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Production of Bioresin from Groundnut (Arachis Hypogaea) Oil.

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ABSTRACT: Continuous use of petrochemicals for production of composite polymer matrices has been declining in recent time not only because of the economic and depletion problems associated with fossil fuels but also due to health and environmental challenges. These and other problems geared the concerted efforts across the globe to explore renewable resources for production of composite polymer matrices. Vegetable or plant oil had been found to be one main valuable source of renewable composite matrices (bioresins). This paper presents experimental report on production of bioresin from groundnut (Arachis Hypogaea) oil. The bioresin was produced via Epoxidation and Acrylation route. Analysis of the epoxidized groundnut oil (EGO) and acrylated epoxidized ground nut oil (AEGO) respectively, showed that the degree of epoxidation (DOE) was 74.2% while the degree of acrylation (DOA) was 60.7%. The density of the bioresin was determined to be 1.4g/cm^3 while the viscosity after treatment with styrene was 374Cp. Confirmation test conducted on the bioresin suggested that the resin is suitable for composite production and thus can serves as alternative resin to the petrochemical types. Commercial production of the bioresin will not only help to ameliorate some of the challenges confronting petrochemical resins for composite applications, it will also contribute to wealth creation and diversification of the economy.

KEYWORDS: Composite material, Synthetic resin, Bioresin, groundnut oil, Iodine value, Epoxidation, Acrylation

I. INTRODUCTION

Composite material is one of the emerging materials widely used nowadays in the fields of Air, Land and Sea transportation among others for production of materials that have high strength to light weight ratio coupled with corrosion resistance, [1].

The material generally consists of two major constituents, reinforcement (fibre) and polymer matrix (commonly called resin). Going by [2] and [3], Polymer matrix (Resin), is a viscous and transparent liquid either from organic or inorganic source that will transform (cured and hardened) into solid when treated with suitable catalyst, accelerator with or without heat. Those from inorganic sources (such as petrol and chemicals) are commonly called synthetic resins while those from organic sources (such as plant or animal) are called bioresin or renewable resins. The bioresins are often biodegradable and non-toxic unlike the synthetic ones.

Resin (polymer matrix) constitutes a significant volume fraction (above 50%) of any fibre reinforced composite material that requires proper impregnation of the reinforcement. Despite the fact that the reinforcement (fibre) carries the bulk of the load that the composite is subjected to, it is hardly possible to use the reinforcement alone as a single component in any load bearing structure without the resin (polymer matrix) while the resin in some cases may be used alone in a low load bearing components. This indicates the importance of resin as a constituent in composite material, [4].

There are different types of resins (bioresins and synthetic resins), however according to [2] any type of resin has several functions; it is a binder that holds the reinforcement (i.e. fibre) in place, it transfers external loads to the reinforcement and redistributes the load to surrounding fibers when an individual fiber fractures and laterally supports the fibers to prevent buckling in compression among others and also protect reinforcement Before recent time, the bulk of the resins (Polyester, Vinyl Ester, Epoxy and Phenolic resins, etc) used across the globe for wide range of engineering activities are synthesized from nonrenewable petrochemicals substances like Xylene, ethylene, propylene; benzene and vinyl chloride by polymerization and other processes. These traditional (convectional) resins have been

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found to have some health and environmental challenges despite its non renewability, [5] and [6]. According to [7], the bulk of the synthetic resins used in Nigeria are imported materials. Despite their adverse effects of importation on economy, the materials are scare and only found in commercial cities and some major towns. These and other challenges geared the concerted efforts by researchers across the globe to source for alternative materials that are not only renewable and sustainable for resin production, but also the resin itself must not pose any health and environmental problems.

There are different renewable sources, edible and non edible oils that have been used to produce bioresins by researchers across the globe. Few of these oils include soya bean oil, Palm oil, Hemp seed oil, Mango seed kernel oil, Cotton seed oil, etc. The use of these oils for bioresin production did not only help to cushion the adverse effects associated with synthetic resins, but also add more value to them and encourage more production thereby busting the economic activities.

One of the renewable oils that is affordable and sustainable in Nigeria and many other countries for bioresin production is ground nut oil (Arachis hypogaea). Going by [8], ground nut is a major crop grown in the arid and semi-arid zone of Nigeria. The crops are either grown for its nuts, oils, its vegetative residues (haulms) or for foreign exchange by exporting them.

Going by the report of [9], physico-chemical properties of four varieties of ground nuts widely grown in Nigeria have been determined. One of them that capture the attention of this work is the most cultivated groundnut (Gargajiya ground nut) in Nigeria especially the northern part that produced over 85% of the country output. The ground nut oil has the highest oil yield of 37.80% and highest iodine value of 81.947mg iodine/100g oil in crude state among the others.

Nigeria is among the countries that produce ground nut in commercial quantities for consumption and export purposes. Going by [10], over 34,000,000 thousand tonnes are produced in the world annually while about 3,000,000 thousand tonnes per annum in Nigeria.

Using ground nut oil for bioresin production will not only help to ameliorates some of the challenges confronting petrochemical resins (synthetic resins), it will also contribute to wealth creation and diversification of our economy.

II. MATERIALS AND METHODS

2.1 Materials

The crude ground nut oil used was bought directly from one of the local millers in Bauchi town. The experiment was conducted in ATBU, Bauchi where the available measuring devices/apparatus, chemical compounds and testing machine were used. Plate 1 shows sample of groundnut from which the unrefined groundnut oil (GO) used was extracted, plate 2.

Plate 1. Sample of groundnut **Plate 2**. Sample of groundnut oil used

2.2 Methods

2.2.1 Production of Epoxidized ground nut oil (EGO) using Performic acid (PFA)

The epoxidation chemical reaction was conducted according to ATSM standard reported by [11]. The reactions were conducted in a 2-neck round bottom flask placed on a hot plate equipped with magnetic stirrer. After inserting the magnetic bit into the reaction vessel, 200 g of the ground nut oil was weighed into the vessel. The required amount of formic acid (FA) and hydrogen peroxide (H_2O_2), calculated for 1:2.5 mole ratios (1ml FA to 2.5ml H_2O_2) was premixed, and charged into the dropping funnel to allow formation of PFA. Under continuous stirring, the PFA was added drop wise at a flow rate of 2 ml per minute using dropping funnel for the first 1hour. The reaction was allowed to continue for about 3 hours to completion.

At the end of the complete reaction of, the epoxidation reaction mixture was transferred to a separating funnel and the organic layer was

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thoroughly washed with distilled water, 2% sodium carbonate and 3% sodium chloride solutions to neutralize the residual acid and remove the resulting salt from the reaction mixture. The final product was then dried at 70°C on the hot plate.

The reactions that preceded the epoxidation process were:

In the first stage, formic acid (FA) was made to react with H_2O_2 to form Performic acid (PFA) and water.

$$FA + H_2O_2 \longrightarrow PFA + H_2O \quad \ldots\ldots (1)$$

In the second stage, the PFA was made to react immediately with the olefinic double bond (DB) of the oil to produce the epoxided oil (EO).

$$DB + PFA \longrightarrow EGO + FA \quad \ldots\ldots (2)$$

where,

FA = Formic Acid,

PFA = Performic Acid,

DB = Double Bonds of the ground nut oil

EGO = Epoxidized ground nut Oil

H_2O_2 = Hydrogen peroxide and H_2O = Water.

Alternatively, the reactions may be written as:

$$\underset{\text{Formic acid}}{HCOOH} + \underset{\text{Hydrogen Peroxide}}{H_2O_2} \longrightarrow \underset{\text{Performic acid}}{HCOOOH} + \underset{\text{Water}}{H_2O} \quad \ldots\ldots (3)$$

$$\underset{\text{Performic acid}}{HCOOOH} + \underset{\text{unsaturated substrate}}{H_3C-\overset{H}{C}=\overset{H}{C}-R} \longrightarrow \underset{\text{Epoxide oil}}{H_3C-\overset{H}{\underset{O}{C}}-\overset{H}{C}-R} + \underset{\text{Formic acid}}{HCOOH} \quad \ldots\ldots (4)$$

Plate 1 shows the epoxidation reaction set up while plate 2 shows sample of the epoxidized ground nut oil produced.

Plate 3. Epoxidation reaction set **up**

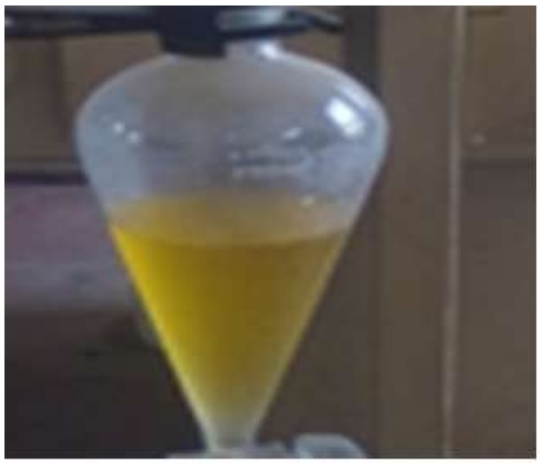

Plate 4. Sample of EGO produced from epoxidation reaction

2.2.2 Determination of degree of epoxidation (DOE)

In this work, theoretical conversion of carbon-carbon double (C = C) bond of the ground nut oil (GO) triglyceride to epoxidized ground nut oil (EGO) is considered. Going by the reports of [12], [13] and [14] respectively, the theoretical method of determining DOE of any renewable oil

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with known iodine value is thus calculated for the ground nut oil. In this method, the theoretical oxirane oxygen content (OOC) conversion in 100 g of oil sample is given by the expression.

$$OOCtheo = \left[\frac{(IV0/2Ai)}{100 + (IV0/2Ai)Ao}\right] A_o \times 100 \quad \ldots\ldots\ldots\ldots(5)$$

Where the atomic weight of iodine, Ai = 126.9, the atomic weight of oxygen, A_0 =16.0, and the initial iodine value (IVo) of the oil sample is 81.9

Also from the above authors, the experimental oxirane oxygen content (OOCexpt) can be calculated after the titration method for 100 g of oil using the formula:

$$OOCexpt = \frac{1.6\ N\ (V-B}{W} \quad \ldots\ldots\ldots\ldots ..(6)$$

Where;

N is the normality of hydrogen bromide (HBr) in acetic acid

V is the volume (ml) of HBr consumed for sample

W is the weight (g) of sample and B is the volume (ml) of HBr for blank

The degree of epoxidation or percentage conversion to oxirane is given by:

$$DOE = \frac{OOCexpt}{OOCt\ heo} \times 100 \quad \ldots\ldots\ldots\ldots(7)$$

Where OOCexpt is the experimentally obtained oxirane oxygen and OOCtheo is the theoretically obtainable oxirane oxygen. The results are found in table 1.

2.2.3 Production of acrylated epoxidized ground nut oil (AEGO)

Acrylated epoxidized mango kernel oil (AEMKO) was prepared according to ASTM standard reported by [15], [16] and [17] respectively. In this study, epoxidized mango kernel oil (EMKO) was reacted with Acrylic acid in a 250 ml round-bottom flask equipped with a magnetic stirrer and a reflux condenser. Hydroquinone which was used as a free radical inhibitor was added to the contents in the flask. The molar ratio of EMKO: acrylic acid was 1:10. The flask was heated to 90°C until the light yellow colour changed to milky colour which indicated complete reaction. The mixture was cooled to room temperature and diluted with toluene before purifying by washing with distilled water. The final product was dehydrated with anhydrous sodium sulfate and the solvent was evaporated using an evaporator.

The chemical equation preceding the reaction may be written and as shown in figure 1.

Epoxidized ground oil + Acrylic acid ⟶ Acrylated epoxidized ground oil …….. (8)

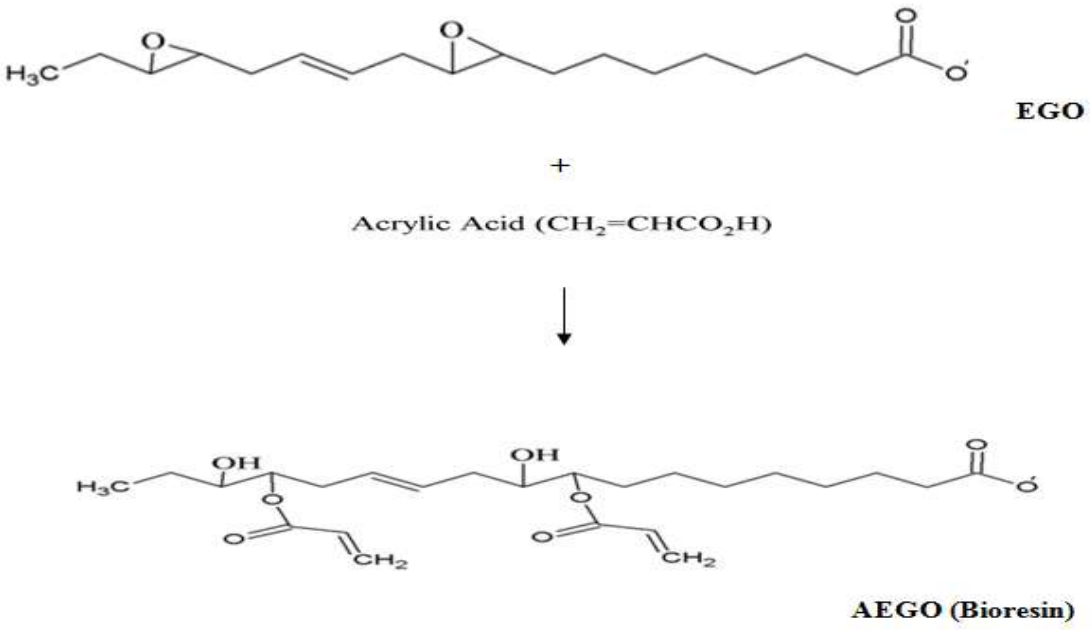

Figure 1. Structures of EGO and AEGO after epoxidation and acrylation chemical reactions.

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Plate 5 shows the acrylation reaction set up while plate 6 shows the sample AEGO (bioresin).

Plate 5. Acrylation reaction in progress

Plate 6. Sample of Bioresin from ground nut oil

2.2.4 Determination of Iodine value of the Acrylated epoxidized ground nut oil (AEGO)

The Iodine value of the bioresin was determined by titration method using American Oil Chemists Society standard (AOCS Cd 1b-87) reported by [18]. After thorough stirring, 21g of the resin and 30ml Hanus solution were placed in a 250ml conical flask and stoppered. This was titrated with 0.1N Sodium thiosulphate ($Na_2S_2O_3$) until the solution became light yellow. 2ml of 1% starch indicator was added and the titration continued until the blue colour disappeared. The iodine value was calculated using the formula shown below.

$$\text{Iodine value (I.V.)} = \frac{(B-S)x\ N\ x\ 12.69}{W} \quad \text{……..(9)}$$

Where, B = bank titre (without oil) = volume of $Na_2S_2O_3$ used

S = sample titre (with oil) = volume of $Na_2S_2O_3$ used

N= normality of Sodium thiosulphate = 0.1

W= weight of oil.

The result of the iodine value of AEGO is found in table 1.

The degree of acrylation (DOA) in this work was calculated using $\frac{IVo - IVa}{IVo}$. ….(10)

where IVo is the iodine value of raw oil and IVa is the iodine value of acrylated oil

III. RESULTS AND DISCUSSION

Table 1: Results of determined properties of bioresin from ground nut oil.

S/NO.	Parameters	value
1	Iodine value (IV) of ground nut oil used	81.9mg iodine/100g oil
2	Theoretical oxirane oxygen content (OOC theo.	4.91
3	Experimental oxirane oxygen content (OOCexpt	3.61
4	Degree of Epoxidation of EGO	74.2%
5	Iodine value (IV) of AEGO produced	32.2mg iodine/100g oil
6	Degree of Acrylation of AEGO	60.7%
7	Viscosity	374cP
8	Density	1.4g/cm^3

Going by [19] and [20], some vegetable oils have high contents of unsaturated fatty acid and the double bond (C=C) in it provides the center stage for conversion into epoxy fatty acid by chemical reaction called epoxidation. Oxirane oxygen content is a measure of the amount of C=C

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which has been transformed into epoxides through the epoxidation reaction. Due to the high reactivity of the oxirane oxygen ring of the epoxidation product, the epoxides (upper part of figure 1) can serve as materials for synthesis of variety of industrial products such glycol, lubricants, plasticizers, paints etc, [13].

In this work, the ground nut was epoxidized by reacting it Performic acid while the epoxidized ground nut oil (EGO) was used as raw material for bioresin production by acrylation method. The degree of epoxidation (DOE) of the ground nut oil which was determined to be 74.2% revealed the extent by which the carbon double bonds (C=C) in the oil was converted to epoxidized ground nut oil (EGO) before been transformed into bioresin through acrylation reaction. In other words 74.2% DOE showed the extent at which the carbon –carbon double bonds in the ground nut oil was converted to Oxirane Oxygen (OO). With proper handling and management of the epoxidation process, the value of the DOE is a total reflection of the level of unsaturation of the oil dictated by its iodine value (i.e 81.9 mg iodine/100 g oil in this case). According to [12] and [13], iodine value of renewable oil is used to quantify the degree of C=C present in a plant oil and is used to monitor the epoxidation reaction. The higher the iodine value of oil, the better the value of DOE and of course the quality of the bioresin produced from the epoxidized oil.

The acrylation reaction conducted in this study is a further modification on the chemical structure of EGO where the epoxy functional triglyceride of the epoxidized ground nut oil was made to react with acrylic acid as shown in figure 1. Going by [13] and [16], the acrylation reaction transformed the epoxy functional groups by incorporating acrylate chemical groups onto the triglyceride thereby yielding vinyl functionalities structure as shown in figure 1. There are many methods of accessing the level of transformation of epoxy functional groups into acrylates. This work attempted to use the iodine values of the raw and the acrylated oils. The remaining iodine value of the raw oil after the acrylation reaction gave broad view about the extent to which the carbon double bonds have been transformed into acrylate groups during the production of the bioresin from the raw oil to acrylated oil. The iodine value of the crude ground nut oil was 81.9mg oil/100g of iodine while that of the bioresin (AEGO) after the acrylation reaction was 32.2mg iodine/100g oil. This gave the degree of acrylation in this work as 60.7% using equation 10. However, the value depends on the level of unsaturation of GO and of course effective management and control of both the epoxidation and acrylation processes respectively.

Resin is a viscous liquid that will transform (cured and hardened) into solid when treated with suitable catalyst, accelerator with or without heat. The viscosity of resin has to be such that can easily be used for production without any stress. The dynamic or absolute viscosity of AEGO after acrylation reaction was 1530 centi-Poise (cP). The high viscosity value was reduced to acceptable value 374 cP by adding about 35% by weight of styrene to the AEGO. This helps to improve processability for manufacturing composite parts by traditional composite processing techniques.

Going by [4], density of resin is one of the physical properties that enable one to know its heaviness (dense nature). It gives idea about the mass of the resin with respect to the volume (space) occupied. The density of the final product determined was $1.4g/cm^3$ and falls within the ASTM standard range of $1.0 – 1.5g/cm^3$.

Confirmation test of the bioresin was done by mixing some quantity with catalyst (Methyl ethyl Ketone) and accelerator (Cobalt amine). The thoroughly mixed content was poured into cylindrical plastic pipes used as the moulds. After left to cure and dry in sun for two days, the demoulded samples are shown in plate 7. The composite produced from the bioresin suggests that it can be used as alternative resin to the synthetic resins.

Plate 7. Sample of neat cast bioresin from ground nut oil.

IV. CONCLUSION.

The following conclusions are made based on the outcome of the study:

1. The bioresin was produced via epoxidation and acrylation chemical reactions route. The degree of Epoxidation (DOE) was 74.2% while that of Acrylation (DOA) was 60.7%. These values reflected the extend at which the carbon double bond in ground nut oil was transformed into epoxy functional groups and the epoxy functional groups into acrylate functional groups of the bioresin respectively. However, they all depend on the level of unsaturation of GO as dictated by its iodine value and of course effective management and control of both the epoxidation and acrylation processes respectively.
2. Both the viscosity and density of the bioresin determined were found to be within ASTM standard. The cast bioresin sample shown in plate 7 gave good promising result of the resin and thus can serve as alternative resin to the synthetic ones.
3. Considering the fact that the source (ground nut oil) from which the bioresin was produced is a material that is readily available, affordable and sustainable in Nigeria and many other countries, the use of the oil for bioresin production in commercial quantity will not only help to ameliorates some of the challenges confronting petrochemical resins (synthetic resins), but will also contribute to wealth creation and diversification of economy.

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