Synthesis and Evaluation of Performance Characteristics of Walnut (Tetracarpidium conophorum) Seed Oil-Modified Alkyd Resin

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Abstract: Walnut seed oil (WSO) was extracted from walnut seed and employed in the production of 50% oil length Alkyd Resin (oil modified polyester) using the monoglyceride method. This involved reacting the oil first with glycerol (alcoholysis) and subsequent treatment of the monoglyceride obtained with phthalic anhydride. The walnut oil and it alkyd resins were characterized and performance characteristics evaluated for use in surface coating formulations. Walnut seed oil gave alkyd resins whose coating properties are comparable to those of commercial alkyd, as its film air-dried within a few hours and showed good chemical resistance in various solvent media such as water, brine, and acid. However, the films showed low resistance to alkali which could be due to alkali hydrolysis.
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Introduction

Alkyd resins are by far the most important class of coating resins. It is estimated that alkyd resins contribute about 70% to the conventional binders used in surface coating today. The popularity of alkyd resins as vehicle for coatings is largely due to their unique properties such as film hardness, durability gloss and gloss retention, resistance to abrasion, etc. impacted on them through modification with drying oil (Aigbodion, et al, 2001).

Generally, the alkyd contributes to coating flexibility, adhesion, durability, and gloss; while the other resins e.g. phenolic resins, confers faster drying rate, improved film hardness and resistance to chemicals. Resins chemists take advantage of the compatibility property of alkyd to prepare new set of binders that meet certain specialized end-use specifications (Zeno et al., 1999, Anthawale and Chamanker 2000, Anthawale, et al., 2000).

The oils that are mostly employed for alkyd resin synthesis are linseed, soybean, castor and tall oils (Oguniyi and Njikang, 2000, Kildiran, et al., 1996, Majumder 1999).

These oils are largely imported to Nigeria for the formulation of coatings for metal cans used in packing of beverages, drugs, food, etc. However, drying oils are available locally, which have remained untapped. These include rubber seed oil, soybean oil, walnut oil and tobacco oil (Adefarati, 1986). These drying oils owe their value as raw materials for decorative and protective coatings to their ability to polymerize or "dry" after they have been applied to surface to form tough, adherent, impervious, and abrasion resistance films. The advantages claimed in surface coating applications include excellent odor and heat bleach ability, good drying properties and more uniform polymer structure (Kirk and Othmer, 1947).

Previous studies (Ikhuoria, et al., 2005, Ikhuoria and Okieimen, 2005, Ikhuoria and Aigbodion , 2006) have shown that rubber seed oil, one of our indigenous oils in Nigeria and its derivatives can be used in alkyd resin synthesis with performance characteristics comparable to imported linseed and soybean oils alkyd resins . Walnut seed is another indigenous seed that is available in Nigeria in abundance and the seed oil has no commercial value. In this study, we hope to extract the oil, synthesize alkyd resin and evaluate the performance characteristics of the resin obtained therein.

Materials and methods sample collection and preparation

The African walnut (*T. conophorum*) used in this study were obtained from a popular market called new Benin market, Benin city, Edo state , Nigeria. The walnut was washed with distilled water and dried in a hot air circulating oven at 65^{0}C to a constant weight for 18-24 hours. The nuts were shelled and the seeds ground using an electric blender. Oil was extracted with n-hexane at 40-60^{0}C in a soxhlet apparatus. The extract was de-solvenized by distillation process to obtain the walnut seed oil, which was used for alkyd resin synthesis without further refining.

Alkyd synthesis

Walnut seed oil-modified alkyds 50% oil length was prepared according to the formulation Table 1.

Table 1: Recipe for the formulation of walnut seed oil alkyd resin

Ingredients	Quantity
Walnut seed oil (WSO)(g)	151.13
Glycerol (GLY)(g)	60.99
Phthalic anhydride (PA)(g)	87.88
Oil length%	50.3

The preparation of the resin was carried out using the alcoholysis method (Ikhuoria *et al*, 2004). In a typical experiment, the walnut seed oil was reacted with glycerol at a temperature range of 230-250^{0}C in a three-necked flask, fitted with a motorized stirrer, Nitrogen gas inlet, a dean and stark trap carrying a water condenser. Alcoholysis was complete when one part of the reaction mixture dissolved in three parts of anhydrous methanol and formed a clear solution. The reaction temperature was cooled to about 180^{0}C, and then, phthalic anhydride and xylene was introduced into the flask. Then the reaction temperature was raised to between 230-250^{0}C and then monitored to completion by determination of the acid value periodically, until it dropped to below 10.

Characterization of samples

The physic-chemical properties of the Walnut seed oil and the resin were determined using ASTM standard methods (ASTM D 1639-90, (1994), ASTM D 1541-60, (1979) and ASTM D 1962-67, (1979))

Performance characteristic of alkyd films

The performance characteristics of the films were determined in terms of drying schedule and chemical resistance. Films of walnut seed oil alkyd were prepared by applying thin spread the resin on clear glass panel and dried at room temperature. The drying process was monitored in terms of the time of set- to- touch, surface -dry and dry-through.

The chemical resistance was determined using ASTM (D 1308-67) standard test method at room temperature. The resistance of the films to different solvent media (water, NaOH, HCl, NaCl) was determined.

Results and discussion

The physic-chemical properties of the Walnut seed oil (WSO) are presented in Table 2.

The colour of walnut seed oil is golden yellow. This makes look it so promising as it compares with soybean oil. It has specific gravity of 0.9320 which implies that it is less dense than water. Its iodine value is 153.05 (gI2/100g), which when based on the drying oil classification (MacDonald, et al., 1994), puts walnut seed oil in the class of a drying oil. This is a very important requirement in alkyd synthesis as the surface formulated with the resin may want to be put to use immediately after coating. Iodine value is also another vital parameter employed in ascertaining the suitability of oil for alkyd synthesis. It shows the level of unsaturation of the oil. This result is indicative of the fact that walnut seed oil is quite suitable in alkyd synthesis as its level of unsaturation will accommodate the cross-linking reactions for alkyd to form dry, hard solid film (Sullivan, 1976). The acid value of walnut seed oil is 11.07 (mg KOH/g), as it is used to measure the level of deterioration of oil. The level of acidity is a very important property in vegetable oils that is related to their use in industrial applications e.g alkyd synthesis. Some time high acid value of oil could be due to hydrolytic reaction during processing of the oil or as result of enzymatic action in the oil bearing seed seed (Cocks, and Rede, 1966). However when desired, the acid content can be reduced (de-acidification) by refined purification processes, especially alkali refining (Aigbodion, et al, 2001).

The saponification value of the walnut seed oil is 203.45 (mg/KOH/g). The saponification value reveals the average molecular weight of the fatty acids of triglycerides present in the walnut seed oil as the mean molecular.

Table 2: physico-chemical properties of walnut seed oil (WSO)

PROPERTIES	
Colour	Golden yellow
Acid value (mg KOH/g)	11.07
Saponification value (mgKOH/g)	203.45
Iodine value (g/100g)	153.05
Specific gravity (30^{0}c)	0.9320

Physic-Chemical properties of walnut seed oil alkyd resin

Table 3 shows the Physico-chemical properties of the alkyd sample prepared from the reaction between the walnut seed oil, glycerol, phthalic anhydride. The colour of the alkyd is dark-brown as compared to that of the precursor oil (WSO).

The darkening in colour of the alkyd could been attributed to high temperatures of reaction, oxidation and the catalyst (MacDonald, et al., 1994).

The iodine value of the alkyds was observed to have decreased considerably to 84.02mg/KOH as compared to that of the crude walnut seed oil 153.05mg/KOH. This could be as a result of dimerization and polymerization reactions at the reactive double bonds of unsaturation of the oil during alkyd synthesis.

The saponification value of the alkyds was observed to have increased greatly considerably to 320mg/KOH as compared to that of the walnut seed oil. Also in comparison to the value of the crude walnut seed oil, that of the alkyd is quite high due to polymerization reaction.

The nonvolatile matter content was observed to 79.05% for the alkyd sample.

Table 3: Physic-chemical properties of walnut seed oil alkyd resin

Properties	
Colour	Dark-Brown
Iodine Value (g/I2/100g)	84.02
Acid value (mg/KOH)	14.02
Saponification value (mg/KOH)	320.02
Non-volatile matter (%)	79.05

Performance characteristics of WSO alkyd films

Chemical resistance of walnut seed oil modified alkyd films

Table 4 shows the chemical resistance of the alkyds prepared with walnut seed oil.

Films of these samples show excellent resistance to acid, brine and water but poor resistance to alkali. The poor alkali resistance of alkyds may be explained on the basis that they consist essentially of ester groups, which are known to be susceptible to hydrolysis by alkali.

Table 4 Chemical Resistance of Walnut Seed Oil Modified Alkyd Films

Solvent media	
Alkali (0.1m KOH)	2
Acid (0.1m H_2SO_4)	1
Brine (5%, w/w NaCl)	1
Water (cold)	1

1= film not removed, 2=film removed

Drying Schedule of Walnut Seed Oil alkyd

The drying schedule of the alkyd filmsis shown in Table5. It was observed that the alkyd was set to touch after 30minutes, surface dry after 2hrs. and completely dried after 8hours. Based on this result, it can be inferred that walnut seed oil alkyd could be used as binder in surface coating formulation as it showed comparable coating properties to other reported oil modified alkyd.

Table 5: Drying schedule of walnut seed oil alkyd

Characteristics	Time
Set to touch(mins)	30
Surface dry(hr)	2
Dry through(hr)	8

Conclusion

Results obtained from this study shows that the walnut seed oil modified alkyd resins exhibited good performance characteristics. This is an indication that walnut seed oil will play a great role in various industrial applications such as in the formulation of surface coatings. Considering present practices in Nigeria where imported oils, such as linseed oil resin, constitute the technical resin used in the coating and its allied industries, substituting these with walnut seed oil alkyd from our locally sourced oil seems to be a step in the right direction. It is our wish that further studies be carried out on the alcoholysis of other locally available vegetable oils.

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