Synthetic Modification of Sunflower Oil

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Abstract. This report is based on the synthesis of thermoset resins from sunflower oil. Sunflower oil with an iodine value of 120 g I / 100 g oil containing 30 % oleic acid and 59 % linoleic acid was epoxidized by reaction with a peroxy acid (formed in-situ by the reaction between hydrogen peroxide and formic acid). The ratio of ethylenic unsaturation to hydrogen peroxide to formic acid used was 1:1.5:0.5. The maximum conversion of iodine generated was 82.45 % for seven h of epoxidation at 65 °C, and the oxirane oxygen content at that same condition was 4.6 %. Thermoset resins synthesized from sunflower oil were further modified using acrylic acid. All the resins generated were characterized using FT-IR spectroscopy. The results showed that the generated resins could be used in composite production for automobile, construction, and furniture applications.

Keywords: sunflower oil; epoxidation; thermoset resins; acrylation; Oxirane Oxygen Content.

INTRODUCTION

Petrochemical-based polymers have been of great use due to their low cost, high mechanical performance, good heat sealability, and good barrier properties. One of the most important uses is in the composite making. Composite materials were made by embedding synthetic fibres such as carbon, aramid, glass, or natural fibres into a polymer matrix. However, the composite material produced from petrochemical-based polymers and earlier mentioned systematic fibres is not biodegradable. Also, these petrochemical-based polymers emit volatile organic compounds, negatively influencing human health and the environment [1]. Owing to the environmental problems generated by the disposal of conventional plastics and related polymers from petrochemicals, there has been intensified research into polymers originating from renewable resources [2].

Polymer matrix could be obtained from thermoplastic or thermoset polymers. Some examples of biobased thermoplastics may be polylactic acid or starch-based thermoplastics. Thermoset has the advantage of low viscosity, which makes fibre impregnation easy and room temperature processing by infusion techniques possible. The setback of the thermoset is that it cannot be remoulded after curing [3].

The most interesting raw material candidate for bio-based thermoset can be found amongst plant seed oils such as sunflower, castor, groundnut, soybean, cottonseed, linseed, or rapeseed. Plant oil is also known as a natural triglyceride. Triglycerides are esters of fatty acids and glycerol [4-5]. It needs to be functionalized to add crosslinkable sites to the fatty acids of the triglycerides or so that they can undergo further chemical reactions, so to say [6]. This chemical modification utilizes the unsaturated double bonds in the fatty acids part of the triglyceride. A good number of bio-based resins can be synthesized from plant oils. For example, epoxidized sunflower oil [7], acrylate epoxidized soybean oil (AESO), methacrylate soybean oil (MSO), and methacrylic anhy-

dride modified soybean oil (MMSO) [2]. Following composite application, these bio-based resins are then impregnated with natural fibres (referred to as reinforcement or fillers), such as flax, hemp, viscose, or lyocell fibres, to produce biodegradable composites. Scientists, researchers, and educational institutes are making great efforts [8].

The development of these bio-based resins has helped in the reduction of the use of fossil resources. They have been used in different applications, such as paints, inks, coatings, and plasticizers, and many technical products, such as housing (doors, composite decking, window frames, and hot tubs), aerospace (wings, tails, propellers, and fuselages), pipes and fittings, boat, storage tanks swimming pool panels and more popularly in the building of vehicle parts.

This is due to their biodegradability and inexpensive nature [1, 9]. This work discussed in detail the procedures and the outcome of the modification of sunflower oil. Using conventional plastics and related polymer materials derived from petrochemicals has posed more significant environmental concerns. There is a need for available alternatives from the bio-based origin; hence, this study.

Given the environmental issues associated with the disposal of conventional plastics and related polymers from petrochemicals, this project aims to develop novel thermosetting polymers derived from sunflower oil, which is of renewable origin. Therefore, the target is to create lighter weight, higher strength, and more eco-friendly materials and offset the reliance on petroleum-based materials in making thermoset resins. These resins may be used in composites which can be applied in the automotive industry to save energy (due to low weight), reduce carbon dioxide emission, and improve fuel efficiency. This study will cover the epoxidation and further modification of pure sunflower oil with acrylic acid.

MATERIALS AND METHOD

Materials. Pure sunflower oil was obtained from New Market (Aba, Abia State, Nigeria). Formic acid (85 %) was purchased from Linsko chemicals Lt. (Aba, Abia State, Nigeria); hydrogen peroxide (30 wt%) was also obtained from Linsko Chemicals Lt. (Aba, Abia State), although the first sample test was done with a little

amount of H_2O_2 from Chemical Engineering Analysis Laboratory (MOUAU, Abia State, Nigeria). The chemicals mentioned above were used to epoxidize the oil. For further modification, acrylic acid (94%) was purchased from Linsko Chemicals Lt. hydroquinone (99%) was used as a cross-linking inhibitor and sodium carbonate, used for washing derived samples, was also purchased from Linsko chemicals Lt.

Resin Synthesis. Two different resins were synthesized from sunflower oil: Epoxidized Sunflower Oil resin (ESO) and Acrylated Epoxidized Sunflower Oil resin (AESO). The conventional method was used for the epoxidation of pure sunflower oil.

Experimental setup. Epoxidation reactions were carried out in a three-necked round-bottom flask (250 ml capacity) equipped with a magnetic heater/stirrer and placed in an oil bath, the temperature of which was controlled by the temperature regulator of the magnetic heater/stirrer to meet the desired temperature of the mixture inside the flask. The central neck of the flask was covered with a hollow cork through which a thermometer was introduced to record the temperature of the reaction mixture. In contrast, the remaining two necks were fitted with a reflux condenser and a reagent introduction tube; covered with a cork at the end (Figure 1).

Figure 1 – Experimental setup
(*also used for the acrylic modification process*)

Epoxidation procedure. The epoxidation method reported by [24] was used with slight variation in procedure, and this was repeated for all the experimental runs with the same concentration but different reaction times. A known

amount of sunflower oil (30 g) was placed in the flask, the calculated amount of formic acid was added to the flask after about five minutes, and the mixture was stirred continuously for 30 mins. Then 16.15 g of 30 wt% aqueous hydrogen peroxide was added dropwise to the reaction mixture, as an 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, that is, ethylenic unsaturation: H_2O_2:HCOOH. After entirely adding hydrogen peroxide, the mixture was heated under reflux at the desired temperature (65 °C) and with rapid stirring. The rapid stirring was maintained throughout the experiment to achieve fine oil dispersion and avoid zones of high peroxide concentration that could lead to an explosive mixture. The reaction setup was repeated 5, 6, and 7 hours after the first 4-hour setup. The equation of reaction for the process is given below.
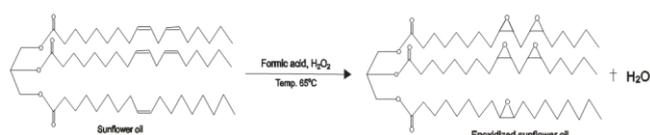
Scheme 1 – Synthesis of epoxidized sunflower oil

Washing of samples. The collected samples (ESO) were then immediately washed with sodium carbonate dissolved in distilled water to remove the free acids and other unreacted components. 10 g of Na_2CO_3 was first dissolved in 100 ml of distilled water. Then, another 100 ml of distilled water was further added to the mixture. The total mixture was added to the sample and separated by a funnel. Subsequent extraction was used to recover the remaining pieces after washing.

Determination of the Number of Chemicals Per Sample. Calculating the chemical required for the epoxidation reaction of the desired amount of oil, using formic acid as the oxygen carrier, is summarized below. Based on the literature, a typical fatty acid composition profile for sunflower oil is presented in Table 1.

Table 1 – Unsaturated fatty acid composition and molecular weight in sunflower seed oils

Fatty acids	Molecular formula	Composition (wt%)	Molecular weight (g/mol)
Oleic acid	$C_{18}H_{34}O_2$	59	282.47
Linoleic acid	$C_{18}H_{32}O_2$	59	280.45

The total mole of sunflower oil is expressed as the concentration of double bonds (DB) in the oil (a total of 89 %) → (n_t)

Mass of sunflower oil (chosen) = 30.0 g; Density of sunflower oil = 0.9188 g/ml; Volume of sunflower oil = 30.0/0.9188 = 32.65 ml.

$$n\ Oleic\ acid = \frac{0,3 \times 30}{282.47} = 0.0319.$$

$$n\ Linoleic\ acid = \frac{0,59 \times 30}{280.45} = 0.0631.$$

n_t = 0.0319 + 0.0631 = 0.095. A total mole of sunflower oil = 0.095 mol.

Formic acid. Mole ration of formic acid to DB = 0.5:1.

Formic acid (85 wt%), molecular weight = 46.03 g/mole, density = 1.22 g/ml. Mole of formic acid = 0.5, n_t = 0.5(0.095) = 0.0475 mol. Mass of formic acid = 0.0475(46.03) = 2.186 g.

$$Mass\ of\ formic\ acid\ solution = \frac{100 \times 2.186}{85} = 2.57\ g$$

Volume of formic acid required per sample = 2.57/1.22 = 2.11 ml.

Hydrogen peroxide. Mole ration of hydrogen peroxide to DB = 1.5:1

Hydrogen peroxide (30 wt%), molecular weight = 34.01 g/mole, density = 1.10 g/ml; Mole of hydrogen peroxide = 1.5(0.095) = 0.1425 mole. Mass of hydrogen peroxide = 0.1425(34.01) = 4.85 g.

$$Mass\ of\ hydgen\ peroxide\ solution = \frac{100 \times 4.85}{30} = 16.15\ g$$

Volume of hydrogen peroxide needed per sample = 16.15/1.10 = 14.68 ml.

Characterization of the epoxidized oil

Iodine Value and Oxirane Content analyses. These analyses were done on the epoxy resin to verify the degree of conversion of the pure oil to an epoxide.

FT-IR analysis. The first FT-IR Spectroscopy (Fourier transform infrared spectroscopy) analysis was done to verify the functionalization of the resin with the peroxyl acid (that is, hydrogen peroxide reacted with formic acid) in comparison with the known properties of the pure sunflower oil as obtained from the literature.

Synthesis of acrylate-modified sunflower oil. This is due to further modification of the epoxy resin with acrylic acid. The epoxidized sunflower oil (14.09 g) was heated at room temperature, while acrylic acid (4.6 g) containing hydroquinone (0.011 g; 0.25 wt% acrylic acid) was added for 30 minutes. The reaction mixture was heated under reflux for 6 hours at 120 °C with constant stirring. Excess acrylic acid (1.8 g) containing hydroquinone (0.0042 g) was added for 5 mins, and the reaction proceeded for another 2 hours at the same temperature. The mixture was cooled to room temperature, and the obtained product acylated epoxidized sunflower oil (AESO), was isolated. The synthesis was repeated for the remaining epoxidized samples.
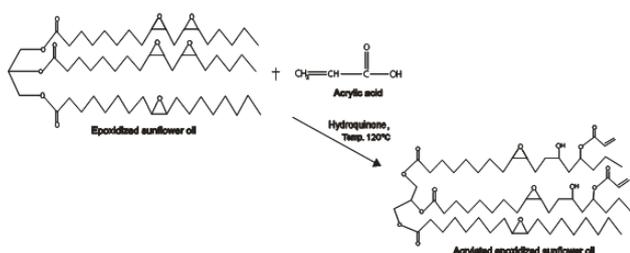

Figure 2 − Synthesis of acylated epoxidized sunflower oil

Characterization of acylated sunflower oil

FT-IR spectroscopy analysis was also employed to identify the fictionalization of the structure of the modified resin, and the comparison was made for the pure and epoxidized oil.

RESULTS AND DISCUSSION

Determination of Iodine Value and Conversion

The iodine value of sunflower oil was calculated using the equation below:

$$Iodine\ value = \frac{(B-S) \times M \times 12.69}{W},\qquad(1)$$

where S – volume of $Na_2S_2O_3$ solution required for titration of the sample (ml); B – volume of $Na_2S_2O_3$ solution required for titration of the blank (ml), W = weight of sample used (g); M – Molarity of the $Na_2S_2O_3$ (0.1 M).

The initial value of sunflower oil (IV_o) is expressed as iodine value at t = 0 (h), $M = 0.10$ M, $W = 0.20$ g, $B_1 = 23.75$ ml, $B_2 = 23.76$ ml, $B_3 = 23.74$ ml, $B_{AV} = 23.75$ ml, $S_1 = 4.81$ ml, $S_2 = 4.84$ ml, $S_3 = 4.84$ ml, $S_{AV} = 4.83$ ml.

$$IV_o = \frac{(23.75-4.83) \times 0.1 \times 12.69}{0.20} = 120.05\ g\ I\ /100\ g\ oil$$

$$X_\% = \frac{IV_o - IV}{IV_o} \times 100,\qquad(2)$$

where IV_o – Initial iodine value; IV – Iodine value at certain conditions; Reaction temperature = 65 °C (constant); Stirring speed = 750 rpm (constant).

a) Reaction time = 4 h, $W = 0.20$ g, $S_1 = 14.83$ ml, $S_3 = 14.83$ ml, $S_3 = 14.86$ ml, $S_{AV} = 14.84$ ml.

$$IV = \frac{(23.75-14.84) \times 0.1 \times 12.69}{0.20} = 56.53\ g\ I_2\ /100\ g\ oil$$

$$X_\% = \frac{120.05-56.53}{120.05} \times 100 = 52.91\ \% .$$

b) Reaction time = 5 h, $W = 0.20$ g, $S_1 = 16.39$ ml, $S_3 = 16.42$ ml, $S_3 = 16.39$ ml, $S_{AV} = 16.40$ ml.

$$IV = \frac{(23.75-16.40) \times 0.1 \times 12.69}{0.20} = 46.64\ g\ I_2\ /100\ g\ oil$$

$$X_\% = \frac{120.05-46.64}{120.05} \times 100 = 61.15\ \% .$$

c) Reaction time = 6 h, $W = 0.20$ g, $S_1 = 19.36$ ml, $S_3 = 19.37$ ml, $S_3 = 19.33$ ml, $S_{AV} = 19.35$ ml.

$$IV = \frac{(23.75 - 19.35) \times 0.1 \times 12.69}{0.20} = 27.92 \; g \; I_2 / 100 \; g \; oil$$

$$X_\% = \frac{120.05 - 27.92}{120.05} \times 100 = 76.74 \; \% \; .$$

d) Reaction time = 7 h, W = 0.20 g, S_1= 20.42 ml, S_3= 20.45 ml, S_3= 20.42 ml, S_{AV} = 20.43 ml.

$$IV = \frac{(23.75 - 20.43) \times 0.1 \times 12.69}{0.20} = 21.07 \; g \; I_2 / 100 \; g \; oil$$

$$X_\% = \frac{120.05 - 21.07}{120.05} \times 100 = 82.45 \; \% \; .$$

The reaction conversions for 4–7 h are summarized in Figure 3 below.
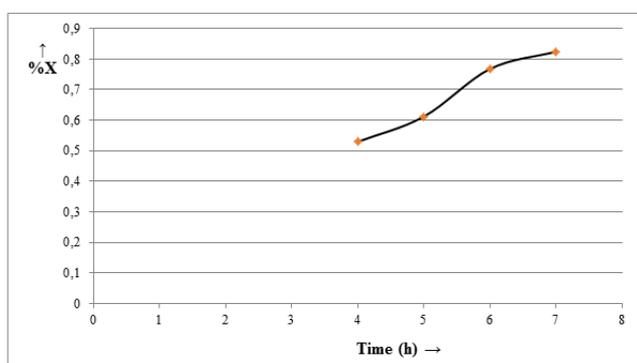

Figure 3 − Effect of time on Conversion to iodine value

Determination of oxirane oxygen content

The number of oxirane groups indicated by the percentage of oxirane was calculated using the equation below.

$$Oxygen \; content = \frac{(B-S) \times M \times 16 \times 100}{W \times 1000}$$

where S – volume of NaOH used for sample (ml); B = volume of NaOH used for blank (ml); M – Molarity of the NaOH – 0.1 M; W – weight of sample used (g).

The volume of NaOH used for blank (ml)

B_1 = 22.89 ml, B_2 = 22.89 ml, B_3 = 22.92 ml, B_{AV} = 22.90 ml, Reaction temperature = 65 °C (constant), Stirring speed = 750 rpm (constant).

a) Reaction time = 4 h, W = 0.20 g, S_1= 19.31 ml, S_2= 19.36 ml, S_3= 19.32 ml, S_{AV} = 19.33 ml.

$$Oxygen \; content = \frac{(22.90 - 19.33) \times 0.1 \times 16 \times 100}{0.2 \times 1000} = 2.86 \; \%$$

b) Reaction time = 5 h, W = 0.20 g, S_1= 19.00 ml, S_2= 19.02 ml, S_3= 19.01 ml, S_{AV} = 19.01 ml.

$$Oxygen \; content = \frac{(22.90 - 19.01) \times 0.1 \times 16 \times 100}{0.2 \times 1000} = 3.11 \; \%$$

c) Reaction time = 6 h, W = 0.20 g, S_1= 18.96 ml, S_2= 18.89 ml, S_3= 18.96 ml, S_{AV} = 18.97 ml.

$$Oxygen \; content = \frac{(22.90 - 18.97) \times 0.1 \times 16 \times 100}{0.2 \times 1000} = 3.14 \; \%$$

d) Reaction time = 7 h, W = 0.20 g, S_1= 17.25 ml, S_2= 17.10 ml, S_3= 17.10 ml, S_{AV} = 17.15 ml.

$$Oxygen \; content = \frac{(22.90 - 17.15) \times 0.1 \times 16 \times 100}{0.2 \times 1000} = 4.60 \; \%$$

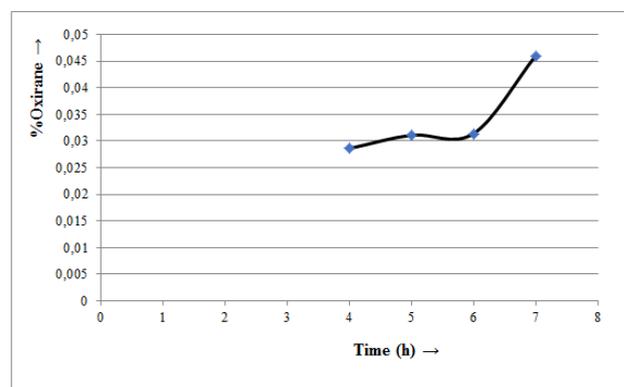The oxirane conversion for 4–7 h are summarized in Figure 4.

Figure 4 − Effect of time on conversion to oxirane content

Resins from Epoxidation and Acrylation Reactions. Four epoxy resins were synthesized from pure oil. Further modification of the epoxidized oils with acrylic acid yielded four acrylates epoxidized resins. Figure 5 shows examples of one out of the polishes from the epoxidation and further improvement (with acrylic acid) of pure sunflower oil.
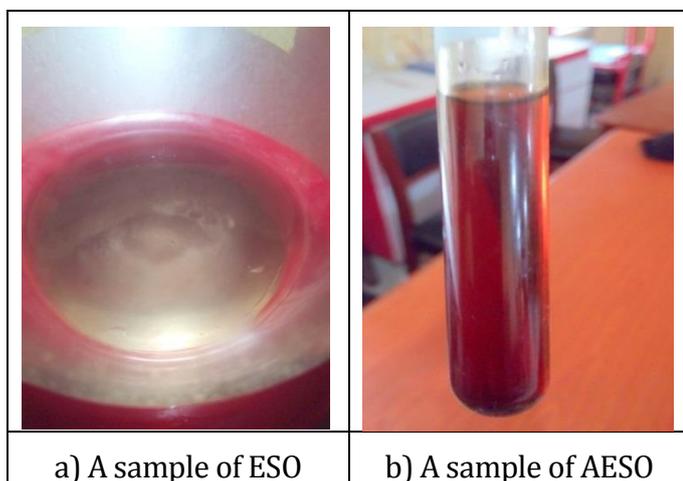
| a) A sample of ESO | b) A sample of AESO |

Figure 5 – Examples of generated epoxy and acrylate-modified resins

FT-IR spectroscopy analysis. The FT-IR spectroscopy of the untreated oil and the epoxy and further modified resins of sample 3 are shown in Figure 6. This sample was chosen because it showed the highest response. The FT-IR spectra were used to verify the ESO functionalization with acrylic acid and to compare the ESO and the acrylate resin with the untreated oil.

The iodine value and oxirane oxygen content are important properties in the characterization of epoxidized vegetable oils. While the Iodine value indicates the remaining unsaturation after the epoxidation reaction, the oxirane oxygen content indicates the epoxy groups present in the products. In the preparation of polymer, epoxy resins with lower iodine values and higher oxirane oxygen content are desired. The reduction in iodine values indicates the consumption of the unsaturation during epoxidation. But there did not represent conversion solely to epoxy groups because epoxy ring degradation generates side reactions.

The effect of time on iodine value and reaction conversation is shown in Figure 3. The result indicated that the conversion of iodine value in the sunflower oil increases linearly with an increase in reaction time. Also, the effect of reaction time on oxirane content is shown in Figure 4. The result indicates that oxirane content increases with time. Unsaturated double bonds in the oil were converted to an oxirane ring through an epoxidation reaction, as indicated by the decrease in iodine value. Maximum conversion of 82.45% (with iodine value of 21.07 g I2 / 100 g oil) was achieved at seven h reaction time and 65 ℃. The corresponding oxirane content was gotten to be 4.60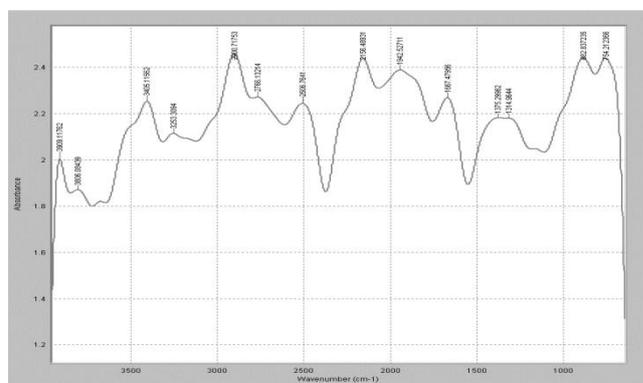 % at the same conditions. Hence the optimum operating condition for the epoxidation reaction was achieved at a reaction time of 7 h.
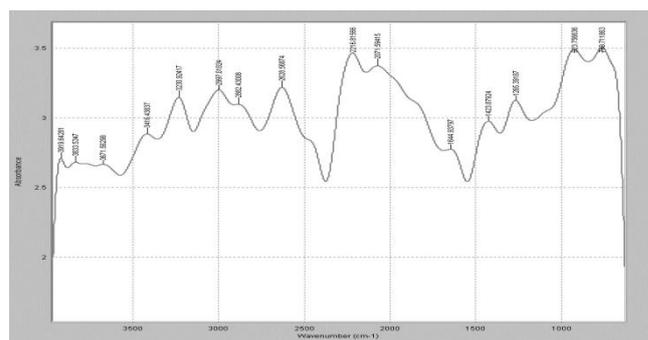
a) Untreated Oil
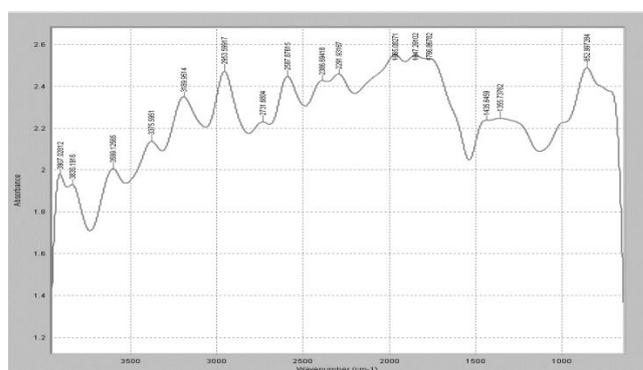
b) ESO

c) AESO

Figure 6 – FT-IR spectra of untreated, epoxidized, and acrylic-modified sunflower oil

For modification with acrylic acid, the esterification reaction took place between the epoxidized sunflower oil and acrylic in the presence of hydroquinone (as a cross-linking inhibitor). The epoxy group reacted with the carboxylic acid to form esters. The reaction occurred between the acid's carboxyl group and the epoxy and hydroxyl group of the epoxides. This resulted in the formation of acrylate epoxidized sunflower oil.

In the FT-IR spectra, it can be seen that the presence of carbon-carbon double bonds (C=C) in the untreated sunflower oil was indicated by the appearance of a peak at 1520 cm^{-1}. The single rise marked the absorption band for the epoxy group in ESO at 842 cm^{-1}, achieved after seven h reaction time and 65 °C temperature. This peak was missing in the untreated oil. The hydroxyl absorption is shown by the slope, down from 3900 cm^{-1}. The peak indicates the IR spectra for the acrylic group at 1690 cm^{-1}. This peak is absent in both the epoxy resin and the untreated sunflower oil, which shows that the acrylate resin was formed.

CONCLUSIONS

The environmental issues associated with petrochemical polymer materials brought about the need for using materials from renewable sources. Renewable raw materials are environmentally friendly, biodegradable, low-cost, and readily available. The most interesting raw materials candidate for bio-based thermosets can be found among plant seed oils, also known as triglycerides. Sunflower oil is an excellent example of plant seed oil. An effort is being made to produce 100% bio-based thermosetting materials. This report is based on the synthesis of thermoset resin from sunflower oil. From the results, it could be seen that biobased material could serve as a possible replacement showing that the generated composite could be used in automobile, construction, and furniture applications.

We are recommend further studies to be carried out, first by the use of other methods of vegetable oil modification apart from epoxidation and acrylation. Secondly by the extension of the reaction time to 10 hours and above (also beginning from zero hours), to determine the response at a higher number of hours. We also recommend using computer software such as design expert to model the process.

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