Synthesis of Alkyd Resins from *Sesamumradiatum* (Black Sesame) Seed Oil

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ORIGINAL RESEARCH

Abstract- The utilization of vegetable oils as renewable feedstocks is gaining more grounds in the polymer industry as replacement for petroleum-based feedstocks due to environmental challenge. There is a dire need to meet the recent increased demand for vegetable oil feedstock for oil-based alkyd resins production. Hence, black sesame (Sesamum radiatum) oil, a non-conventional raw material was investigated for alkyds production. The oil was extracted, characterized and refined. Medium-oil alkyds, alkyd-x and alkyd-y, with 48% and 52% oil contents respectively, were synthesized via two-stage alcoholys is-poly esterification process with glycerol and phthalic anhydride. Oil yield, density, specific gravity, viscosity; iodine, acid and saponification values were 28.2%, 0.934 g/ml, 0917, 0.045 poise, 106.6 gI2/100g oil, 0.73 mgKOH/g and 188 mgKOH/g of oil respectively. Densities, specific gravities, viscosities, and acid values of alkyd-x and alkyd-y were obtained as 0.886g/ml and 0.933 g/ml, 0.869 and 0.915, 60.4 m.Pa.s and 65.5 m.Pa.s, 14.55 mg KOH and 11.93 mg KOH respectively. Successful polyesterification was confirmed on FTIR spectra. Pencil hardness test indicated highest hardness at 5H for alkyd-x while gloss retention was 60.2%. .

Keywords- Alkyds, Black Sesame oil, Polyesterification, *Sesamumradiatum* oil.

1 Introduction

Sesamum radiatum (black sesame) is an annual edible leafy vegetable, flowering plant which is popularly cultivated in Asian and African countries (Watson & Beevy, 2022; Nzikou et. al, 2010). Although, the black sesame seed is usually high in oil, up to 50% of seed weight, it is not yet a commercialized oilseed (Watson & Beevy, 2022). The oil has a pale yellow color and an appealing grain-like aroma. It is high in polyunsaturated fats, rich in vitamins A, B, and E as well as in many minerals (Nzikou *et. al*, 2010). The seed oil has been regarded as useful in lowering cholesterol and notable in oleic and linoleic acids. The oil is valued for its high quality, stability and resistance to oxidative rancidity, especially after hydrogenation (Chakraborty *et. al*, 2017). Various works have been reported on the industrial applications of sesame oil for preparation of sulphonated oil (Nkwor *et. al*, 2021), epoxidized oil (Obiegwu & Kalu, 2021), biodiesel (Mujtaba *et. al*, 2020), bio nanoocomposites (Alarfaj *et, al, 2020*) among others.

Recently, more attention is being paid to renewable raw materials (Sulaiman *et al*.,2022) and environmentally friendly alkyd coatings because the lifecycle of alkyd paints showed less effect on the environment than those based on acrylic dispersions (Shibi *et. al*, 2017). In spite of the problems associated with many new coatings' resin developed over the years, alkyd resins continue to remain of interest. Alkyds are mostly preferred owing to their versatility and relatively low costs.

Sesamum radiatum seed oil is a typical underutilized seed oil in Nigeria, with potential application for alkyd resins production for the paints industry. They are polyesters developed from the poly condensation of polyhydric alcohol, dibasic acids as well as monobasic fatty acids. They are used in the production of various finishes which include paints, varnishes and lacquers. Oil is a significant raw material for producing modified alkyd resins. The oil constituent of the paint usually determines the quality properties of the alkyds such as drying time, resistance, and consistency (Odetoye *et. al*, 2012), having a major effect on the curing and physical characteristics of the final film produced. Alkyd paints are regarded as long-lasting on surfaces and resilient to wear and tear.

Tung, castor and linseed oils have been widely utilized in the production of alkyd resins (Odetoye *et. al*, 2012). The higher degree of unsaturation in the oil chain of an alkyd corresponds to shorter drying times for its coatings (Bender, 2013). Classification of alkyds is based on the ratio of fatty acids to the remaining constituents of the resin. Long oil alkyd contains over 55% fatty acids, medium oil alkyd contains between 45 and 55%, while short oil class usually has about 30% fatty acids. Most of the fatty acids are from vegetable oils (such as soybean), though fish oil may also be used (Bender, 2013). Although, few works (Mustapha *et al*., 2023; Chinweuba & Chendo, 2017; Igbo *et al*., 2014) have been reported on the more popular sesame (*Sesamiumindicum*) oil-based alkyd resin preparation, there is dearth of research on black sesame (*Sesamiumradiatum*) oil based alkyd resins. Hence, we report black sesame oil alkyd for the first time. This study is aimed at producing alkyd resins from black sesame (*Sesamum radiatum*) seed oil of Nigerian origin.

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Section D- MATERIALS/CHEMICAL ENGINEERING & RELATED SCIENCES
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2 Materials and Methods

2.1 Materials and Sample Preparation

Dried Sesamum radiatum (black sesame) seeds were obtained from a farmer at Oja Oba market in Ilorin West, Kwara State, Nigeria. The black sesame seeds were cleaned by hand picking /removal of impurities and unwanted matter. The seeds were then ground using a mechanical grinder to ease solvent penetration and boost the extraction of the oil (Elleuch *et. al*, 2007).

Fig. 1: Seeds of *Sesamum radiatum*

2.2 Extraction of the Seed Oils

Soxhlet extractor setup was used for the extraction process using n-hexane as the solvent. 100 g of ground seeds were charged into the thimble and placed in the extractor heated with the aid of heating mantle, set at 70 °C for 2 hours per each run. Then, the solvent was recovered by distillation in the set up at same temperature 70 °C.

2.3 Physicochemical Characterization of *Sesamum radiatum* Oil

2.3.1 Degumming of Sesamum Radiatum Oil

Dry degumming was employed for the refining of the sesame oil. A 75 g mass of the Sesamum radiatum seed oil was charged with 25 ml of 0.1% phosphoric acid and stirred. About 0.08g, 2% acid-activated bleaching earth was added at a temperature of 90°C. The mixture was allowed to settle. After a contact time of 12 hours, the spent earth was separated from the oil by filtration. The main purpose of degumming was to remove the phospholipids and gums from the oil (Gupta, 2017).

2.3.2 Acid, Iodine, and Saponification Value Determinations

The level of unsaturation (iodine number) of the oil was determined using Wijs/Hanus method. DIN53241-1:1995-05 (Das and Dash, 2014). The AOAC methods (AOAC, 2000) were employed for acid and saponification value determinations of black sesame oil. The acid value was based on titration in ethanol and petroleum ether using phenolphthalein as an indicator. The determination of saponification value was done by completely saponifying the oil, by adding a known amount of KOH, the excess of which was determined by titration. The samples were also analyzed on a gas chromatography-mass spectrophotometer (Agilent 5975C) using Helium gas as a carrier while compound identification was achieved using the NIST library. The sesame oil spectra were also recorded on Fourier Transform Infrared Spectrophotometer.

2.3.3 Determination of Density, Specific Gravity, and Viscosity

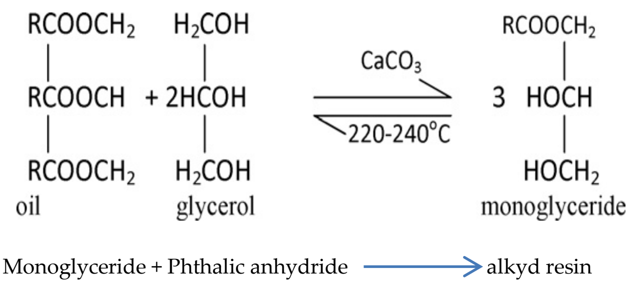
The density of the sample was obtained using the formula; Density = Mass of oil divided by the volume of oil weighed (Chetz,1999). The absolute viscosity of the oil was measured in S.I. units of Pa.s (Issam and Cheun, 2009). Ostwald viscometer was used in the determination of the sesame seed oil viscosity. The specific gravity (SG) was calculated using the formula, SG = Mass of oil divided by the mass of equivalent volume of water.

2.4 Synthesis of Sesamum Radiatum Oil-Based Alkyd Resins

Medium-oil alkyds (Table 1), alkyd-x and alkyd-y, with 48% and 52% oil contents respectively, were synthesized via two-stage alcoholysis-polyesterification process (Scheme 1) using glycerol and phthalic anhydride. The 48% *Sesamum radiatum* oil-based alkyd (alkyd-x) was synthesized by charging 25 g of sesame oil to a three-necked flask (Fig. 2) connected to a condenser, furnished with temperature monitoring, stirrer, nitrogen source, and trap. After heating the oil to 200 ^{0}C, 12.5 g glycerol and 0.25 g calcium carbonate were added to the oil. After the addition, the mixture was heated to 240 ^{0}C for 2 hours then cooled to 140 ^{0}C and then 15 g of phthalic anhydride was added. At this point, the reactants were heated again to 240 °C and the reaction was monitored towards acid number decrease to 15 mgKOH/g. The reaction was quenched by immersing the reaction vessels in cold water. Acid number indicates free fatty acid quantity (Islam & Jamari, 2014). The 52% *Sesamum radiatum* oil-based alkyd (alkyd-y) was prepared similarly with the composition indicated in Table 1.

Table 1. Formulation of black sesame medium oil alkyds

Materials (g)	Alkyd-x(48%)	Alkyd-y (52%)
Sesame oil	25.0	25.0
Phthalic anhydride	15.0	12.2
Calcium carbonate	0.25	0.25
Glycerol	12.5	11.0



Scheme 1. Alcoholysis- polyesterification

2.5 Characterization of Alkyds

2.5.1 Physicochemical Properties

The physicochemical characteristics of *Sesamum radiatum* oil alkyds were determined accordingly as described earlier in 2.3.3.

2.5.2 Pencil Hardness and Film Adhesion Tests

The value for the hardness test was recorded as the hardest pencil which does not scratch the alkyd film surface (Turner, 1998). Pencils used were between 5B and

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5H. The adhesion test was done based on the methods described in ASTM D3359-2009. The peeled area was observed by a magnifier, and results were based on percentage of the film removal (Razee et. al, 2017). The gloss retention time was measured using ASTM D523 standard test method with spectrum at 60°C. The percentage of the gloss was calculated using:

$$PGR = \frac{Gloss_{final}}{Gloss_{initial}} \times 100$$

Fig. 2: *Sesamum radiatum* oil alkyd resin synthesis

2.5.3 FTIR Analysis

The alkyds and the oil samples FTIR spectra were recorded on the Fourier Transform Infra-Red Spectrophotometer with frequency in the wavenumber range of 4000 to 400cm-1 at the Kwara State University Laboratory, Malete, Kwara State, Nigeria.

3 Results and Discussion

3.1 Extraction and Characterization of Sesamum Radiatum Oil

Table 2 indicates the physicochemical characteristics of the oil. The acid value of 0.73 mg KOH/g oil obtained shows that the oil has desirable low free fatty acids (LFFA) content and is relatively less than the value of 2.8 mg KOH/g oil (Igbo *et. al*, 2014) obtained earlier. The iodine value of 106.6 gI2/100g of oil indicates the semi-drying oil class which was a major consideration for its utilization in alkyd resin production. The value is relatively lower than 120gI_2/100g and 112gI_2/100g obtained in two earlier works respectively (Igbo *et. al*, 2014; Chakraborty *et. al*, 2017). The saponification value of 188 mg KOH/g oil is similar to the value of 190 mg KOH/g oil obtained in another work (Chakraborty *et. al*, 2017) for black sesame oil.

Table 3 indicates the fatty acid content of Sesamum radiatum oil. The GC-MS result implies that black sesame oil is composed mainly of linoleic acid (41%) which is an unsaturated fatty acid contributing to the iodine number. Fatty acid profile of the black sesame oil indicated the predominant presence of oleic and linoleic acids that were reflected in the degree of unsaturation and semi-drying nature of the oil.

Table 2. Physicochemical characteristics

Parameters	*Sesamum radiatum* Black sesame oil
Specific gravity	0.917
Density (g/ml at 25°C)	0.934
Colour	Light yellow
Acid value (mgKOH/g oil)	0.73
Iodine value (gI_2/100g oil)	106.6
Saponification number (mgKOH/g of oil)	188
Viscosity (Pa.s)	0.045 at 38°C
Percentage oil content (%)	28.2%

Table 3 Fatty acid profile of the black sesame oil

Fatty Acids	Composition (%)
Linoleic	41
Oleic	39
Palmitic	8
Stearic	5

3.2 Preparation of Sesamum Radiatum Oil Based Alkyd Resins

Figure 3 indicates that while polyesterification reaction progresses, the acid value decreases. This drop was more pronounced at the early stage of the reaction due to the depletion of the abundant free acid during the course of reaction (Odetoye *et al*.,2013).

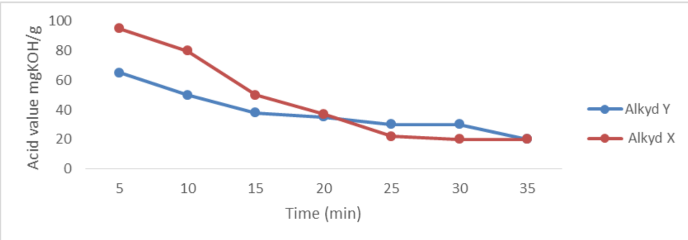

Fig. 3: Acid value vs reaction time (polyesterification)

3.3 Sesamum Radiatum Oil Alkyds Characterization

3.3.1 The Physicochemical Characteristics of the Sesamum Radiatum Oil Alkyd Resin's Oil

Table 4 shows the physicochemical properties of the alkyd samples. The dark colours of alkyd-x and alkyd-y may be the effect of high-temperature conditions during the synthesis (Otabor and Ikhuoria, 2019). The acid value of the alkyd samples was obtained in the range of 6.02 to 14.6 mg KOH/g. A similar occurrence was obtained in previous studies using Sesamumindicum (Mustapha et al., 2023), melon seed oil, palm oil, Jatropha oil (Odetoye *et. al*, 2012), Melina seed oil, and rubber seed oil (Igbo *et. al*, 2014; Uzoh *et. al*, 2019; Otabor and Ikhuoria, 2019).

3.3.2 Colour, Pencil Hardness and Film Properties of the Alkyds

Table 5 shows some physical properties of the films of Sesamum radiatum oil-based alkyd resins. The pencil hardness was found to be slightly higher for alkyd-x, which contains higher amount of phthalic anhydride. An increase in phthalic anhydride increases pencil hardness due to the rigidity of the aromatic moiety present in the polymer chain (Bora *et. al*, 2014). The pencil hardness of the coating is comparable to that of Jatropha oil alkyds

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Table 4. Physiochemical properties of *Sesamum radiatum* oil-based alkyd resins

Parameters	*Sesamum radiatum* Alkyd-x	*Sesamum radiatum* Alkyd-y	Palm oil alkyd (Islam *et al.*, 2014	*Sesamumindicum* alkyd (Mustapha et al,2023)
Percentage yield (wt%)	78.4%	73.9%	67.0%	-
Color	Dark brown	Coffee	Light brown	Brown
Acid value(mg/KOH/g)	14.55	11.93	4.27	6.02
Viscosity (mPa.s) at 25°C	60.4	65.5	92.1	21.96
Specific gravity	0.87	0.92	0.89	1.06
Density	0.89	0.93	0.92	-
Samples	**Color**	**Pencil hardness**		**Adhesion**
Alkyd-x	Dark brown	2H		Passed
Alkyd-y	Coffee	H		Passed

(Odetoye et. al, 2012). The similarity can be due to the semi-drying property of both oils. These adhesion characteristics of both resins are considered to be reasonably good. The percentage gloss retention was gotten at 60.2%.

3.3.3 FTIR Analysis of Oil and Alkyds

FTIR spectra in Figs. 4 to 6 indicate the structure and functional groups of the oil and alkyds which were found comparable to earlier work (Nzikou *et. al*, 2012). For the oil (Fig 5) the absorbance peak at around 722cm-1 was due to aliphatic –(CH_2)– group vibrations while the peaks around 1039 cm^{-1} were due to the C-C stretching frequency. The characteristic C=O stretch frequency of ester and C–H stretch of alkane can be shown by the peaks around 1746cm^{-1} and 2854cm^{-1}, respectively. The O-H stretching resonance was shown with the wide absorption band at 3650- 3100.

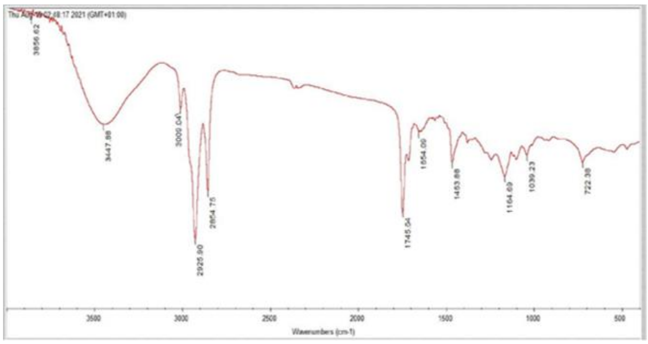

Fig. 4: Black sesame oil FTIR spectrum

For alkyd-x, peak at 750cm-1 shows the aromatic –CH bending vibrations while peak at 923 cm^{-1} represents C-C stretch pulsation. C-O-C stretch vibrations are portrayed at 1042 cm^{-1} and 1291 cm^{-1} correspondingly for aliphatic and aromatic moieties. The peaks at 1714 cm^{-1} for the carbonyl group(C=O) stretching vibrations were obtained for the same for oil, at 2887 cm^{-1}. The peak representing asymmetry and symmetric vibrations for –CH_2 appeared at around 2945 cm^{-1} and 3405 cm^{-1} showing stretching vibration for –CH moiety. Similarly, in the alkyd-y spectrum, the aromatic –CH bending vibrations are shown by the peak at 746 cm^{-1}. The peaks around 990cm-1 is due to C stretching vibration and C-O-C stretching vibration can be described by the peaks at 1042cm^{-1} and 1290cm^{-1} correspondingly for aliphatics and aromatics (Chakraborty *et. al*, 2017). The characteristic of ortho-substituted aromatic hydrocarbon is indicated at peaks around 1580 cm^{-1} and 1599 cm^{-1}.

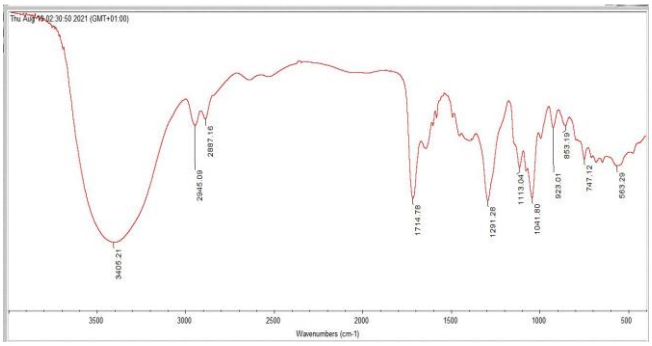

Fig. 5: Alkyd-x FTIR spectrum

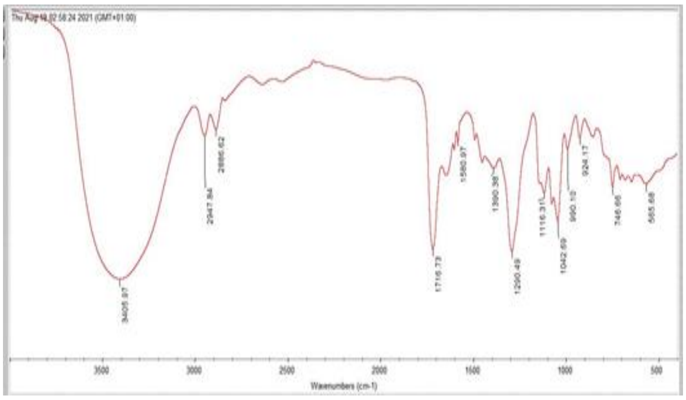

Fig. 6: Alkyd-y FTIR spectrum

4 CONCLUSION

The extracted *Sesamum radiatum* seed oil which was found to be a semi-drying oil, rich in oleic and linoleic acid, was successfully utilized as a suitable feedstock for the synthesis of medium oil alkyd resins. The physiochemical properties, film properties, and FTIR analyses of the resins confirmed the successful synthesis of the alkyds. Hence, Sesamum radiatum oil-based alkyd resins are a potential binder that needs to be harnessed for the paints industry. Further studies can be done to improve the properties of Sesamum radiatum oil modified alkyd by blending with other polymer resins and with the inclusion of driers.

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