



## In Situ Epoxidation of Sesame Seed Oil for Synthesis of a Bio-based Resin

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**Citation:** Nwosu-Obieogu, K., & Kalu, U. C. (2020). *In Situ Epoxidation of Sesame Seed Oil for Synthesis of a Bio-based Resin*. *European Journal of Sustainable Development Research*, 4(3), em0121. <https://doi.org/10.29333/ejosdr/7830>

### ARTICLE INFO

Received: 14 Dec. 2019

Revised: 20 Feb. 2020

Accepted: 24 Feb. 2020

### ABSTRACT

This study is aimed at the modification of sesame seed oil to develop a biobased resin. Neat sesame seed oil was epoxidized via in-situ conventional method with peroxyacetic acid at 75°C. Biobased resins were synthesized by further modifying the epoxidised oil with acrylic and methacrylic acid respectively at 90°C in the presence of hydroquinone. Conversion rate of 76.54% and high oxirane content of 3.83% at a reaction time of 7 hours was achieved for the epoxidation process. FT-IR spectra of the acrylated and methacrylated epoxy resins of sesame seed oil were identified at 2710 and 3002cm<sup>-1</sup> respectively. This ascertained the functionalization of the acids used for modification and clearly demonstrates the potential of sesame seed oil for biobased resin synthesis.

**Keywords:** epoxidation, acrylation, methacrylation, sesame seed oil

## INTRODUCTION

Recent interest in the use of renewable resources has motivated researchers to develop biodegradable resin due to environmental concerns and high cost posed by petrochemical based resins. (Aleksandar, 2014; Belgacem & Gandini, 2008; Kong et al., 2013; Lopes et al., 2013; Moseiwick et al., 2013; Siyanbola et al., 2013).

Currently the synthesis of biobased polymeric resins from readily available, sustainable, eco-friendly vegetable seeds has paved way for its utilization as functional based material for the production of resins (Blavo et al., 2001; Campanella et al., 2004; Xia & Larock, 2010).

Plant oils are being considered as important renewable raw materials for the production of bio-based polymer materials due to the unsaturated fatty triglycerides it contains (Leveneur, 2017; Nikeshe et al., 2015; Rakotonirainy & Padua, 2001). These unsaturated C=C present in the oil can be modified into reactive group via epoxidation (Chen et al., 2019) hence this has been actualized by various researchers.

Sinadovic-Fiser et al. (2001) have studied the kinetics of the epoxidation of soybean oil in bulk by peracetic acid formed in situ, in the presence of an ion exchange resin as the catalyst, the kinetic model proposed was validated, and the optimal conditions for obtaining 91% conversion, 5.99% epoxide content in product were found to be 0.5 mole of glacial acetic acid and 1.1 mol of hydrogen peroxide per mole of ethylenic unsaturation at 75°C, over the reaction time of 8 hours.

Goud et al. (2007) worked on the kinetics of epoxidation of Jatropha oil using peroxyacetic/peroxyformic acid in the presence of an acidic ion exchange resin as catalyst in or without toluene. The kinetic model proposed was validated and the activation energy for the epoxidation was found to be 53.6KJ/mol.

The kinetics of the epoxidation of rubber seed oil was investigated by Okiemen et al. (2002), hence there was a good fitting between experimental and the actual data, which indicates that the oil was suitably epoxidised.

Epoxidized vegetable oil not only improves the stability of oils, but also provides adequate reactivity to form chemical linkages with other polymer chains (Cai et al., 2008; Campanella et al., 2004), hence the need to further modify epoxidised oil via acrylation, methacrylation or hydroxylation to produce various range of thermosets. These thermosets present improved physical properties such as higher flexibility, adhesion and resistance to water and chemicals (Xia & Larock, 2010). Nwosu-Obieogu et al. (2017) developed biobased polymeric resins from modified linseed and sunflower oil, the FTIR analysis showed that the oils were suitably modified.

Sesame seed (*Sesamum Indicum L.*) a member of the family *Pedaliaceae* is among the earliest crops processed for oil production. (Anilakumar et al., 2010; Hassan, 2012), it is grown in Asia and Africa, applied in medicine, pharmaceuticals and nutrition. It is very rich in unsaturated fatty triglycerides (Crews et al., 2006), not good for frying due to its decomposition at low

temperature, hence the need to utilize it effectively through conversion to biobased resins and biofuels. (Bang et al., 2014; Musik & Milchert, 2017; Saydut et al., 2008).

Gharby et al. (2015) characterized the chemical and nutritional constituents of sesame seed oil grown in Morocco, the results revealed a high degree of unsaturation with linoleic acid (46.9%) followed by oleic acid (37.4%), which is an indication that it can be functionalized.

Music et al. (2018) compared epoxidation of sesame oil with performic acid and peracetic acid, performic acid gave a higher epoxy number than peracetic acid, hence this work tends to add value to sesame seed oil by epoxidation and further modification via acrylation and methacrylation of the epoxidised oil.

## MATERIALS AND METHODS

Materials used in this work include Sesame Seed (2.5kg), purchased from Mgbowo market, Enugu state, Nigeria; H<sub>2</sub>O<sub>2</sub> (30wt%), obtained from Chemical Engineering Analysis Laboratory, MOUAV, Abia State, Nigeria; Acetic acid (95%), Acrylic Acid (94%), Methacrylic Acid (99%), hydroquinone powder (99%), used as a free radical inhibitor, Sodium Carbonate, oven, grinder, mortar and pestle, muslin cloth, three necked round bottom flask, oil bath, thermometer, electronic weighing balance, condenser, heater, separation funnel, 250ml beakers, test tubes, stirring rods, retort stand and watch.

### Epoxidation Procedure

The sesame oil was extracted using mechanical expression from its seed. The epoxidation method reported by Goud et al. (2007) was adopted in this work with little variation in procedure. Sesame oil (60g) was placed in the flask, 4.3g of acetic acid was added to the flask after about five minutes, and the mixture was stirred continuously for 30mins. Then 29.89g of 30wt% aqueous hydrogen peroxide was added drop wise to the reaction mixture, as oxygen donor, at a rate such that the hydrogen peroxide addition was completed within half an hour; considering the completion of hydrogen peroxide addition as zero time. The mole ratio of the components used was 1:1.5:0.5. After the complete addition of hydrogen peroxide, the mixture was heated under reflux at the same desired temperature of 75°C and with rapid stirring. The rapid stirring of 200rpm was maintained throughout the experiment to achieve uniform dispersion of oil and to avoid zones of high peroxide concentration that could lead to explosion. The reaction setup was repeated for 5, 6 and 7 hours after the first 4 hour setup. The collected samples (ESO) were then immediately washed with sodium carbonate dissolved in distilled water to remove free acids and other unreacted components. 20g of Na<sub>2</sub>CO<sub>3</sub> was first dissolved in 100ml of distilled water. Then, another 100ml of distilled water was further added to the mixture. The total mixture was separated using a separation funnel.

### Analytical Techniques

#### Iodine value

The iodine value of the oil sample was determined by the Wiji's method of the Association of Oil Chemists. 0.5 g of the sample was poured in a conical flask. 10 ml of carbon tetrachloride was added to the oil and was shaken to allow the oil dissolve. Also 20 ml of Wiji's iodine solution was later added to the mixture. It was stirred vigorously, stoppered and kept in the dark for 30 minutes. Subsequently, 15 ml of potassium iodide solution followed by 100 ml of distilled water was added. The mixture was titrated against 0.01N sodium thiosulphate solution. A reagent black was also titrated as well.

Iodine value of epoxidized samples was calculated after analysis using the formula:

$$IV = \frac{(B - S) \times M \times 12.69}{W}$$

Where:

IV = Iodine value of samples

S = Volume of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> used for sample (ml),

B = Volume of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> used for blank (ml),

W = Weight of sample used (g),

M = Molarity of the Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> used.

Conversion was calculated with the formula below:

$$C_{GO} = \frac{IV_o - IV}{IV_o} \times 100$$

Where:

IV<sub>o</sub> = Iodine value before treatment

IV = Iodine value after treatment

#### Oxirane Oxygen content

The percentage of the oxirane oxygen was determined by direct method established by using hydrobromic acid solution in glacial acetic acid. The content oxirane oxygen (OO) was calculated according to the consumed amount of the halogen atom (Swern et al., 1947).

**Table 1.** The percentage of iodine value of the epoxidized sesame oil at different time intervals

Time (hr)	Iodine value (%)
4	27.14
5	39.99
6	65.26
7	76.54

**Table 2.** The percentage of oxirane oxygen content of epoxidized sesame oil at different time intervals

Time (hr)	Oxirane value (%)
4	1.38
5	1.51
6	2.43
7	3.83

The Oxirane Oxygen Content of the analyzed samples was calculated using the formula:

$$OV = \frac{(B - S) \times M \times A_o \times 100}{1000W}$$

Where:

S = Volume of NaOH used for sample (ml)

B = Volume of NaOH used for blank (ml)

M = Molarity of the NaOH used

W = Weight of sample used (g)

A<sub>o</sub> = Atomic weight of oxygen

### Synthesis of Acrylated Sesame Seed Oil

The epoxidized sesame seed oil (30.0g) was heated at a room temperature while acrylic acid (9.79g) containing hydroquinone (0.02g, 0.25wt %) was added at 30 minutes. The reaction mixture was heated under reflux for 6hours at 90°C with constant stirring. The mixture was then cooled to room temperature. The obtained product, Acrylated Epoxidized Sesame Oil (AESO) was washed with distilled water and then isolated.

### Synthesis of Methacrylated Sesame Seed Oil

The epoxidized sesame oil (30.0g) was heated at a room temperature while methacrylic acid (9.79g) containing hydroquinone (0.02g) was added at 30 minutes of the experiment. The reaction mixture was heated under reflux for 6hours at 90°C with constant stirring. The mixture was then cooled to room temperature and washed with distilled water. The obtained product, Methacrylated Epoxidized Sesame Oil (MESO) was isolated.

### FT-IR Analysis

FT-IR spectroscopy analysis was employed using Nicolet iS50 model to identify the various samples of pure, epoxidised and acrylated and methacrylated epoxidised sesame seed oils.

## RESULTS AND DISCUSSION

The result indicated that the percentage conversion of iodine value and oxirane value in the epoxidized sesame oil increased with reaction time, hence maximum conversion of 76.54 (with iodine value of 24.68gl<sub>2</sub>/100goil) in **Table 1** as well as 3.83% for oxirane value in **Table 2** was achieved at 7hours reaction time which is in agreement with the findings of (Goud et al., 2007). From the FT-IR spectra shown in **Figures 1-4**, it is observed that at the wave number 3890,700 the pure sesame oil tends to form a hydroxyl group with an unsaturated carbon-carbon bond in **Figure 1**. The epoxidized sesame oil became saturated and formed an epoxy group at wave number of 1120 in **Figure 2**. The acrylated and methacrylated epoxy resins of sesame oil were obtained at the wave number of 2710 and 3002 respectively to form the acrylic and methacrylic groups in **Figures 3** and **4** respectively, which is a pointer to the fact that sesame seed oil has been modified.

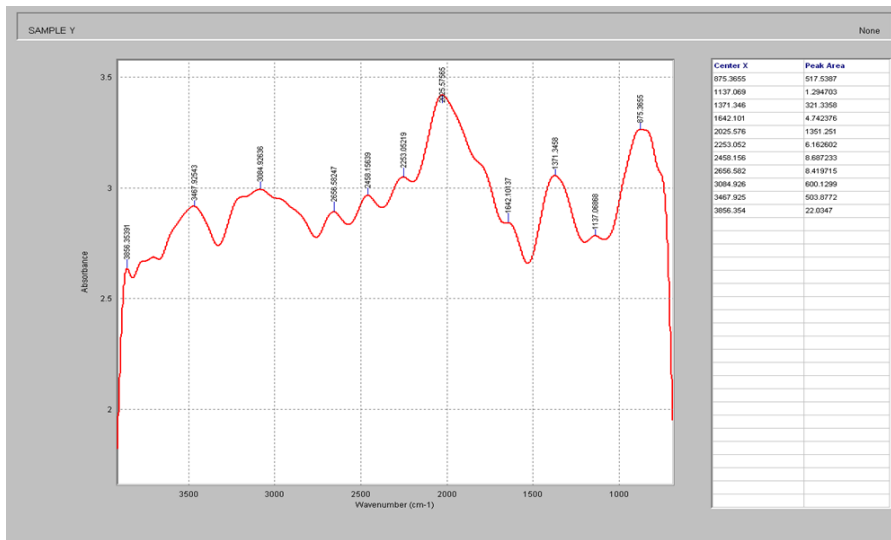


Figure 1. FT-IR of pure sesame seed oil

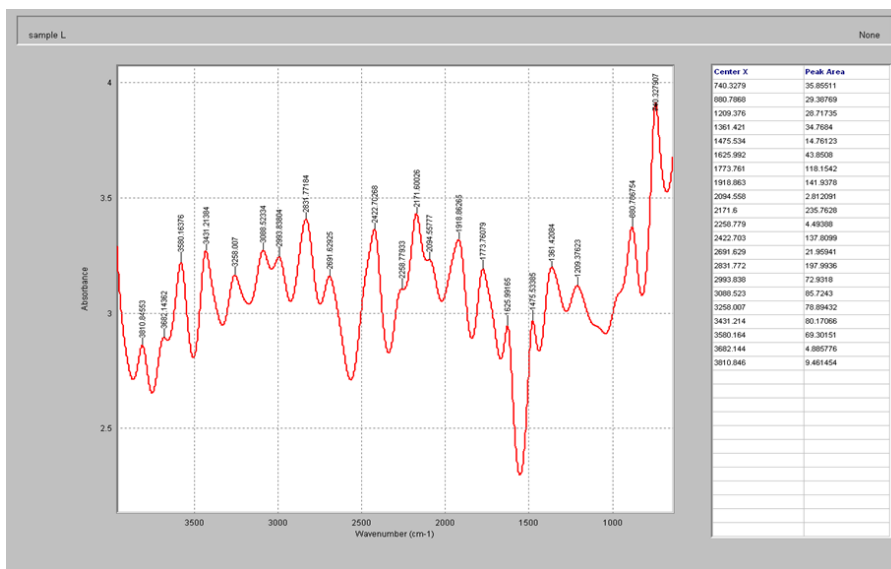


Figure 2. FT-IR of epoxidised sesame seed oil

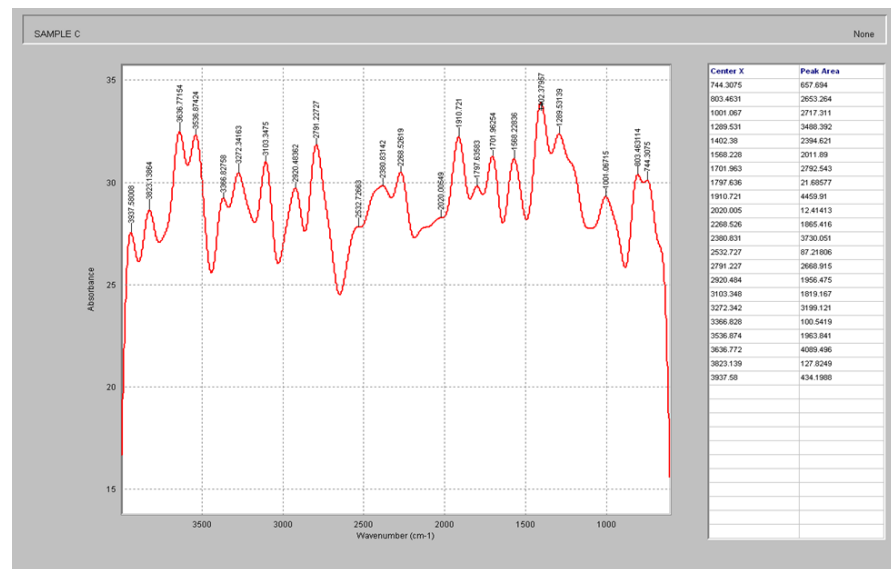


Figure 3. FTIR of acrylated sesame seed oil

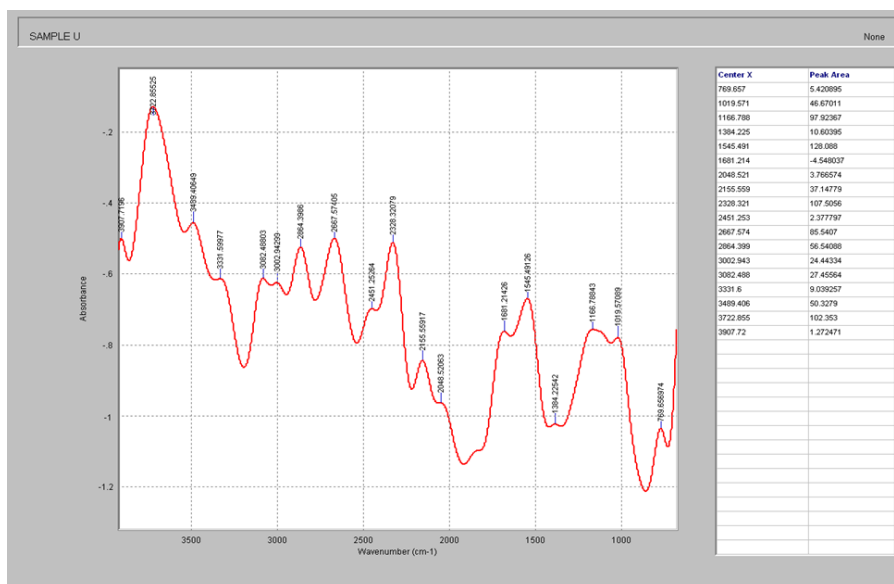


Figure 4. FTIR of methacrylated sesame seed oil

## CONCLUSION

Increase in the concern about environmental pollution from petrochemical-derived polymer products, has made plant seed oil a potential replacement. From the results obtained in this work, It was found that sesame seed oil is a good starting material for oil epoxy synthesis and further modification via acrylation and methacrylation to produce biobased resin. Hence the information is for possible utilisation and application of sesame seed oils for the synthesis of bioresins and composites preparation.

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