Fig. 4. These were different for the different formulation with time.

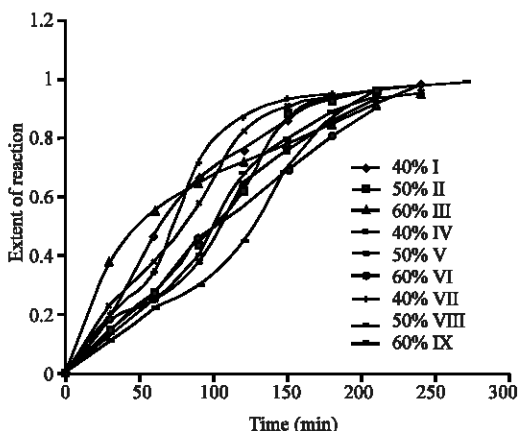


Fig. 4: Variation of extent of reaction with time

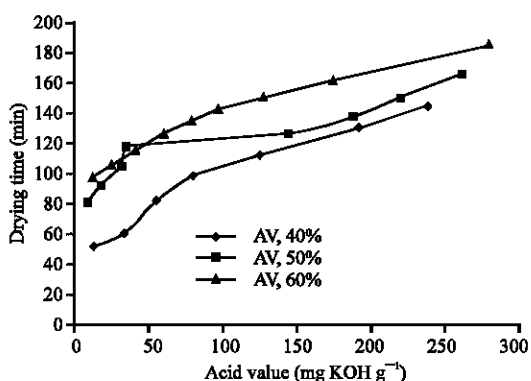


Fig. 5: Effect of acid value on drying time

Drying tests: Figure 5 shows the effect of acid value on the drying time (set-to-touch condition) of the alkyd resin film produced from modified castor oil. It was seen that the drying time decreased with decrease in acid value. This was as a result of the reaction of the acid groups leading to a decrease in the acid value of the resin and consequently enhancing drying.

The effect of degree of polymerization and average molecular weight on the drying time of the alkyd resin film is shown in Fig. 6 and 7. In addition it was seen that the drying time of the alkyd resin film decreased with increase in both average molecular weight and the degree of polymerisation. Thus, the alkyd resin film dried faster toward the end of the reaction when higher molecular species were formed. This position agrees with research reports on the formation of nucleation sites with increase in molecular weight such that the rate of drying increases.

Figure 8 and 9 show the effect of alkyd resin oil length on the drying time. It was seen that the short (40%) oil lengths reaches the set-to-touch conditions faster than the medium (50%) and the long (60%) oil lengths, respectively. This was attributed to the decrease of the

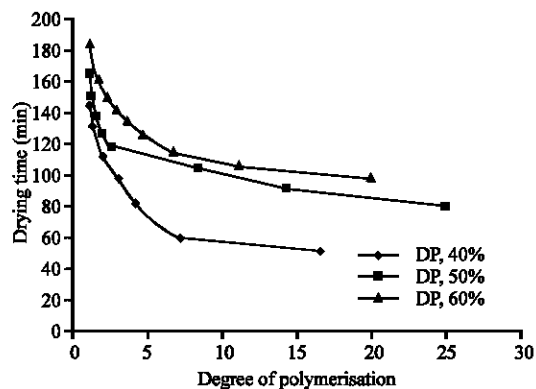


Fig. 6: Effect of degree of polymerisation on drying time

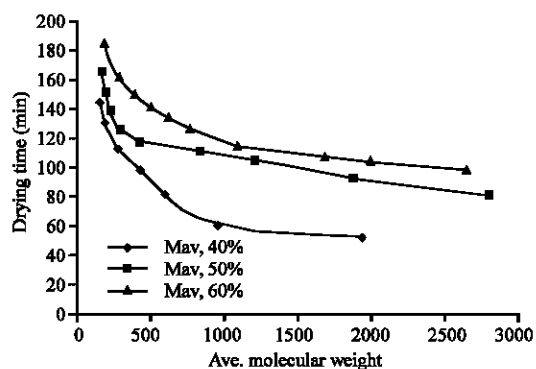


Fig. 7: Effect of average mol. weight on drying time

solubility of the alkyd in the solvent (xylene) as oil length decreases, increasing the amount of solvent embedded in the alkyd resin. This conforms to literature reports regarding to the oil type of drying mechanism used by alkyds to attain a dry state. However, this trend seemed to be reversed for the drying times required to attain tack-free conditions. In this case, the long (60%) oil length reached the tack-free stage faster than the medium (50%) oil length and the short (40%) oil length, respectively. This drying behaviour agrees with literature position. It was also observed that of the dryers used to improve drying characteristics, cobalt and manganese were most effective while zinc and cadmium had the least effectiveness (Fig. 8 and 9). The use of manganese was preferred because of environmental considerations. Similarly, among the catalysts used, it was seen that PbO gave the best result. However, due to environmental considerations, this catalyst cannot be used on an industrial scale. Even though it was seen that the short oil length (40%) resin had a shorter processing time, it consumed the highest quantity of phthalic anhydride which increased production costs. Thus, the long oil length (60%) was preferred in terms of phthalic anhydride consumption and drying time.

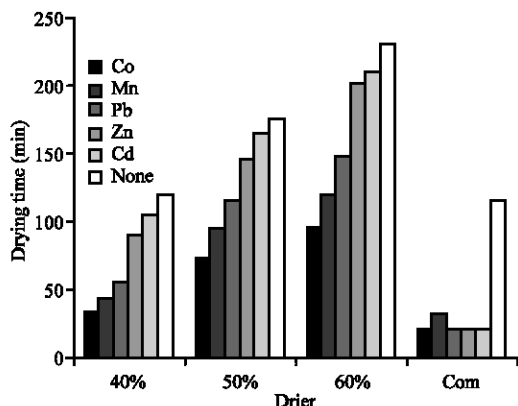


Fig. 8: Effect of drier on drying time

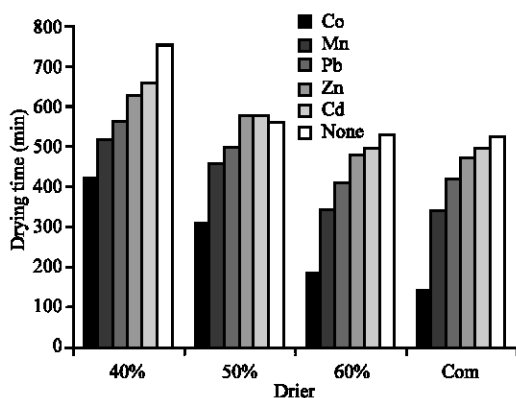


Fig. 9: Effect of drier on drying rate (Tack free)

Comparison made between the drying time of the alkyd resins produced in this research and commercially available alkyd resin produced by Intracil, an alkyd resin manufacturing company based in Emene, Enugu State, showed that the commercial alkyd resin dried faster both in the catalysed and uncatalysed states. This was attributed to the differences in the properties of fatty acid used in the formulations.

CONCLUSION

It has been shown in this research that castor oil can be modified and used for the production of alkyd resins with quick drying properties. Thus castor oil can be used as a substitute for linseed and soyabean oils. The drying performance of the resin can be enhanced by the addition of metal dryers. It has also been shown that the long oil length resin was cheaper to produce and possessed the fastest drying time.

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