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Production of Bioresin from Sweet Orange (Citrus Sinensis) Seed Oil

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ABSTRACT
Sweet Orange (Citrus sinensis) is one of the common fruitsgrown in commercial quantity in Nigeria and many other countries across the globe. The seeds of the fruits are usually thrown awayby consumers and users as waste. This paper attempts to extract oil from the seeds and produce Bioresin from the extracted oil via Epoxidation and Acrylation Processes. The oil was extracted using Soxhlet extraction method with n-hexane as solvent. The Physico-chemical Properties of the oil determined were: Moisture content of seed (6.37), Oil yield (37%), Specific Gravity (0.920 g/cm^3), Iodine value (56.4 mg iodine/100 g), Free Fatty acid (3.11mg NaOH/g oil), Acid value (6.19mg NaOH/g oil), Saponification value (193.25 mg KOH/g oil) and Peroxide value (6.7mg/g oil)respectively. The bioresin was produced via Epoxidation and Acrylation processes. Analysis of the Epoxidation process showed that theDegree of Epoxidation (DOE) was 59.2% while the Degree of Acrylation (DOA) from Acrylation process was 49.1%.The viscosity of bioresin producedwas reduced from 1530 Cp to 363Cp acceptable standard by adding Styrene to it. The density of thebioresin was 1.32 g/cm^3.Confirmationtest on the Bioresin was done by producing cast moulding sample of it using the same Catalyst(Methyl Ethyl Ketone Peroxide, MEKP) and Accelerator (Cobalt amine) use in producing cast Polyester resin. The appearance of the solid composite showed some degree of promising bioresin that can serve as alternative resin to the synthetic polyester resin.

KEYWORDS: Sweet Orange seed oil,Physico-Chemical properties, Epoxidation, Acrylation, Bioresin, Synthetic resin, Composite material.

I. INTRODUCTION

Polymer matrix commonly called Resin is one of the two major constituents of fibre reinforced composite material.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 crude oil or chemicals) are commonly called synthetic resins while those from organic sources (such as plant or animal) are called bioresin or renewable resins. Resins are mostly used to produce fibre reinforced composite material by combining it with suitable reinforcement that can easily be impregnated [1].

It was noted by [2] that 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.

Despite the awareness and increasing applications of composite materials in the fields of Air, Land and Sea transportation among others, the bulk of Resins used for wide range of Engineering activities across the globe are Synthesized from nonrenewable petrochemicals substances, which are found to have some economic and health challenges.[1]

In order to ameliorate some of the challenges associated with synthetic resins, many researchers across the globe have conducted researches on use of renewable and sustainable organic substances for production of renewable (bioresins). It was found that plant or vegetable base oil offer a sustainable and with growth of scale, potentially a cost competitive option to petrochemical polymers [1].

These Biopolymers are produced from triglycerides which have active sites acquiescent of

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chemical functionalization and or reactions suitable for the production. These sites in the triglycerides enable them to be directly epoxidized followed by Acrylation process to produce the bioresin in most cases[3] and [4].

According to [3] and [5], Epoxidized Oil (EO) polymers by themselves may be suitable as a polymeric matrix if blended with synthetic epoxy resin. But where pure bioresin is desired, further modifications can be made on the chemical structure of EO to modify functionalities. One such modification involves acrylation of the epoxidized oil.

Acrylation is a chemical reaction where epoxidized oil structure is modified for further functionalities. In this process, epoxy functional triglyceride of theepoxidized oil is made to react with acrylic acid to incorporate acrylate chemical groups onto the triglyceride thereby attaching vinyl functionalities to its structure [3], [5] and [6].

Acrylation process helps to convert the unreacted epoxides in the oil to impart further functionalization to the triglyceride thereby improving the polymer performance. After this modification, a polymer in the form of Acrylated Epoxidized Oil (AEO) is obtained. The conversion of EO to AEO allows, lower curing temperatures, shorter curing times and improved material properties and pave way for the use of same catalyst and accelerator used for polyester resin composite production. [3], [5] and [6]..

The aim of this study is to produce Bioresin from sweet orange seed oil via Epoxidation and Acrylation processes.

Base on [7], Nigeria is one of the countries that have rich and fertile soils to grow wide varieties of plants and vegetables including sweet orange fruits in commercial quantities for consumption and industrial purposes. [8]has it that Nigeria is among many countries that produce orange fruits in commercial quantities for consumptions and industrial uses, (over 150,000 – 200,000 tonnes per annum). The fruits are readily available in nooks and cranny of the country during the peak of harvesting season (February – July every year).The seeds of the fruits are discarded by the consumers and users as waste.

The outcome of research into the use of sweet orange seed oil for bioresin production will not only help to reduce some of the challenges confronting petrochemical resins (synthetic resins) globally and at our local level where the bulk of them are imported materials, it will also contribute to wealth creation and diversification of the economy when concerted efforts are made to produce the bioresin in commercial quantity.

II. MATERIALS AND METHODS

2.1 Materials/Equipment

Among the materials, chemicals, equipment, tools and devices used for the work are found in Table 1.

Table 1: List of materials, chemicals, equipment, tools and devices used for the work.

	Materials and chemicals	Equipment/Devices
1	Sweet orange seed oil	Buck infrared spectrophotometer (model 530)
2	Formic Acid	Digital weighing machine (LA 164. B. Brain)
3	Hydrogen peroxide	Measuring cylinder
4	Sodium hydroxide	Griffin temperature and adjustable oven
5	Potassium hydroxide	Conical flask
6	N-Hexane solvent	U-tube Viscometer
7	Sodium thiosulphate	Pipette
8	Acrylic Acid	Burette

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9	Hydroquinone	prolab efflux viscometer
10	Toluene	stop watch
11	Distilled water	2-neckround bottom flask
12	Anhydrous Sodium Sulfate	Hot plate equipped with magnetic stirrer
13	Styrene	Separating funnel
14	Methyl Ethyl Ketone Peroxide (MEKP)	Magnetic bit
15	Cobalt amine	Tripod stand
16	Hydrogen bromide	PVC cylindrical hollow pipe

2.2. METHODS

2.2.1. Processing of Sweet Orange Seeds for Oil Extraction

In this work sufficient quantities of rotten sweet orangesthrown away by farmers, marketers and consumers respectively in Bauchi town, Nigeria were searched and collected. The seeds were removed, washed with water and sun dried for five days to reduce its moisture content prior to grounding intosuitable texture for oil extraction. Plate Iin appendix A shows the samples of sweet orange and the seeds containing the oil .

2.2.2. Extraction of Oil from Processed Seeds

The oil was extracted using Soxhlet extractor apparatus with n-hexane as the solvent in accordance with[9].The extraction steps were repeated severally until the quantity of oil needed was attained.Plate II in appendix B shows the setup for oil extraction and sample of oil extracted from sweet orange seeds.

2.3 Physico-Chemical Properties of Sweet Orange Seed Oil

2.3.1 Determination of Moisture Content of Ground Sweet Orange Seeds.

The method described in [10] was used in which the moisture content was calculated using equation (1).

$$\text{Percentage Moisture} = \frac{Wi - Wf}{Wi} \times 100 \quad \ldots (1)$$

Where,

Wi = initial weight of ground African sweet orange seeds sample before drying

Wf = final weight of ground African sweet orange seeds sample after drying

2.3.2 Determination of the Percentage of Oil Yield

The percentage oil yield was determined based on [9] and the numerical value was calculated using equation (2)

$$\text{Percentage Oil Yield} = \frac{\text{weight of oil}}{\text{weight of sample on dry matter basis}} \times 100\% \quad \ldots (2)$$

2.3.3 Determination of Relative Density of the Oil

The procedure used by [11] was adopted where the relative density was calculated using equation (3).

$$\text{Relative Density of Oil} = \frac{W3 - W2}{W1} \ldots (3)$$

Where,

W3 = weight of bottle and pure oil sample

W2 = weight of empty bottle

W1 = weight of equal volume of water = weight of bottle and distilled water - weight of empty bottle.

2.3.4. Determination of Free Fatty Acid of the Oil

The free fatty acid of the oil was determined by titration method described in Association of Official Analytical Chemists [12]. At the end of the titrations the free fatty acid (FFA) was calculated using equation (4).

$$\text{FFA} = \frac{\text{Titre volume x M x 28.2}}{\text{Weig ht of oil}} \ldots (4)$$

Where,

M = Morality of (NaOH).

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2.3.5. Determination of Acid Value of the Oil

In order to determine the acid value of the oil, the procedure for determination of free fatty acid described in [13]was repeated and the end point of the titration was used to calculate the acid value using equation (5)

Acid value (AV) = % FFA x 1.99 … (5)

2.3.6. Determination of Saponification Value (S.V) of the Oil.

The Saponification value (S.V.) was determined by titration method and the value was calculated using equation (6) in accordance to [10].

Saponification value (S.V) = $\frac{(B-R)\times 28.05}{\text{weight of sample}}$… (6)

Where,

B = Blank titre value.

R = Real titre value.

2.3.7. Determination of Peroxide Value (P.V) of the Oil.

The peroxide value (PV) was determined by titration method and the value was calculated using equation (7) in accordance to [13].

Peroxide value = (R × B) × $\frac{\text{Molarity of } Na_2S_2O_3}{\text{weight of oil sample}}$… (7)

Where.

R = Real titre value determined

B = Blank titre value

2.3.8. Determination of Iodine Value (I.V) of the Oil.

The Iodine value (IV) of the oil was determined by titration method and its value calculated using equation (8) in accordance to [13].

Iodine value (IV) = $\frac{(B-S)x\ N\ x\ 12.69}{W}$… (8)

Where,

B = bank titre,

S = sample titre

N= normality of Sodium thiosulphate

W= weight of oil.

2.4 Epoxidation of Sweet Orange Oil using Performic Acid (PFA)

Theepoxidation chemical reaction was conducted on sweet orange seed oil according to ISO standard described by[14] and [15]. 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, 100 g of the 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 another 3 hours to completion.

At the end of the 4 hours, complete reaction of the first test, the epoxidation reaction mixture was transferred to a separating funnel and the organic layer was 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. This step was repeated until the desired quantity of ESOSO was obtained. Plate III in appendix C showed Epoxidation process set and sample of ESOSO produced.The reactions that preceded the epoxidation process were written thus:

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

$FA + H_2O_2 \longrightarrow PFA + H_2O$ … (9)

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

$DB + PFA \longrightarrow EO + FA$ … (10)

Where,

FA = Formic Acid,

PFA = Performic Acid,

DB = Double Bonds of the oil

EO = Epoxidized Oil

H_2O_2 = Hydrogenperoxide and H_2O = Water.

Alternatively, the reactions may be written as:

$HCOOH + H_2O_2 HCOOOH \longrightarrow + H_2O$ … (11)

Formic Acid + Hydrogen Peroxide → Performic Acid + Water

2.4. 1 Determinationof theoretical Oxirane Oxygen Content (OOC)

The theoretical Oxirane Oxygen Content (theoOOC) was calculated according ISO standard reported by [14]and [15]. In this calculation, the numerical values of the variables were inserted in equation (11) to determine the Oxirane Oxygen Content.

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Thus, theoOOC = $\left[\frac{(IV0/2Ai)}{100+(IV0/2Ai)Ao}\right] A_o$ x 100 … (12)

Where,

Ai (Atomic weight of iodine), = 126.9,

A_0(Atomic weight of oxygen), =16.0

IVo (Initial iodine value of the oil sample) =56.4

2.4.2 Determinationof Experimental Oxirane Oxygen Content (OOC)

In order to determine the experimentalOxirane Oxygen Content (exptOOC), another chemical reaction by titration method was conducted using Hydrogen Bromide (HBr) on 100 g raw Sweet Orange Seed Oil. The experiment was conducted in line with ISO standard reported by [14]and [15].The numerical values of the variables from the experiments were inserted into equation (12) to determine experimentalOxirane Oxygen Content.

Thus, OOC expt. = $\frac{1.6\,N\,(V-B)}{W}$ … (13)

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 (100g) and

B is the volume (ml) of HBr for blank

2.4.3 Determination of Degree of Epoxidation (DOE)

The relative percentage conversion to Oxirane Oxygen Contentor the degree of epoxidation (DOE) was calculated using ISO standard as in [14] and [15]. This simply involves dividing the experimental value of Oxirane Oxygen Content determined by the theoretical value.

Thus DOE= $\frac{expOOC}{theoOOC}$x 100. … (14)

Where,

expOOC (g/100 g sample) is the experimentally obtained Oxirane Oxygen Content

theoOOC is the theoretically obtainable maximum Oxirane Oxygen Content.

2.5 Production of Acrylated Epoxidized Sweet Orange Seed Oil (AESOSO)

Acrylated EpoxidizedSweet Orange Seed Oil (AESOSO) was prepared according to ISO standard as reported by [3] and [16]. In this work, Epoxidized Sweet Orange Seed Oil (ESOSO) 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 ESOSO: Acrylic Acid was 1:10. 50 g of ESOSO and 500g Acrylic Acid were placed in the flask and 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 above procedure was repeated to achieve the quantity of bioresin desired. Plate 1Vin appendix D showed Acrylation process set and sample of Acrylated Epoxidized Sweet Orange Seed Oil (AESOSO) produced. The reaction that preceded the process may be written as in equation (15).

Epoxidized oil + Acrylic acid ⟶ Acrylated epoxidized oil … (15)

2.6 Determination of Iodine Value of Acrylated Epoxidized Sweet Orange Seed Oil

The Iodine value of Acrylated Epoxidized Sweet Orange Seed Oil (AESOSO) simply called the Bioresin was determined by titration method using American Oil Chemists Society standard [17]. The result obtained is shown in Table 2.

2.7 Determination of Viscosity and Density of Acrylated Epoxidized Sweet Orange Seed Oil

The Viscosity of Acrylated Epoxidized Sweet Orange Seed Oil was determined using Brookfield viscometer apparatuswhile the density was determinedon the basis of mass to volume ratio as described by[11].The results of these tests are found in table 3.

2.8 Confirmation test on Bioresin Produced

The confirmation test on the bioresin was done according to [18] and [19], by producing solid composite of the resin using the same catalyst (Methyl Ethyl Ketone Peroxide, MEKP) and accelerator (Cobalt mine) normally used in producing solid structure from polyester resin. Plate V shows the solid composite produced from both bioresin and polyester resins respectively.

III. RESULTS AND DISCUSSIONS

The results ofPhysico-Chemical Properties of Sweet Orange Seed Oil Extracted are shown in table 2. Table 3 shows the results of Epoxidation and Acrylation processes and other determined properties of bioresin from Sweet Orange Seed Oil.

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Table 2: Physico-Chemical Properties of Sweet Orange Seed Oil Extracted.

Physico-Chemical Properties	Value
Moisture content	6.37
Percentage yield of Oil(g oil/100 g dry matter)	37%
Relative density of oil (g/cm3)	0.92
Free Fatty Acid value (mg NaOH/g oil)	3.11
Acid value(mg NaOH/g oil)	6.19
Iodine value (mg iodine/100 g)	56.40
Saponification value(mg KOH/g oil)	193.25
Peroxide value(mg/g oil)	6.7

The percentage oil yield from the seeds is a measure of the quantity of oil and others substances contain in it [9] and [10]. The value gives an insight into the quantity of oil in the seed and thus sharpens the decision on whether to proceed with more extraction or change to other fruits seeds with possibly better yields and requisite properties for bioresin production. The oil yield in this work was 37%. Although the oil yield was low, however, considering the fact that the source (sweet orange seeds) are waste materials discarded by the consumers and users, the low yield value may be tolerated since they are abundantly available and sustainable for use during the peak of harvesting season.

From the definition of [20], relative density is the ratio of mass of a given volume of substance (oil) to equal volume of water at room temperature). Relative density enables one to know the heaviness (dense nature) of the oil when compared with that of distilled water. From the results, the relative density of the oil was0.92g/cm^3.The value implies that the oil is less dense when compared with distilled water. This is due to possible absent of heavy element or hydroxyl groups in it [3].

Free fatty acids (FFA) content of oil is responsible for formation of soap and when the free fatty acid level of oil is above 5% as found in animal fats and cooking oil, the free fatty acids combine with catalyst to form soap which contributed to emulsion formation and subsequently difficulty to separate [11]. High water content in oil sample leads to increase in free fatty acids level because water in oil will oxidize in the present of air and water and many of the alkyl groups of the triacyl glyceride oxidize to fatty acid. [21]. In this work the free fatty acid value of the oil was 3.11mg NaOH/g oil.

Acid value of seed oil is the number in milligrams (mg) of sodium hydroxide (NaOH) required to neutralize the free fatty acid and carboxylic acid group in one gram (1g) of the oil [22]. The acid value is a measure of total acidity of the lipid, involving contributions from all the constituent fatty acids that make up the glyceride molecule and the lower the acid value of an oil, the fewer the free fatty acids it contains which makes it less exposed to the phenomenon of rancidification, [23]. Acid value of oil gives idea about the oil tendency to spoilage and shelf life and thus its quality, [11]. Acid value measures the degree of saturation of oil and thus the higher acid value indicates higher saturation level of free fatty acid and carboxylic acid group present in the oil [24].

In this work the acid value of sweet orange seed oil extracted was 6.19mg NaOH/g oil oil. The high acid value of the oil indicates that it has high free fatty acids and carboxylic acid group in it. This implies that oil is partially saturated and will limits its usefulness for bioresin production.

Iodine value of seed oil is the number of milligrams of iodine consumed by 100g of the oil, [22]. Iodine value of oil according to [4], measures the degree of unsaturation of oil. This unsaturation is in the form of carbon double bond which reacts with

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iodine compound. The higher the iodine value the more the carbon double (C=C) bond are present in the oil and the more the level of unsaturation of the oil. On the basis of bioresin production, iodine value is used to monitor the epoxidation reaction and a successful epoxidation reaction will see a high proportion of those C=C converted into epoxides. The double bonds in the oil are used as reactive sites in the epoxidation reaction and other functionalized processes. A successful epoxidation reaction will see a high proportion of the C=C converted into epoxides.

In this study the iodine values of the oils vary from 56.4 mg iodine/100g oil.The iodine value of the oil is within the bench mark of 50.3 mg iodine/100g oil for resin production.

The saponification value of seed oil is a useful tool for the evaluation of the chain length (molecular weight) of fatty acids occurring in the triacylglycerols in oil, [3]. Base on [11] and [17], Saponification value helps to determine the magnitude of potassium hydroxide (in mg) needed to neutralize the acids and saponify the esters contained in 1 g of the lipid. High saponification value of oil indicates high Lauric acid content of the oil which determines its suitability for making soap, Alkyl resin, wetting agents, Detergents etc. In this work the Saponification value of sweet orange oil was 193.25 mg KOH/g oil. The higher the Saponification value, the better the oil for bioresin production.

Considering the work of [17], Peroxide value is one of the most widely used tests for oxidative rancidity in oils. It is a measure of the concentration of peroxides and hydroperoxides formed in the initial stages of lipid oxidation. Generally, the peroxide value should be less than 10 mg/g oil in the fresh oil, [25]. on the other hand reported that peroxide value of oil gives information about the oils oxidative propensity which also affects the shelf life of the oil. Oil with high peroxide values are unstable and easily become rancid. [24]reported that peroxide value of oil is an indication of deterioration of the oil. This means that oilswith higher peroxide values are easily spoiled (low shelf life) and are more unsaturated than lower ones. More unsaturated oils are known to absorb more oxygen and develop higher peroxide value than oil with lower unsaturation level.

In this work, the result of the peroxide value of the oil was6.7 Meg /g of oil. Low peroxide values of the mango seed kernel oils indicate that the oil have longer shelf live and more stable than high one.

Table 3: Results of Epoxidation process and other determined properties of bioresin from Sweet Orange Seed Oil

S/NO.	Parameters	value
1	Theoretical oxirane oxygen content (theo. OOC)	3.43
2	Experimental oxirane oxygen content (expt.OOC)	2.03
3	Degree of Epoxidation (DOE) of ESOSO	59.2%
4	Iodine value (IV) of SOSOextracted	56.4 mg iodine/100g oil
5	Iodine value (IV) of AESOSO (Bioresin) produced	28.7 mg iodine/100g oil
6	Degree of Acrylation (DOA) of AESOSO (Bioresin)	49.1%
7	Viscosity	363cP
8	Density	1.32g/cm^3

Epoxidized Sweet Orange Seed Oil(ESOSO) which serves as a raw material for bioresin production by acrylation process was produced with Degree of Epoxidation (DOE), 59.2%. The value of the DOE obtained was a reflection of the level of unsaturation of the raw oil as dictated by its iodine value (56.4 mg iodine/100 g oil) and handling of the Titration process of experimental Oxirane oxygen content determination. The 59.2% DOE simply tells that only 59.2% of the raw oil transformed into epoxidized oil. This means that there are still 40.8% of the oil that still unsaturated and still requires more functionalization.

According to [3] and [4], this unsaturated portion of the epoxidized oil will appear as carbon double in the FTIR spectra of the oil with other substances in the oil. The epoxidation process

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transformed the triglyceride molecule of the raw oil into epoxy functional triglyceride molecule.

Base on [3], epoxidized oil polymers by themselves may be suitable as a polymeric matrix if blended with synthetic epoxy resin.

The Acrylation reaction conducted in this work was a further modification on the chemical structure of ESOSO. According to [3] and [16], Acrylation is another functionalization process where the epoxy functional triglyceride of the epoxidized oil was made to react with acrylic acid so as to incorporate acrylate chemical groups onto the triglyceride thereby yielding vinyl functionalities structures.

The DOA from the Acrylation process was 49.1%. This was based on Iodine values of the raw oil and acrylated oil. The DOA figure simply implies that only 49.1% of the raw oil transformed in bioresin and even the bioresin still has some traces of unsaturated molecule in it that will limit its effectiveness as binder in composite material.

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 viscosity of AESOSO produced was 1530 Cp.This was too high for composite processing techniques. Going by the report of [3], there is need to decrease the viscosity by adding Styrene to it so as improve processability for manufacturing composite parts by traditional composite processing techniques.

The addition of Styrene AESOSO decreased the viscosity to 363Cp which is within the standard range (100 to 500 Cp at 20^{C}).

The density of the bioresin is one of the physical properties that enable one to know its heaviness (dense nature). It gives idea about the mass of the bioresin with respect to its volume. The density of the bioresin was determined on the basis of mass to volume ratio. As shown in Table 3, the result was $1.32g/cm^3$ and falls within the ASTM standard range of $1.0 – 1.5g/cm^3$ for most resins. This simply mean that the bioresin can be used without further work on its viscosity and density and any composite specimen from it can be compared with those from synthetic resin such as polyester resin.

Confirmation test on the Bioresin was done by producing cast moulding sample of it using the same Catalyst (Methyl Ethyl Ketone Peroxide, MEKP) and Accelerator (Cobalt amine) use in producing cast Polyester resin. The appearance of the solid composite compared favourably with cast polyester resin. This showedsome degree of promise on the bioresin and thus can serve as alternative resin to the synthetic polyester resin.

IV. CONCLUSION.

The following conclusions are made based on the outcome of the research work:

1.The sweet orange seed oil was extracted with oil yield of 37% and Iodine value of 56.4 mg oil/100 g oil. The iodine value showed the unsaturation level of the oil and the extent on which functionalization processes can be effective.

2. The epoxidation chemical reaction was conducted using performic acid route. The theoretical and experimental Oxirane Oxygen Content (OOC) of the oil were 3.43% and 2.03% respectively while the degree of epoxidation (DOE) was 59.2%. The value of the DOE obtained is a reflection of the level of unsaturation of raw oil as dictated by its iodine value.

The acrylation chemical reaction was conducted using acrylic acid route. The (DOA) estimated titration method was 49.1%. The value of the DOA is a reflection of the level of unsaturation of the oil as dictated by its iodine value and of course effective management and control of both the epoxidation and acrylation processes respectively.

3. The viscosity and density of the bioresin were determined to be 363Cpand $1.32g/cm^3$respectively.

4. Confirmation test on the Bioresin was done by producing cast moulding sample of it using the same Catalyst (Methyl Ethyl Ketone Peroxide, MEKP) and Accelerator (Cobalt amine) use in producing cast Polyester resin. The appearance of the solid composite compared to the polyester resin cast composite showed some degree of promising bioresin that can serve as alternative resin to the synthetic polyester resin, much especially that the source of the oil is a waste material that is readily available, affordable and sustainable in Nigeria and many other countries.

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APPENDICES

Appendix A

Plate I: Samples of Sweet Oranges and Seeds containing Oil

Appendix B

Plate II: Setup for oil extraction and sample of oil extracted from sweet orange seeds

Appendix C

Plate III: Epoxidation process setup and Sample of ESOSO produced

Appendix D

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Plate IV: Acrylation process setup and Sample of AESOSO produced

Appendix E

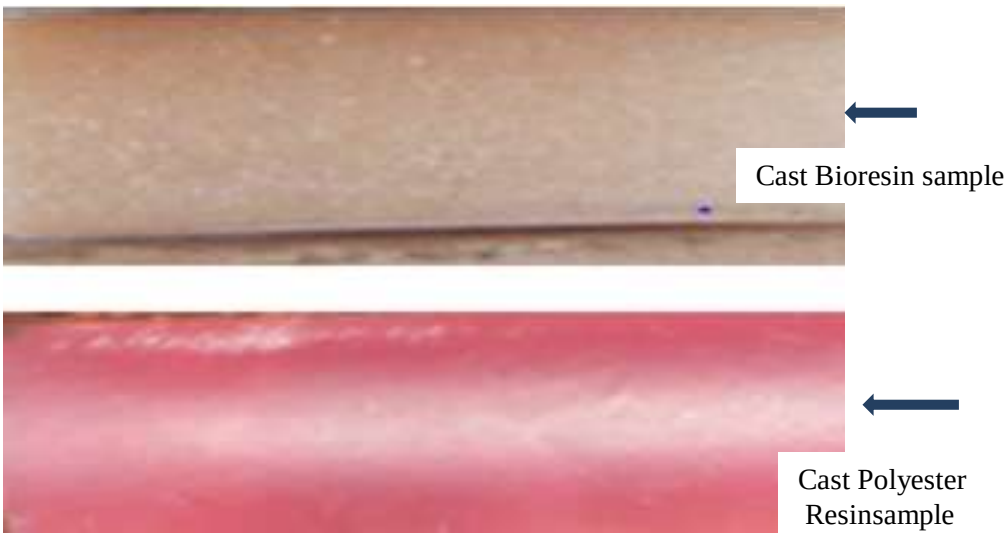

Plate V: Sample of cast bioresin from sweet orange seeds and cast polyest