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Synthesis, Characterization, Antimicrobial Activity and Performance Evaluation of Alkyd Resin derived from Mahogany Seed Oil

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ABSTRACT

Mahogany *Khaya senegalensis* A. juss commonly known as African mahogany belongs to the family *Meliaceae*, a popular medicinal plant among the Nupes and Yorubas in Nigeria. The stem bark aqueous extract is traditionally used by Yoruba and Nupe tribes to treat malaria, jaundice, oedema and headache. *Khaya senegalensis* seeds have been reported to contain about 67% oil content by weight. The oil is rich in oleic acid (66%) and used in West African cosmetics. In this research Mahogany Seed Oil (MSO) was obtained from the local market and employed in the preparation of the alkyd resin (oil modified ester) using the monoglyceride method. First, the oil was reacted with glycerol (alcoholysis) to form a monoglyceride which was further reacted with phthalic anhydride (polycondensation) to form the alkyd resin. The MSO and its corresponding alkyd resin were characterised by fourier transform infrared spectroscopy (FTIR). The alkyd resin was found to have antimicrobial activity against *Escherichia coli*, *Salmonella typhi* and *Staphylococcus aureus* as evaluated using paper disc diffusion method. The prepared alkyd resin was subsequently used to prepare surface coatings which exhibited properties that are comparable to those of commercial alkyds, as its films air-dried within few hours. Also, the films exhibited good chemical resistance in various solvent media such as brine, water and dilute acid but low resistance to alkali which could be due to alkaline hydrolysis. The surface coating also shows a very good fastness to light which suggests the potentials of Mahogany seed oil alkyd resin as binder in the preparation of surface coatings with promising antimicrobial properties.

Keywords: Alcoholysis, Glycerol, Phthalic anhydride, Xylene, Alkyd resin, Vegetetable Oil

Introduction

Vegetable oils (VO) are triglycerides which typically consist of glycerin and saturated and/or saturated fatty acids. The composition of the fatty acids contained in oil will determine its industrial use. The general formula of triglycerides is shown in figure 1. From the chemical point of view, triglycerides were found to have shown two

reactive sites, the carboxylic acid group of the fatty acid chain and the double bond in the unsaturated fatty acid chain (Odetoye *et al.*, 2008). The oils that are mostly employed for alkyd resin synthesis are linseed, soybean and tall oils. These oils are largely imported to Nigeria for the formulation of coatings for metal cans used in

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packaging beverages, foods, drugs, etc. However, vegetable oils are available locally, which remained untapped. These include mahogany seed oil, castor seed oil, tobacco seed oil, etc. The values of these vegetable oils as raw materials for decorative and protective coatings is due to their ability to polymerize or dry when applied to surface forming tough, adherent, impervious, and abrasion resistance films (Momodu *et al.*, 2011).

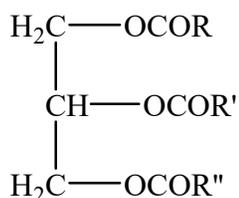


Figure 1: General structure of triglycerides.

Purification of Vegetable Oil Studies on bleaching of vegetable oils with activated charcoal and clays have been shown to be dependent on such factors as the nature of the oil (including type of colouring matter and level of unsaturation), type and quality of bleaching agent (Akolisaibemesi, 2007). Edible oil purification including activated carbon is done with powdered activated carbon (PAC). The less application of granular activated carbon is usually due to many operational constraints associated to it. The use of PAC for edible refining is always in conjunction with bleaching earth. For relative small scale operations, ready for use bleaching earth/activated carbon mixtures are offered by established bleaching earth manufacturers. Performance improvements may occur when dosing of PAC with some delay after bleaching earth (Norit, 2014).

Vegetable Oils (VOs) as Natural Polymeric Coatings are triglycerols of fatty acids. They contain suitable functionalities in their backbone such as hydroxyls, double bonds, epoxies, esters and other functional groups that can undergo several chemical reactions. Alkyd Resins (AR) are oil modified polyesters consisting of a polyol (usually glycerol, trimethylol propane or pentaerythritol), a multi functional acid (phthalic acid or trimellitic acid) and an unsaturated fatty acid formed by poly-condensation reaction. They find important application as binders in surface coatings. They are classified as short (30 – 42%), medium (43 – 54%), long (55 – 68%) and very long ($\geq 68\%$), based on the percent weight fraction of vegetable oil in the resin (Manawwer *et al.*, 2014). Alkyds resins are the reaction products of polybasic acids, polyhydric alcohols and monobasic fatty acids or oils. It is a chemical combination between polyester polymers and oil or oil derived fatty acids which enhances the mechanical properties, drying speed durability of these oleo-resinous vehicles formed over and above those compared with the oil themselves. These resins, nowadays comprise about half of all resins used in the production of surface coating materials produced by the industries. Though there are large number of synthetic resins utilize in the in formulations of paint by industries, the alkyd resins have become the most utilize one because of its versatility and low cost together with a broad spectrum of performance properties (Shaker *et al.*, 2012). The structure of a typical alkyd resin is given in Fig 1. About 60 – 70% of

an alkyd resin comprises of biodegradable raw materials e.g. fatty acids, glycerol, pentaerythritol and the rest as non-biodegradable e.g. phthalic acid. Alkyds are available in two forms i.e. ‘drying’ or ‘non-drying’ alkyds; the former refers to alkyds with drying vegetable oils, containing polyunsaturated fatty acids while the latter refers to alkyds obtained from non-drying vegetable fatty acids. They show a good gloss retention, durability, and weathering resistance while poor chemical resistance, particularly in alkaline media due to the presence of higher number of ester groups (Dutta *et al.*, 2006).

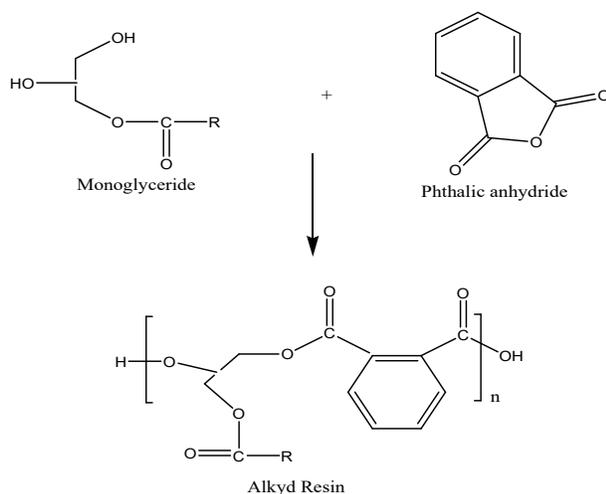


Figure 2: Chemical conversion of monoglyceride to alkyd resin.

Materials and methods

Materials

Mahogany seed oil was purchased from Kasuwar Kurmi market in Kano city, Nigeria. All chemicals and solvents used were of analytical grade and were used as received. The glassware used were thoroughly washed, rinsed with distilled water and dried in an oven overnight before use. All weighings were carried out on an

electric Mettler balance model H30AR, iodine value, saponification number, acid value, percentage free fatty acid, specific gravity was determined according to standard procedure. FTIR spectral analysis of the mahogany seed oils and alkyd resin samples were recorded in the range of 4000 – 650 cm^{-1} using FTIR spectrometer, Agilent Technologies, viscosity measurements of alkyd resin and formulated paints samples were carried out in the Instrumental Laboratories of the Department of Pure and Industrial Chemistry, Bayero University, Kano, Nigeria. Antimicrobial activity studies were carried out at the Research Laboratory of the Department of Microbiology, Bayero University, Kano, Nigeria.

METHODS

Physico-Chemical Characterization of Mahogany Seed Oil

The physio-chemical properties of the castor and mahogany seed oil samples including: refractive index, iodine value, saponification number, acid value, percentage free fatty acid, specific gravity and FTIR spectral analysis were determined in accordance to American Oil Chemists Society methods (AOCS, 1996).

Synthesis of Mahogany Seed Oil Seed Oil Alkyd Resin

The measured quantity of the oil sample (mahogany seed oil) was poured into the three-necked flask and heated to about 120°C to remove moisture. The measured quantity of glycerol was added, at this temperature before raising the temperature to 230°C. After 30minutes a small quantity of the reaction mixture (aliquot) was taken to check for solubility in methanol, which indicated the formation of the monoglyceride and the end of the first stage. At the beginning of the second stage, the temperature was lowered to about 180°C and the measured quantity of phthalic anhydride was added, followed by addition of xylene (120 ml) into the reaction mixture to aid the distillation of

water of esterification by forming an azeotrope. The temperature was gradually increased to 240 – 250°C and maintained for about 4 hours. Aliquots were withdrawn from the reaction mixture at one-hour intervals to check for drop in acid value. The reaction was halt by immersing the reaction vessel in cold water. Nitrogen was used to blanket the surface of the reaction mixture during the reaction. (Onukwli *et al.*, 2008). The amount of various ingredients used in the synthesis of Mahogany seed oil alkyd resin are presented in Table 1.

Table 1: Formulations of alkyd resin

Raw materials Resin	MSO-
Oil (g)	89.00
Glycerol (g)	62.00
Phthalic anhydride (g)	148.12
Oil length (%)	30.00

Physico-chemical characterisation of the alkyd resin

The physicochemical properties of the alkyd resins prepared from the mahogany seed oil; such as colour, viscosity, acid value and FTIR spectral analysis were determined using American oil chemists' society methods. (AOCS, 1996) and the results are shown in Table 2.

Antimicrobial activity of alkyd resins

The activity was investigated by employing a disc diffusion method, in this method the agar plates were incubated with an isolated test organism (*E. coli*, *Salmonella typhi* and *Staphylococcus aureus*) by spreading uniformly. One disc from each sample was placed in the petri-dishes with sterile forceps. The dishes were incubated for 24 hours at 37°C. After 24 hours, the antibacterial activity of test compound was found by measuring the zone of inhibition and the values

were compared with the standard drug (Ciprofloxacin) (Karigar *et al.*, 2010) as shown in Table 7.

Formulation of the alkyd paints

Three different paint formulations containing 0g, 10g, and 20g of the alkyd resin from both castor and mahogany seed oils were produced for comparison. In each formulation, red ferric oxide was mixed with white spirit before adding to the alkyd resin. Also paint additives such as extenders, thickeners and driers were added and were stirred to obtain a homogeneous mixture. Table 8 shows the various formulations of the alkyd paints prepared.

Performance evaluation of the mahogany seed oil alkyd paint films

The performance characteristics of the films were determined in terms of chemical resistance, drying schedules, and light fastness. Films of mahogany seed oil alkyd paints were prepared by applying a thin spread of the resin on clear glass panel and dried at room temperature. The drying processes were monitored in terms of the time of set-to-touch, surface-dry and dry-through (Momodu *et al.*, 2011). 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, KOH, H₂SO₄, NaCl) was determined. Table 9, 10, and 11 show detailed results of chemical resistance, drying schedules and light fastness test respectively.

RESULTS AND DISCUSSION

Physico-chemical characterisation of the mahogany seed oil

The results of the physico-chemical properties of the oils are shown in Table 1. The iodine value of the MSO was 90.30, less than 100, hence classified is as non-drying oil, iodine value measures the unsaturation of oil. The fact that,

the iodine values is lower than 100 is an indication that, the seed oil has a lower degree of unsaturation. In general, the greater, the iodine value, the higher the degree of unsaturation and the tendency of the oil to undergo oxidative rancidity (Ayo *et al.*, 2007). The saponification value of oil is an indication of the average molecular mass of fatty acids present in oil. The result shows that the saponification value of the mahogany seed oil is found to be 199.71 mg/g, slightly above the value reported by Ayo *et al.*, (2007) i.e. 195.58 mg/g. This indicated that the mahogany seed oil contains mainly fatty acids of high molecular weights. The acid value of the oil was found to be 10.87 for the mahogany seed oil. The acid value is the measure of the extent to which the constituent glycerides have been decomposed by lipase actions, and has been shown to be a general indication of the edibility of the oils (AOAC, 1980). However, the refractive index of the oil was 1.4576. It shows the values fell within the range of edible oils. The specific gravity for the oil was 0.9004, which implies that it is less dense than water (Momodu *et al.*, 2011). The percentage free fatty acid for the mahogany seed oil as shown on Table 2 is; 4.908%.

Table 2: Physico-chemical characterisation of the mahogany seed oil.

Property	Mahogany seed oil
Acid value	10.873
FFA (%)	4.908
Iodine value	90.301
Refractive index	1.4576
Saponification value (mg/g)	199.71
Specific gravity (25°C)	0.9004
Moisture content (%)	13.0

Also, the percentage moisture content of the oil was found to be 13%. This is probably because

crude oil samples as obtained from the local market might contained impurities that could cause hydrolysis of the ester linkages, thereby increasing the free fatty acid level (Nkafamiya *et al.*; 2010).

Physico-chemical properties of the prepared and commercial alkyd resin

Table 3 shows the physico-chemical properties of the alkyd resin prepared from the reactions between the mahogany seed oil, glycerol, phthalic anhydride. The color of the alkyd is dark brown for the mahogany seed oil compared to its corresponding precursor oil. The darkening in the colour of the alkyd could be attributed to the high temperature of the reaction, oxidation and the catalyst (MacDonald *et al.*, 1994). The acid values and viscosities of the alkyd are lower compared to the commercial standards C-AKD and L-AKD (Shaker *et al.*, 2012).

Table 3: Physico-chemical properties of the prepared and commercial alkyd resin

Property	MSO-Resin	C-AKD	L-AKD
Colour	Dark brown	Brown	Brown
Acid value (mg/g)	12.00	25.80	35.60
Viscosity (cp)	3.78	10.00	12.80

FTIR spectroscopy of Glycerol, Mahogany Seed oil (MSO) and Alkyd Resin (MSOR)

Figure 3 and Table 4 show the FTIR spectrum and peaks of interest for the Glycerol. From the table, the absorption band at 3291 cm^{-1} indicates OH-stretching due to alcohol, peak that appeared at 2881 cm^{-1} corresponds to sp^3 C-H stretching, while, the peak at 1110 cm^{-1} corresponds to C-O stretching of an ester. Figure 4 and Table 5 show the FTIR spectrum and peaks of interest for the mahogany seed oil (MSO). The peak at 2922 cm^{-1} corresponds to sp^3 C-H stretching, the peak that appeared at 1745 cm^{-1} corresponds to

C=O stretching of an ester while peaks at 1100cm⁻¹ and 1162cm⁻¹ correspond to C-O stretching of an ester.

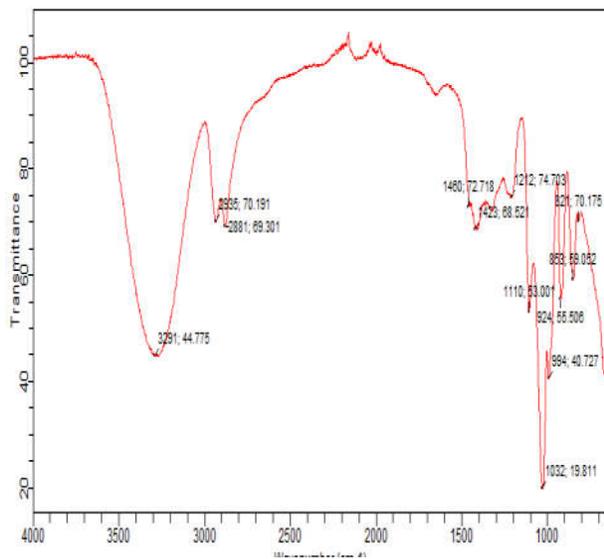


Figure 3: FTIR spectrum of glycerol

Table 4: FTIR Absorption Frequencies of glycerol

Bands (cm ⁻¹)	Functional group
3291	O – H stretching due to alcohol
2881	C – H stretching
1110	C – O stretching

Figure 5 and Table 6 show the FTIR spectrum and peaks of interest of the mahogany seed oil modified alkyd resin (MSOR). From the table, it can be seen that the O-H group in glycerol which was observed at 3291cm⁻¹ (fig. 3) disappears from the spectrum of the MSO-Resin (fig. 5). Also, the appearance of the absorption band at 1601cm⁻¹ indicates the presence of C=C stretching for an aromatic from the phthalic anhydride. Other band of interest, that were found to be present in the MSO-R spectra is the 1257cm⁻¹ which corresponds to C=O stretching of an ester.

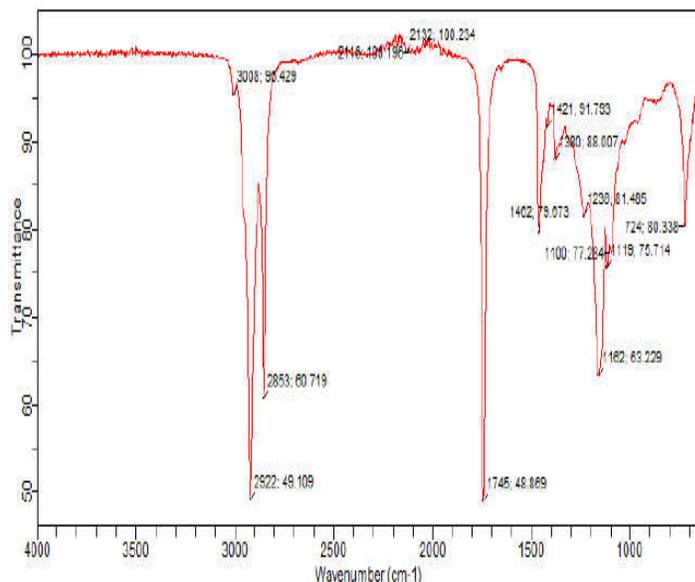


Figure 4: FTIR spectrum of Mahogany Seed oil (MSO)

Table 5: FTIR Absorption Frequencies of Mahogany Seed Oil (MSO)

Bands (cm ⁻¹)	Functional group
2922	sp ³ C–H stretching vibration
1745	C=O Stretching for esters
1100, 1162	C–O Stretching for esters

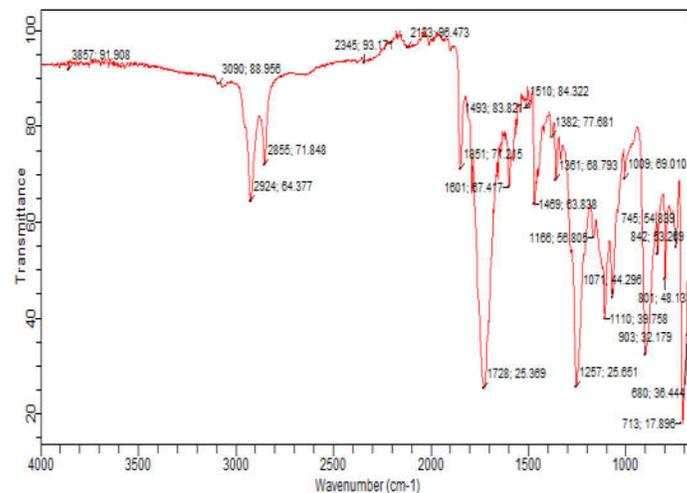


Figure 5: FTIR of Mahogany Seed Oil Alkyd Resin (MSO-Resin)

Table 6: FTIR Peak positions of Mahogany seed oil Alkyd Resin (MSO - Resin)

Bands (cm ⁻¹)	Functional group
1728	C=O Stretching due to conjugation with aromatics
1601	C=C Stretching for aromatics
1257	C-O Stretching for ester

Antimicrobial Properties of the synthesised MSO-Resin

Table 7 show the antimicrobial activity test for the mahogany seed oil modified alkyd resin (MSO Resin). The diameter of Zones of inhibition (mm) was measured for each treatment. The resin showed minimal activity against all the tested organisms at all concentrations.

Table 7: Antimicrobial Evaluation of the MSO-Resin

ISOLATES	MSO- Resin Concentrations			Control (Ciproflaxacin)
	25 mg/ml	50 mg/ml	100mg/ml	2 mg/ml
<i>E.coli</i>	07	09	12	35
<i>S. typhi</i>	07	09	10	32
<i>S.aureus</i>	07	06	06	31

Table 8: Formulation of the mahogany seed oil alkyd resin paints.

Components (g)	MSO-R ₁	MSO-R ₂	MSO-R ₃
Resin	0	10	20
Pigment	15	15	15
Extender	5	5	5
Thickener	2	2	2
Drier	0.3	0.3	0.3

MSO- R₁ = Mahogany seed oil resin paint containing 0g resin
 MSO- R₂ = Mahogany seed oil resin paint containing 10g resin
 MSO- R₃ = Mahogany seed oil resin paint containing 20g resin

Table 8, shows the constituents utilised in the formulations of the mahogany seed oil modified alkyd resin paint. From the table, three different formulations containing 0g, 10g and 20g of the mahogany seed oil modified alkyd resin were prepared and labelled as MSO-R₁, MSO-R₂ and MSO-R₃ respectively.

Formulation of Paint using mahogany seed oil alkyd resin as binder

Three different paint formulations i.e MSO-R₁, MSO-R₂ and MSO-R₃ were prepared using different amount (g) of mahogany seed oil alkyd resin as binder as presented in Table 8.

Performance evaluation of the prepared Mahogany seed oil alkyd resin paint

The performance of the mahogany seed oil alkyd resin paint was evaluated using a thin paint film. The quality parameters evaluated are chemical resistance, drying schedule and light fastness property.

Analysis of Chemical resistance of paint films

Table 9 shows the film chemical resistance characteristics of the different formulations of the mahogany seed oil modified alkyd paints. The films of the different formulations of the alkyd paints exhibited excellent resistance to acid, brine and water but poor resistance to alkali, this may be attributed to hydrolysis of the ester group by the alkali as confirmed by Momodu *et al.*, 2011.

Table 9: Chemical resistance of the mahogany seed oil alkyd paint films

Resistance	Different Paint Formulations		
	MSO-R ₁	MSO-R ₂	MSO-R ₃
Water	2	2	2
Brine	2	1	1
Dilute H ₂ SO ₄	2	1	1
Dilute KOH	1	1	1

1 = Film not removed 2 = Film removed

Drying schedule of Mahogany seed oil alkyd paint

Table 10 shows the drying schedule of the different formulations of oil modified alkyd resin paints. For the set-to-touch drying test the result was 15, 33 and 36 minutes for the MSO-R₁, MSO-R₂ and MSO-R₃ respectively. While, for the surface dry test the results are 30, 80 and 110 minutes for MSO-R₁, MSO-R₂ and MSO-R₃ respectively. The results obtained revealed that

mahogany seed oil alkyd resin paints generally have good drying property.

Table 10: Drying schedule of the different formulations of Mahogany seed oil alkyd paint

Characteristics	MSO-R ₁	MSO-R ₂	MSO-R ₃
Set to touch (mins)	15	33	36
Surface dry (mins)	30	80	110
Dry through (hour)	2	16	20

Light fastness ratings of different mahogany seed oil alkyd paints

Table 11 shows the light fastness ratings of the different alkyd resin paint formulations after exposure to high intensity artificial light for 96 hours. The fastness ratings obtained are 7, 6, and 4 for the MSO-R₃, MSO-R₂ and MSO-R₁ samples respectively. In general, the results obtained suggest that all the samples show very good to excellent light fastness property. This indicates the suitability of this paint formulation for outdoor applications.

Table 11: The light fastness rating of different mahogany seed oil alkyd paint formulations

Sample	Grade	Degree of Fading	Light Fastness Assessment
MSO-R ₁	4	Appreciable fading	Moderate
MSO-R ₂	6	Slight fading	Very good
MSO-R ₃	7	Very slight fading	Excellent

CONCLUSION

The physicochemical analyses of mahogany seed oil was successfully carried out, the oil was

successfully converted to alkyd resin (MSOR) by alcoholysis with glycerol and polycondensation with phthalic anhydride. The alkyd resin was further used in the formulation of a surface coating (alkyd paint). The coatings exhibit good chemical resistance, good drying schedule and moderate to excellent light fastness properties. In addition, MSOR shows some antibacterial activity against *E. coli*, *staphylococcus aureus* and *salmonella typhi* as evident from the observed zone of inhibition using disc diffusion method. This suggests the potentials of locally available mahogany seed oil as raw material for the synthesis of antimicrobial alkyd resin for application as binder in surface coating.

Conflict of Interest

The Authors hereby declare that there is no conflict of interest in this work.

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