

Application of Fourier Transform Infrared (FT-IR) Spectroscopy to the Study of the Modification of Epoxidized Sunflower Oil by Acrylation

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Commercial sunflower oil was epoxidized at the laboratory-scale. The epoxidized sunflower oil (ESFO) was modified following the acrylation reaction. Modification was carried out simultaneously using acrylic acid (AA) and triethylamine (TEA). To optimize the reaction conditions, the effects of four temperatures (40, 60, 80, and 100 °C), the ESFO:AA (100:100) ratio, and 0.2% TEA were investigated. The rate of conversion was analyzed with both FT-IR and titration of the oxirane ring. After that, the temperature with the highest conversion was selected and used throughout for all modification reactions. Then, four ratios (100:100, 100:90, 100:80, and 100:75) of ESFO:AA were analyzed at four different concentrations of TEA (0.2, 0.3, 0.4, and 0.5%) to determine the best estimate for both the ESFO:AA ratio and the catalyst concentration. Conversion rate was analyzed using FT-IR spectroscopy by measuring the concentrations of ester, carbonyl, and alcohol groups. Moreover, oxirane ring concentration was estimated using the titration method (with gentian violet as indicator) and FT-IR spectroscopy (epoxy ring absorptions at 1270 cm^{-1} and 877 cm^{-1}). Based on conversion yield, the optimum ESFO:AA ratio corresponds to 100:80; the best temperature reaction was at 60 °C, and the best TEA concentration was 0.2%. The critical amounts of reactants needed to reach maximum conversion were established. The final acid value of the acrylated ESFO after washing (pH = 7) was 2.1 mg potassium hydroxide (KOH)·g⁻¹. All results show that FT-IR spectroscopy is a simple, low-cost, rapid method for investigating the kinetics of a reaction.

Index Headings: Sunflower oil; Acrylation; Fourier transform infrared spectroscopy; FT-IR spectroscopy; Optimization; Characterization.

INTRODUCTION

Plastics are widely used because they possess the qualities required for many applications. Although the extended life of plastic is due to its nonbiodegradability, that also makes it a source of pollution. Most polymers, such as polyethylene, polypropylene, polystyrene, polyethylene terephthalate, and polyvinyl chloride, however are derived from petrochemicals. Such resources will, arguably, be depleted within the next 100 years. Although the use of oil and related reserves for transportation and heating are serious concerns, the chemical industry will also be faced with real issues associated with the use of an essentially nonrenewable feedstock for most of its products.

The use of annually renewable feedstocks for the production of new plastics can have both economic and environmental benefits. Fundamental research in the production, modification, enhancement, and application of these materials is important.¹

Vegetable oils are renewable raw materials. Their conversion

to useful intermediates for polymeric materials is significant because of their low cost, ready availability, and possible biodegradability. Vegetable oils, such as soybean oil, palm oil, and rapeseed oil, are primarily extracted from the seeds of oilseed plants and have many applications, such as for foods, fuels (biofuels), lubricants, paints, cosmetics, pharmaceuticals, plasticizers, and construction materials. They are also attractive monomers for polymer chemistry because of their natural abundance and reactive functionality.¹

Vegetable oils based on triglycerides, which are biodegradable natural products, have the ability to be polymerized through various polymerization techniques, such as free-radical polymerization, cationic polymerization, thermal polymerization, or ring-opening polymerization in the presence of cross-linking agents. Various biodegradable resins based on epoxidized soybean, linseed, and castor oils have been made.²⁻⁵

Biodegradable polymers are those that degrade because of the action of microorganisms, enzymes, or both. Natural polymers are, by definition, those that are biosynthesized by various routes. Proteins, polysaccharides, nucleic acids, lipids, natural rubber, and lignin, among others, are all biodegradable polymers, but the rate of that biodegradation can vary from hours to years depending on the polymer's functional groups and degree of complexity.⁶

Sunflower oil is a renewable resource that can be epoxidized.⁷⁻⁹ Epoxidized sunflower oil (ESFO) has potential as an environmentally friendly, reactive material for polymer industries.

In this study, sunflower was first epoxidized and then modified by acrylation, based on results from Fourier transform infrared (FT-IR) spectroscopy. Once modified by acrylic acid (to which ESFO is very reactive), the ESFO has more functional groups as a result of the grafting of acrylate groups onto the triglycerides (alcohols, esters, and C=C double bonds) as shown in Scheme 1. The acrylation reaction was investigated to get optimum reaction conditions. The acrylated epoxidized oils will be used to develop new synthetic routes to biodegradable polymeric materials using renewable resources.¹⁰⁻¹²

Furthermore, acrylated triglycerides can be widely used in industry by blending with reactive diluent like styrene, to improve its processability and control the polymer properties. It is also possible to obtain polymers with different moduli and glass transition temperature (T_g). Consequently, a range of properties and, therefore applications can be found.

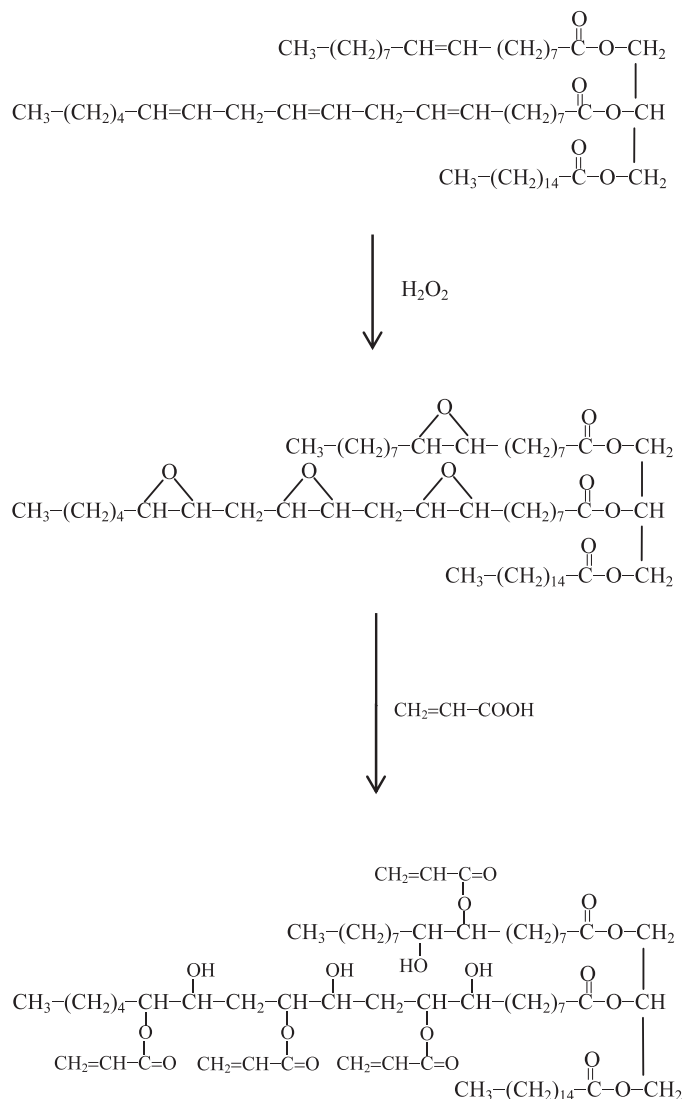
EXPERIMENTAL APPROACH

Materials. The ESFO (dynamic viscosity 198 cSt, density 0.91) was prepared as described previously.⁷ The level of

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SCHEME 1. Schematic representation of both epoxidation and the acrylation reaction products from sunflower oil.

oxirane oxygen was 6.1%. Acrylic acid (AA), triethylamine (TEA), hydrobromic acid (HBr) 35%, glacial acetic acid 99.9%, spectrum-grade potassium bromide (KBr), analytical grade ethanol (96% v/v), and gentian violet, as an indicator, were the commercial products used.

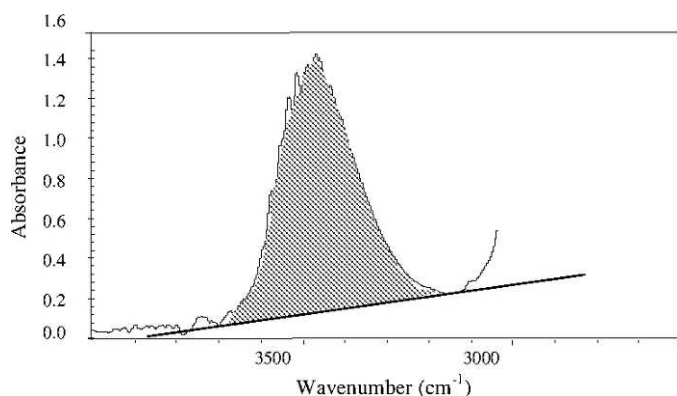


FIG. 1. Schematic representation of the area of absorption band.

Modification of Epoxidized Sunflower Oil. Reactions were carried out in a temperature-controlled, laboratory-scale reactor (a 150 ml, three-necked flask, equipped with a reflux condenser, a thermometer, and a magnetic stirrer). Different

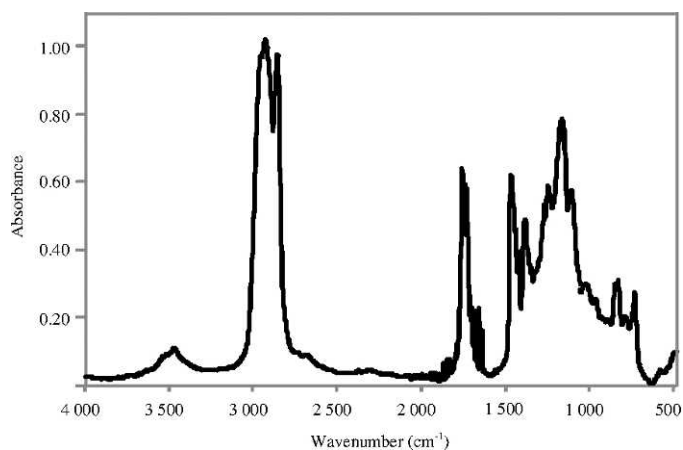


FIG. 2. The FT-IR spectrum of epoxidized sunflower oil (ESFO).

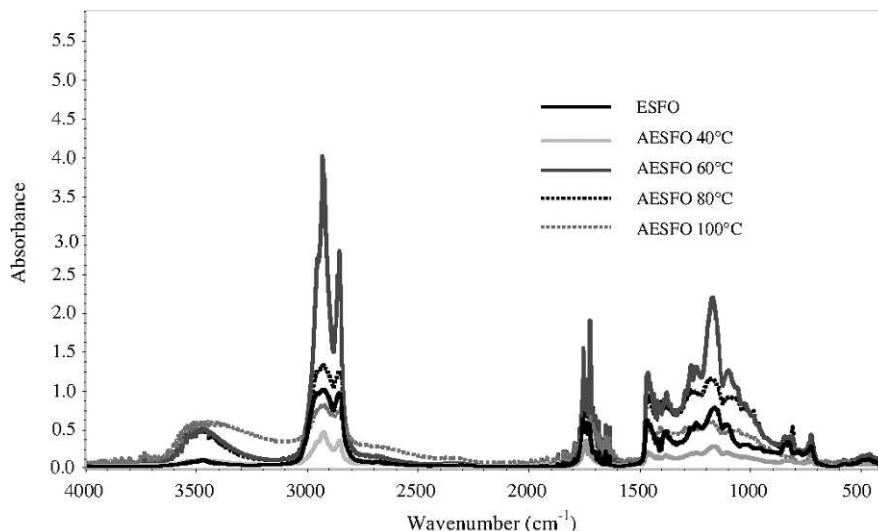


FIG. 3. The FT-IR spectra of acrylated epoxidized oils (AESFOs) at different acrylation temperatures compared with that of epoxidized sunflower oil (ESFO).

TABLE I. The primary peaks from AESFO at different temperatures.^a

	3671–3193 cm^{-1} (–OH stretching)	3099–2759 cm^{-1} (–CH=CH ₂)	1830–1620 cm^{-1} (C=O)	1440–1395 cm^{-1} (C–O)
AESFO (40 °C)	012.529	044.825	017.467	006.086
AESFO (60 °C)	084.887	354.953	094.591	044.591
AESFO (80 °C)	076.152	182.448	081.641	035.095
AESFO (100 °C)	109.646	080.634	057.513	018.005
ESFO	006.873	142.488	037.603	026.075

^a The ESFO:AA ratio is 100:100 by weight, with 0.2% TEA.

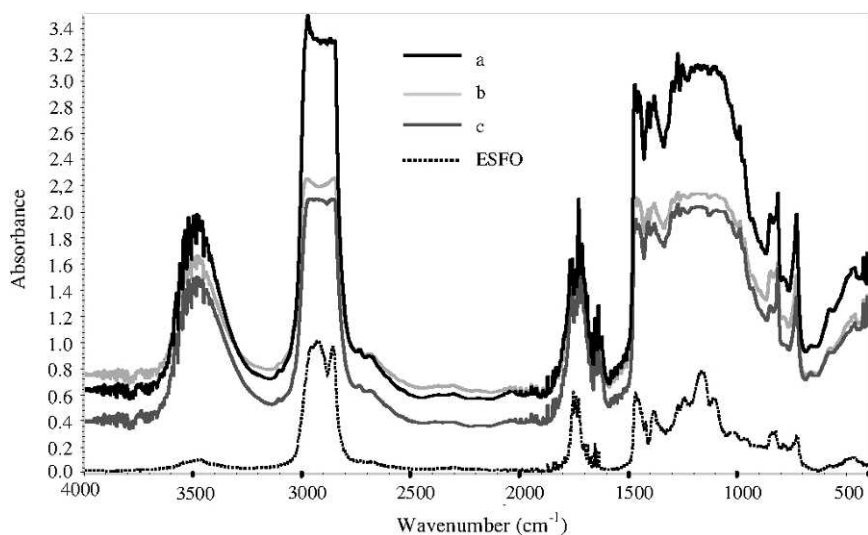


FIG. 4. The FT-IR spectra of acrylated epoxidized oils (AESFOs) (a) AESFO 100:80 (0.2% TEA), (b) AESFO 100:80 (0.4% TEA), (c) AESFO 100:90 (0.2% TEA) as compared with FT-IR spectrum of epoxidized sunflower oil (ESFO).

parameters were optimized: temperature, ESFO:AA ratio, amount of tertiary amine added, and reaction time. Conversion rate was analyzed by both FT-IR and titration of oxirane ring.

Temperature Optimization. In the laboratory-scale reactor, ESFO was with AA at ratio of 100:100 by weight using four different temperatures: 40, 60, 80, 90, and 100 °C. The TEA concentration was maintained at a constant 0.2% over all acrylation reaction. The ratio of the epoxy group to AA was

6.1:100 (0.381 mol of epoxy per 100 g of ESFO) and the ratio of epoxy group to carboxylic acid (COOH) was 6.1:62.5.

ESO:AA RATIO AND CATALYST

The temperature producing the highest conversion was 60 °C. Four ratios by percentage weight of ESFO:AA were examined: 100:100, 100:90, 100:80, and 100:75. The TEA concentration was increased at 0.2% to 0.5% at intervals of 0.1

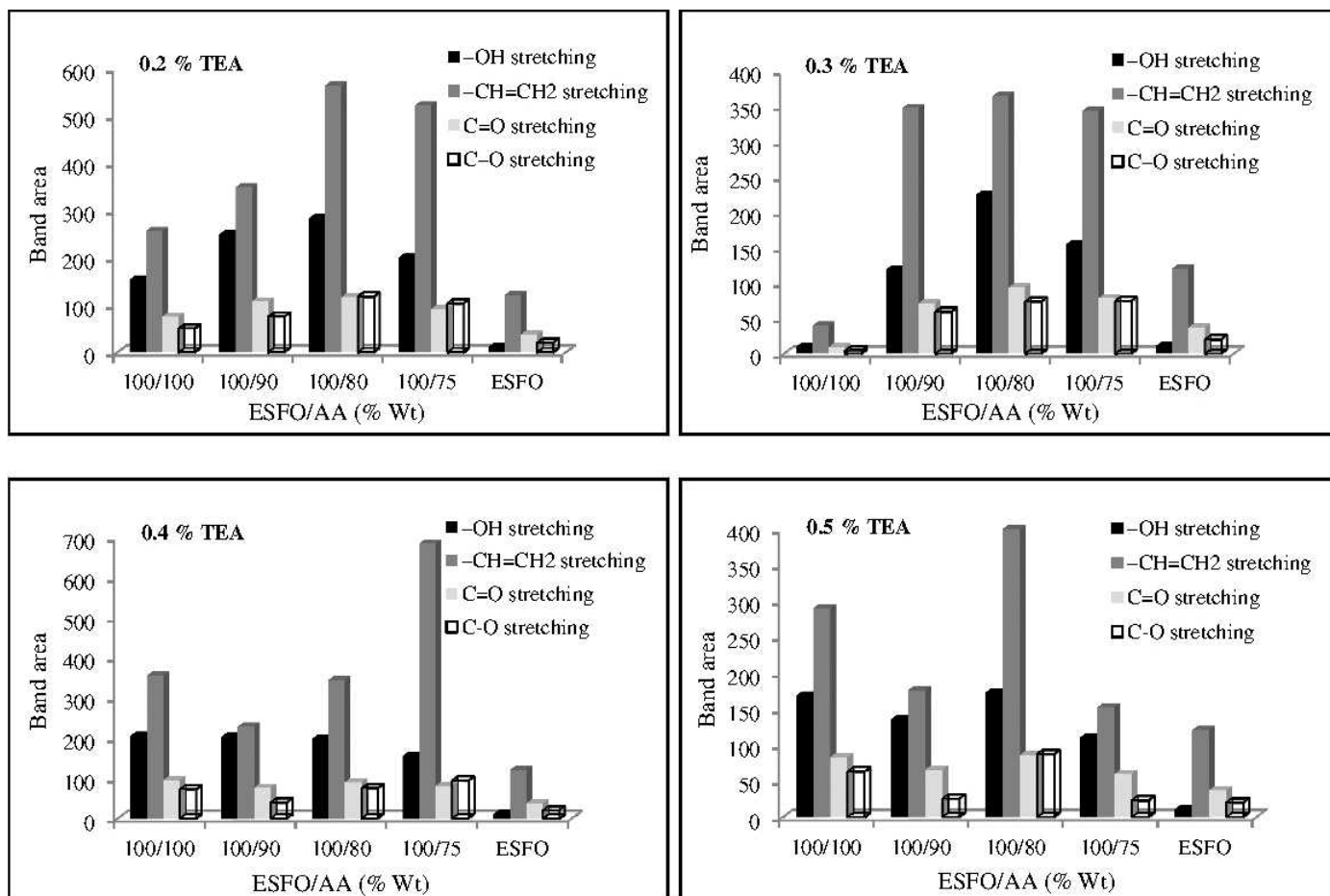


Fig. 5. Absorption-band active sites as a function of the ESFO:AA ratio at 0.2, 0.3, 0.4 and 0.5% TEA, compared with those of ESFO.

for each ESFO:AA ratio to provide the best estimate of both the ESFO:AA ratio and the catalyst concentration.

Reaction Time. After the best conditions were determined, three formulations were selected to study the effect of time on reaction level.

FT-IR Characterization. The FT-IR spectra were recorded on a 680 Nicolet thermo spectrometer (Thermo Scientific) at ranges from 4000 to 400 cm^{-1} . Absorbance spectra were acquired at 4 cm^{-1} resolution, and the signal was averaged over 32 scans using films of liquid ESFO and acrylated ESFO (AESFO) distributed on the surface of the KBr disks.

Titration of Oxirane Groups (Oxirane Index). The epoxy functionality was determined using a simple titration of epoxidized solution by HBr acid.¹³ Hydrobromic acid was diluted in acetic acid at 0.1 N. A quantity of 0.4–0.5 g of ESFO was weighted into a 50 mL conical flask. Finally, 10 mL of acetic acid and 4–5 drops of gentian violet indicator were added. The solution was stirred with a magnetic stirrer, which continued agitating throughout titration of the ESFO solution

by the hydrobromic acid. Equivalence was obtained when the purple solution was replaced with green-blue. This operation was repeated three times.¹³

Titration of Acid Value. Acid value was determined from the beginning of reaction following the 2009 International Organization for Standardization (ISO) 660 standard. Results were expressed in milligrams of KOH per gram of oil.

Viscosity Measurements. Viscosity was determined following the ISO standard 3104.^{14,15}

RESULTS AND DISCUSSION

The FT-IR spectroscopy was used for monitoring the reaction by qualitatively identifying the main signals corresponding to the epoxy group, the carbonyl of aliphatic esters, the secondary alcohols, and the acrylate double bonds, and were primarily quantitative by measuring the absorption-peak areas under identical conditions using a unified baseline (Fig. 1).¹⁶

TABLE II. Oxirane index of different modified oils from ESFO.^a

	ESO:AA (100:100) by weight				ESO:AA (100:90) by weight				ESO:AA (100:80) by weight				ESO:AA (100:75) by weight			
TEA (%)	0.5	0.4	0.3	0.2	0.5	0.4	0.3	0.2	0.5	0.4	0.3	0.2	0.5	0.4	0.3	0.2
Oxirane index	2.28	2.35	3.8	3.25	3.21	1.63	3.14	1.93	3.8	3.22	3.07	1.54	3.6	3.5	3.8	2.97

^a Temperature 60 °C, oxirane index 6.1.

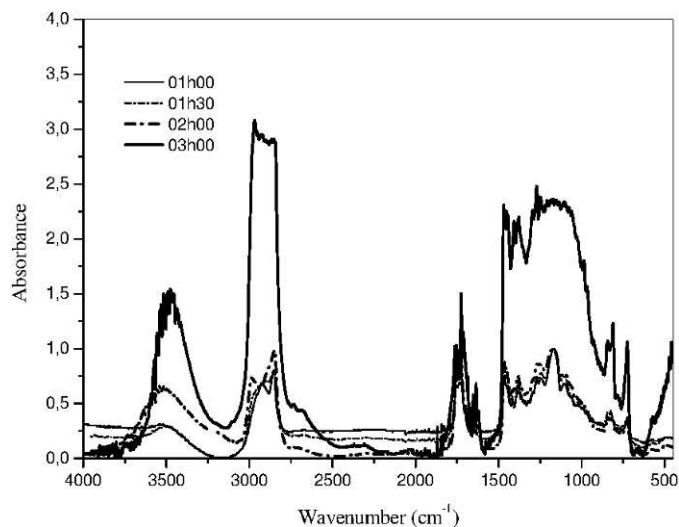


FIG. 6. The FT-IR spectra for time monitoring of the acrylation reaction of ESFO:AA 100:80 by weight (0.2% TEA).

Effects of Temperature. The FT-IR spectrum of ESFO is shown in Fig. 2. The C–O–C from oxirane-ring vibrations appears at 1270 cm^{-1} and 877 cm^{-1} . The FT-IR spectra of AESFO at the various temperatures are shown in Fig. 3. We can clearly see an increase in the concentration of the functional groups. The areas of different bands were calculated to estimate the concentration of each group in the different reactions.

Peaks at $3095\text{--}3075\text{ cm}^{-1}$ correspond to the stretching vibration of the double bonds: --CH=CH_2 (because of the presence of acrylates); signals at $3635\text{--}3620$ correspond to the --OH stretching (the free form of --OH), and the absorption at $1620\text{--}1650$ corresponds to the C=O stretching of ester carbonyl. Finally, the C--O stretching of the aliphatic ester is at $1440\text{--}1395\text{ cm}^{-1}$.^{17,18} The identification of these signals is the complementary evidence that modification has occurred.

Functional-group concentrations were calculated and are summarized in Table I. The best evolution of bands is at 60°C .

Effects of ESO:AA Ratio and Catalyst Amounts. Three spectra from all acrylation reactions are shown in Fig. 4: AESFO 100:80 (ESFO:AA) at 0.2% TEA, AESFO 100:80 (ESFO:AA) at 0.4% TEA, and AESFO 100:90 (ESFO:AA) at 0.2% TEA; also included is the ESFO spectrum to show the epoxidized oils have been modified. Band intensities were different from one reaction to another, which indicates the rate of conversion. Peaks corresponding to the stretching vibration of the double bonds --CH=CH_2 (of acrylates), the --OH stretching (free form of --OH), C=O stretching (of ester), and C--O stretching (of aliphatic ester) have increased in the concentration, compared with those of ESFO. These concentrations have been calculated, and the results are presented in Fig. 5 for TEA concentration percentages of 0.2, 0.3, 0.4, and 0.5%. These results were also supported by titrating the oxirane oxygen, which diminished in concentration; results are shown in Table II.

Effect of Reaction Time. The reaction was carried using an AESFO of ESFO:AA (100:80) percentages by weight and 0.2% TEA. The results of infrared analysis are illustrated in Fig. 6. After 3 h from the beginning of reaction, good conversion rates were recorded. The epoxy ring index was 1.32 at the end of the reaction. The drop in both acid value and oxirane oxygen index as a function of reaction time are plotted in Fig. 7.

AESFO Specifications. The acrylated epoxidized oils were whitish and slightly transparent, and their acid values ranged from 1.93 to $2.35\text{ mg KOH}\cdot\text{g}^{-1}$ after washing until pH 7 was reached, with a viscosity range of $440\text{--}558\text{ cSt}$ (25°C) and a density of 0.98 (25°C).

CONCLUSIONS

The results of this study show that ESFO modification occurred. The issues to be noted are the following:

- Qualitative FT-IR analysis showed the presence of the main

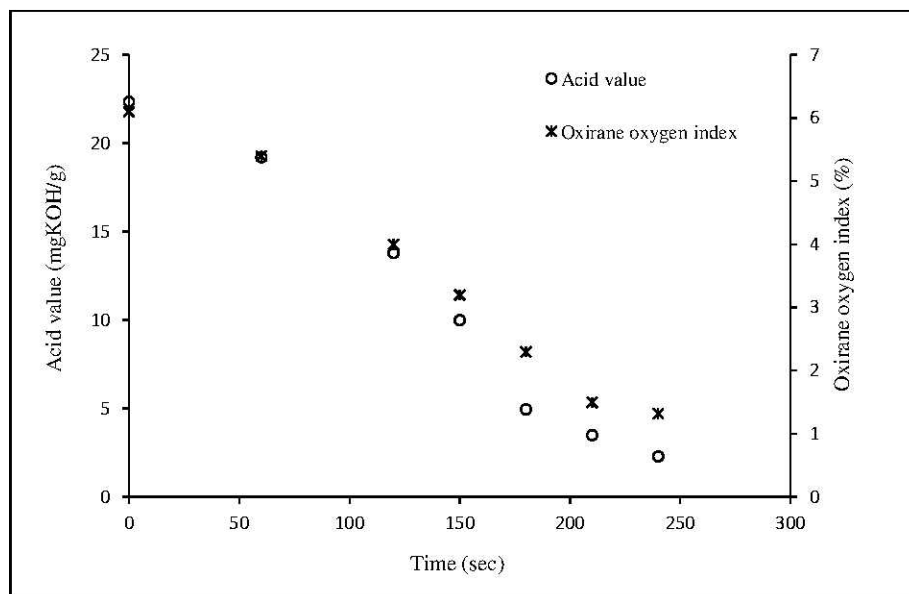


FIG. 7. Variation of both acid value and oxirane oxygen index as function of time the formulation ESFO:AA 10:80 by weight (0.2% TEA).

reactive sites: C–O and –C=O stretching of aliphatic esters, –OH of secondary alcohols (free form of –OH), and stretching the vibration of the double bonds –CH=CH₂ of the acrylates, confirms that modification of ESFO occurred.

- A remarkable increase in the reactivity of the modified oils (when grafted with AA) was determined by quantitative evaluation of FT-IR peak areas.
- A wide range of conversion percentages was obtained.
- Some of the remaining epoxies (which may be traces) have been confirmed and determined by the titration method using hydrobromic acid.
- Use of FT-IR spectroscopy is simple, low cost, rapid and can be used to investigate the modification reaction of ESFO by acrylation.

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