AMERICAN JOURNAL OF INNOVATION IN SCIENCE AND ENGINEERING (AJISE)

ISSN: 2158-7205 (ONLINE)

VOLUME 1 ISSUE 1 (2022)

Indexed in

doi | Crossref | Google Scholar | Directory of Research Journals Indexing DRJI | INDEX COPERNICUS INTERNATIONAL | OCLC WorldCat

PUBLISHED BY: E-PALLI, DELAWARE, USA

American Journal of Innovation in Science and Engineering (AJISE)

Volume 1 Issue 1, Year 2022
ISSN: 2158-7205 (Online)
DOI: https://doi.org/10.54536/ajise.v1i1.709
https://journals.e-palli.com/home/index.php/ajise

Synthesis and Characterization of Fatty Polyamide from Dimer Acid Prepared from *Afzelia Africana* seed oil

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Article Information

Received: October 04, 2022

Accepted: October 11, 2022

Published: October 16, 2022

Keywords

Afzelia Africana, Polyamide, Dimer Acid, Surface Coating, Seed Oil, FTIR, Characterization

ABSTRACT

Afzelia africana seed oil was extracted from its oil-bearing seeds via soxhlet extraction with n-hexane as the solvent. The oil was characterized and the percentage yield, specific gravity, refractive index, iodine value, acid value and saponification value were; 24.6%, 0.9184, 1.4708, 105.75 (Wij's), 5.61 (mg KOH/g) and 199.155 (mg/KOH/g) respectively. Dimer acids were synthesized by heating 50 g of the oil at 340 ^oC in nitrogen inert atmosphere using iodine crystals as catalyst. Characterization of the dimer acid indicated that refractive index, iodine value, acid value and saponification value were 1.4904, 126.90 (Wij's),7.01 (mgKOH/g) and 136.043 (mgKOH/g) respectively. Fatty polyamide was synthesized by heating the dimer acid and ethylenediamine at a temperature of 210 ^oC in an inert atmosphere. Fourier Transform Infrared spectroscopy (FTIR) analysis for both the synthesized dimer acid and fatty polyamide was obtained. The dimer acid shows a peak at 1697.41cm^{-1} due to C=O stretch of carboxylic acid, a peak at 1080.17 cm-1 which corresponds to O-H bend of carboxylic acid. A peak corresponding to C-H stretch of alkane group shown at 2916.42 cm-1, a peak at 1111.03 cm-1 due to C-O-C stretch of fatty ester group. The polyamide showed a peak at 1180.47 cm^{-1} which corresponds to C-N stretch of aliphatic amine group. The significant difference in absorption between the synthesized dimer acid and fatty polyamide is the peak at 3533.71 cm-1 which corresponds to amide N-H stretching absorption that was present in the polyamide due to the higher number of hydrogen bonds formed by amide groups. The findings revealed that Afzalia africana seed oil is semi-drying in nature based on its iodine value and has the desirable qualities needed for producing surface coating vehicles.

INTRODUCTION

Surface coating is the application of decorative and protective materials in liquid or powder form to substrates Surface coating are substances that are generally applied to the surface of other materials to change the surface properties, such as color, gloss, resistance to wear or chemical attack, or permeability, without changing the bulk properties. Surface coatings include such materials as paints, varnishes, enamels, vegetable oils, greases, waxes, concrete, lacquers, powder coatings, metal coatings, and fire-retardant formulations (Lambert *et al*, 1998). In general, organic coatings are based on a vehicle, usually a resin, which after being spread out in a relatively thin film, changes to a solid. This change called drying, may be due entirely to evaporation (solvent or water), or it may be caused by a chemical reaction, such as oxidation or polymerization. Opaque materials call pigments, dispersed in the vehicle, contribute color, opacity, and increase durability and resistance (Norries, F.A. (1995). Organic coatings are usually referred to as decorative or protective, depending upon whether the primary reason for their use is to change the appearance or to protect the surface (Anhwange B.A. *et al*, 2004)

Over the years, organic coatings have been formulated based on petroleum products. The diminution of this natural resource and the global crisis centered around it, coupled with various environmental issues such as petroleum gas flaring, oil spillages and other generated industrial and domestic wastes that are discharged into the environment makes it imperative that petroleum feedstock should be substituted with sustainable resource material (Adeyeye, A. *et al*, 1992) Organic coatings are widely used for protection of surface against corrodents and to provide aesthetic appeal. Various types of polymeric organic coatings from renewable resources like lignin, cellulose, and vegetable oils have been reported as potential candidates for surface coating (Finar, I.L. 2006). Vegetable oils are one of the most important renewable resources for production of polymeric materials like alkyd, polyester amide, polyamide, polyether amide, polyurethane, polyester, and poly-epoxy resin in combination with commercial polymers such as polyvinyl alcohol, polystyrene and polymethylmethacrylate (Boxall, J. *et al*,1980). Vegetable oils from linseed, pongamia, olive, castor, Jathropha, soybean, mesuaferrea, cotton seed, neem (Azadirachta indica), tung, corn, and Annonasquamosa are used for the synthesis of polymeric coatings. The utilization of vegetable oil has attracted great attention in both scientific and industrial applications due to easy availability, environmental friendliness, low volatile organic matter, and cost-effectiveness(Iboronke, A.A., *et al*, 2005).

Plant seed oils are composed of triglyceride molecules containing different and varying percentages of saturated and unsaturated fatty acids. However, chemical modifications such as epoxidation, aminolysis, ozonolysis, hydroformylation, polyamidation and urethanation can be performed on the triglyceride oil to tune physico-chemical properties of the seed oils (Iboronke, A.A., *et al*, 2005).

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LITERATURE REVIEW

Afzalia africana plant belongs to the family of Fabaceae. It is a leafy green plant. It is popularly known as "Yiase" in Tiv language and "akparata" in Igbo language speaking of the south eastern part of Nigeria. Afzalia africana plant is known in many localities within Nigeria and other countries, such as Senegal, Ghana, Sierra Leone, Togo, and Ivory Coast. Afzaliza africana is very attractive, medium sized tree with bright green leaves that turn to attractive yellowish color during harmattan seasons in Nigeria. It has upright crown and the dropping branches resemble a eucalyptus from a distance. Afzaliza africana is a deciduous plant that bears 6-10 hard, shiny, oblong black bean-shaped seeds with red orange aril with extractable oil (Peerman, D.E. 1972).

Surface coating covers a wide range of categories and emissions. In different countries of the World, major surface coating operations include aerospace, auto-refinishing, furniture finishing, metal can-coating and paper coating. Emission depends on the types of surface coating operation and the material used for coating. Surface coating materials are primary organic polymers dissolved in a solvent or suspended in an emulsion (Mohammed, M.I. *et al* 2008). The material may be applied to the product by brush or by spraying. In the process of "drying" the solvent or emulsion carrier evaporates. The organic polymer is left behind to coat the surface. Regardless of the application technique, the volatile constituents of the finish are released to the environment. However, the application technique can determine how much finish must be used and the corresponding amount of air emission per product (McMurry, J. 1996)

Fats and oils are naturally occurring esters found in plants and animals as energy storage compounds. They are the members of a larger class of naturally occurring compounds known as lipids, which are a heterogeneous group of organic compounds grouped together on the basis of their solubility properties. They do not solubilize in water but are soluble in non-polar solvents such as diethyl ether, petroleum ether, acetone, n-hexane. This means that fats and oils are isolated from the cells and tissues of plants and animals by extraction using non-polar solvents (McMurry, J. 1996). Therefore, oils extracted from plants can be called "vegetable oils" and fats extracted from animals' tissues are collectively called "animal fats".

Vegetable oils and animals fats can be hydrolyzed because they fall under the class of lipids that contains ester linkages unlike cholesterol and other steroids that belong to the class of lipids without the ester linkages. Although vegetable oils and animal fats appear different; animal fats like butter and lard are solids whereas vegetable oils like soybean oil and *Afzelia africana* seed oil are liquids at room temperature, the difference arising from their chemical composition; they are closely related. The oils are chemically composed of low melting fatty acids mostly unsaturated, while fats are formed from high melting fatty acids mostly saturated fatty acids. Fats and oils are triacylglycerol's (as triglycerides), triesters derived from glycerol and a variety of long chain carboxylic acids. These long chain carboxylic acids are called fatty acids (Saunders, K.J. 1988).

MATERIALS AND METHODS

Study Area

The research was carried out in Makurdi, town of Benue State Capital. The town is located between latitude 70380N – 70500N, and longitude 80240E and 80380E and 104 meters elevation. It is situated in the Benue valley in the North central region of Nigeria.

Sample collection and preparation.

Afzelia africana seeds were obtained from Adikpo, Kwande Local Government Area of Benue State. The seeds were dehusked and then sun-dried for three weeks after which the seed were ground into a meal using mortar and pestle. The seeds meal was then used to extract the oil via soxhlet extraction using n-hexane as the solvent.

Extraction of *Afzelia africana* seed oil

Exactly 351 g of the ground seeds meal was weighed and tiled in a white handkerchief. The meal was then loaded into a thimble fitted onto a 350 mL round-bottom flask containing 250 mL of n-hexane and anti-bumping chips. A condenser was then connected on the open end of the thimble. The set-up was supported by a retort stand after placing the round-bottom flask on the heating mantle of the extractor (soxhlet extractor). The solvent was then heated at 90 0C so that it vaporized and condensed into the thimble and hence, extract the oil from the loaded meal, after which the solvent and oil siphoned back to the round-bottom flask. This process repeated itself automatically for six hours after which oil extraction was complete. The meal was then removed and the solvent was distilled off the oil so as to obtain the extracted oil as well as the solvent for further use.

Percentage oil yield was calculated using the formula;

$$\text{Percentage oil yield} = \frac{\textit{weight of the extracted oil}}{\textit{total weight of the sample}} \times \frac{100}{1} \quad [1]$$

Characterization of the Extracted Oil

Specific Gravity

A clean empty 50 mL density bottle was carefully weighed. This was then filled with distilled water (H_2O) and weighed again with the water inside it. The bottle was then emptied and dried, then filled with the *Afzelia africana* seed oil and the weight of the bottle containing the oil was determined using an electronic weighing machine. The specific gravity was calculated from this relationship, Specific gravity =

$$\frac{\text{weight of empty density bottle}}{\text{weight of density bottle+water}-\text{weight of density bottle+Afzelia africana seed oil}} \quad [2]$$

Refractive Index

The refractive index of the extracted oil was determined with an Abbe refractometer at 30^0C after which temperature correction was made to obtain the correct refractive index of the oil. A small portion (0.1g) of *Afzelia africana* seed oil was spotted on the glass slide of the refractometer, which was connected to a light source. The temperature adjuster was used to adjust the temperature and the refractometer was viewed through the monitoring glass space to take the scale reading, which was the sample`s refractive index. The refractive index was computed using the formula,

Refractive index correction=
scale reading + [(Temperature -20) ^{0}C x 0.000078] [3]

Acid Value

About 25 mL Diethyl ether was measured with a 50 mL measuring cylinder and mixed with 25 mL of 98% ethanol in a clean beaker. 1mL of 1.0% phenolphthalein indicator solution was added to the mixture. This was then neutralized with three drops of 0.1 M of NaOH solution. The neutralized with solvent mixture was then used to dissolved 2.0 g of the *Afzelia africana* seed oil in a conical flask. This was then titrated with 0.1 M NaOH solution, shaking continuously until the pink color persisted for 15 seconds. The acid value was calculated using the relationship,

$$\text{Acid value} = \frac{\text{Title value (mL) X 56.1(mg KOH/g)}}{\text{Weight of the oil}} \quad [4]$$

Iodine Value

The extracted oil (0.3 g) was weighed accurately (with the help of a chopping pipette) into a stoppered 250 mL flat bottom conical flask. A 10 mL measuring cylinder was used to transfer 10 mL of carbon tetrachloride (CCl4) into the flask to dissolve the oil. Exactly 20 mL of Wij`s solution measured with a 50 mL measuring cylinder was added and the flask was stoppered with a stopper already moistened with KI solution. This was mixed properly and allowed to stand for 30 minutes, 15 mL of the 10 % KI solution and 100 mL of distilled water were added afterwards and mixed. The mixture was then titrated with a 0.1 M $Na_2S_2O_3$. $5H_2O$ solution using a 1 % starch indicator just before the end point. The blank was carried out using similar procedure, but omitting only the oil sample to be analyzed. The iodine value was calculated thus,

$$\text{Iodine value} = \frac{\text{(Blank−Titie value) mL X 12.69(Wij's)}}{\text{Weight of oil}} \quad [5]$$

Saponification Value

2.0 g of the extracted oil was weighed into a conical flask with the aid of a dropping pipette. 25 mL of the alcoholic KOH solution was added to it. This mixture was then heated under reflux on a boiling water bath for 1 hour with occasional shaking. At the end of the 1 hour, the flask was removed from the water bath. 1 mL of 1% phenolphthalein indicator was added to the flask. The mixture was then titrated with 0.5 M HCl solution while still hot. The same procedure was observed for the blank omitting only the oil. The saponification value was calculated using the formula,

$$\text{Saponification value} = \frac{\text{(Blank−Titre value) mL x 28.05(mg KOH/g)}}{\text{Weight of oil}} \quad [6]$$

Synthesis of Dimer Acid

The method adopted by (A.O.C.S. 1960) was used to synthesize the dimer acid without modification. The dimer acid was prepared by heating 50g of the extracted oil in the three neck round bottom flask fitted with mechanical stirrer and stream of nitrogen gas at the temperature of about 340 ^{0}C for 40 minutes using 1g of iodine crystals as a catalyst.

Characterization of the Dimer Acid

The same procedure carried out for the characterization of the extracted oil was repeated for the synthesized dimer acid to determine its refractive index, acid value, iodine value and saponification value as described by using 0.1 g, 2.0g, 0.3g and 2.0g of the dimer acid respectively (Heraldsson, G. 1983)

Synthesis of Fatty Polyamide from the Dimer Acid

Exactly 5.625g of the dimer acid and 1.125g of ethylenediamine were introduced in a three necked round bottom flask followed by the addition of 1cm^3 of 85 % orthophosphoric acid and 11.25 cm^3 xylene. The mixture was heated in an inert nitrogen atmosphere at 210 0C for 2 hours (Williams, K.A. (1966).

RESULTS AND DISCUSSION

Oil yield

The light yellow oil (510.51 g) was extracted from 2104.02 g of ground *Afzelia africana* seeds. The percentage yield of the oil was found to be 24.26%. The result signifies that *Afzelia africana* seeds are a good source of vegetable oil. The result is in agreement with the 25.80 % yield

Table 1: shows the results of the physico-chemical parameters of both the *Afzelia africana* seed oil (AASO) and the dimer acid prepared from the extracted oil.

Parameters	Extracted *Afzelia Africana* seed oil (AASO)	Dimer acid synthesized form *Afzelia africana* seed oil (AASO)
Specific gravity	0.9184	-
Refractive index	1.4708	1.4904
Iodine value (Wij's)	105.75	126.90
Acid value (mgKOH/g)	5.61	2.01
Saponification value (mgKOH/g)	199.155	136.043

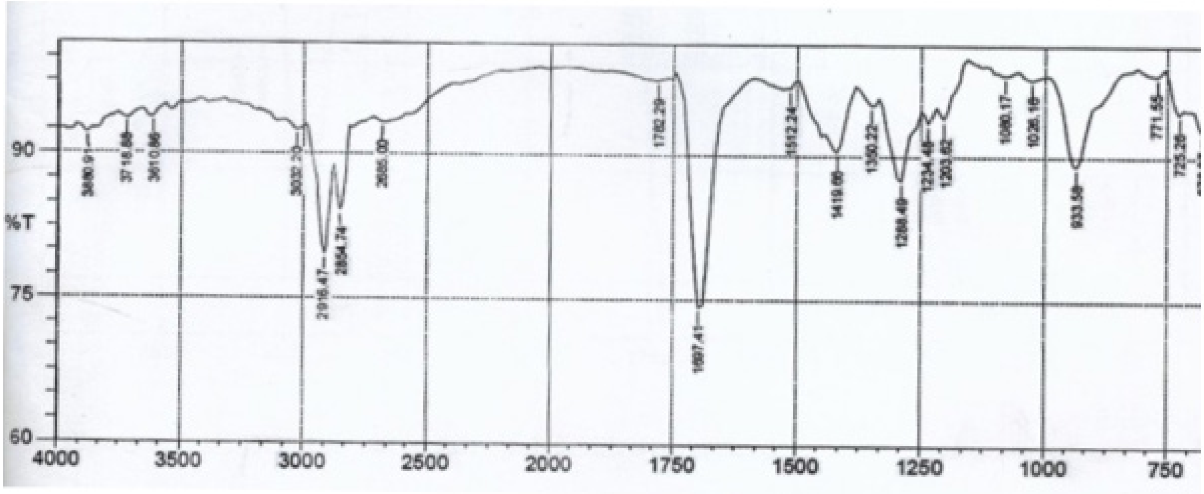

Figure 1: Fourier Transform Infrared spectroscopy (FTIR) of spectrum of the synthesized dimer acid.

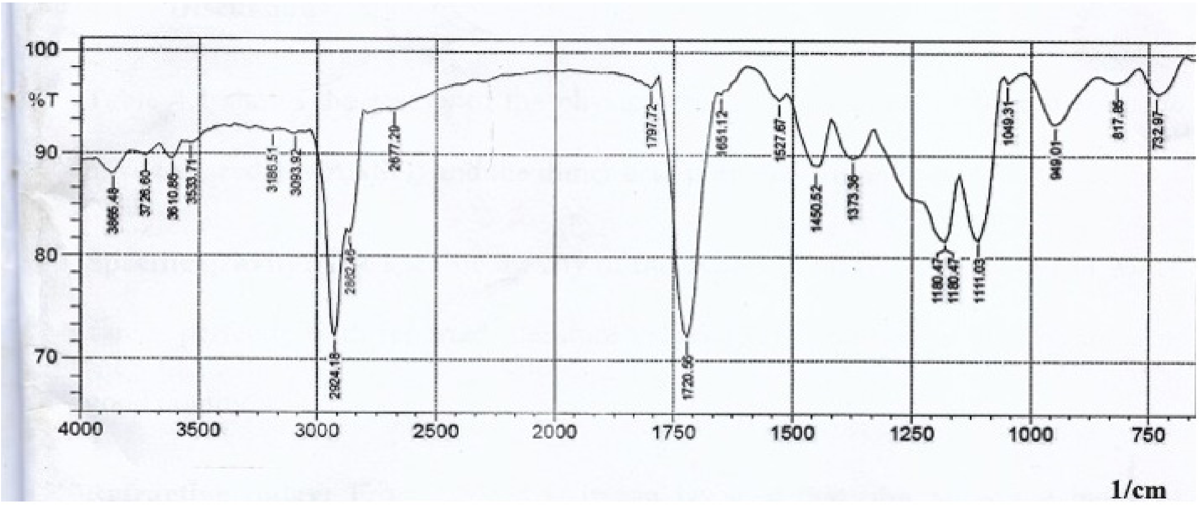

Figure 2: Fourier Transform Infrared spectroscopy (FTIR) spectrum of fatty polyamide synthesized via dimer acid intermediate.

reported by (Adebayo, A.A. 1997) though it was lower. The discrepancy may be as a result of the different extraction procedures used to obtain the oil from the oil bearing seeds.

Specific Gravity
The specific gravity of the extracted oil (AASO) was 0.9184 which agrees perfectly with previous works on the characterization of *Afzelia africana* oil seeds (Premamoy, G. 2002) this shows that the oil is of good quality.

Refractive Index
From table 1, it can be seen that, the refractive index of synthesized dimer acid is slightly higher (1.4708) than that of the extracted *Afzelia africana* seed oil (1.4904). This is due to an increase in the degree of unsaturation as a result of dimerization, since refractive index increases with increase in the degree of unsaturation (Bakker, P.J., 1999).

Iodine value (Wij's)
Iodine value of 126.90 of the synthesized dimer acid is an indication of a higher degree of unsaturation. The decrease in the iodine value of 105.75 for the extracted *Afzelia africana* seed oil (AASO) shows a decrease in the degree of unsaturation. Since, iodine values increase with the degree of unsaturation. It is applied in monitoring progress of hydrogenation, degree of fractionation and for identity characterization of fats (Oboh, F.O. 2004).

Acid value (mgKOH/g)
The acid value for the synthesized dimer acid from the *Afzelia africana* seed oil is higher than that of the extracted oil (5.61). This is due to the fact that, more structural residue were present during dimerization of the oil, since the acid value increases with increasing free fatty acid and structural residue (Freitas R. F.R., *et al.*, 2015).

Saponification value (mgKOH/g)
The saponification value of the extracted oil is higher (199.155) than that of the synthesized dimer acid (136.043) from AASO. This is due to increase in molecular weight of the synthesized dimer acid, since saponification value decreases with increasing molecular weight. Therefore, the higher the saponification value, the lower the molecular weight of the fatty acids and the

better the quality of the oil (Dupuy, B., Mille, G. 1993).

Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The dimer acid shows a peak at 1697.41cm^{-1} due to C=O stretch of carboxylic acid, a peak at 1080.17 cm^{-1} corresponds to O-H bend of carboxylic acid. A peak corresponding to C-H stretch of alkane group shown at 2916.42cm^{-1} a peak at 1111.03cm-1 due to C-O-C stretch of fatty ester group (Williams K.A. 1966). The significant differences in absorption between the dimer acid and fatty polyamide is a peak at 1180.47cm^{-1} which corresponds to C-N stretch of aliphatic amine group and a peak at 3533.71 cm^{-1} which corresponds to the amide N-H stretching absorption that is present in the fatty polyamide due to the higher number of hydrogen bonds formed by amide groups (Haborne, J.B. 1973).

CONCLUSION

Afzelia africana seed oil (AASO) was extracted from its oil bearing seeds and some of its physico-chemical constants were determined. Through the results of this research, *Afzelia africana* seed oil (AASO) is shown to embody the desirable quality attributes necessary for the synthesis of dimer acid and then fatty polyamide. Results from the measurement of the physico-chemical parameters and Fourier Transform Infrared Spectroscopy (FTIR) analysis of *Afzelia africana* seed oil (AASO) based dimer acid and fatty polyamide showed that, it has reasonable quality to be used as a good raw material for synthesis of dimer acid and fatty polyamide (polymeric organic coatings) which can be used as surface coating vehicles.

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