Advances in Analytical Chemistry 2021, 11(1): 1-8
DOI: 10.5923/j.aac.20211101.01

Determination of the Number of Epoxides Groups by FTIR-HATR and Its Correlation with ^{1}H NMR, in Epoxidized Linseed Oil

Juan F. Nieto[1,2], **Enrique Vigueras Santiago**[2], **Susana Hernández López**[2,*]

[1]Programa de Maestría en Ciencia de Materiales
[2]Laboratorio de Desarrollo y Caracterización de Materiales Avanzados (LIDMA), Facultad de Química de la Universidad Autónoma del Estado de México (UAEM), Toluca, C.P., México

---

Abstract By varying the conditions of the epoxidation reaction, samples of epoxidized linseed oil with different epoxidation degrees were obtained. The epoxidation of linseed oil was carried out by the formation of peracetic acid *in situ* using acetic acid, hydrogen peroxide solution, Amberlite IR-120H as the catalyst, and toluene as solvent. The quantification of the number of epoxides was carried out by ^{1}H-NMR and the values obtained were correlated with the absorbance of the epoxy group signal in the FTIR-HATR spectrum. The method used to quantify the absorbance of the epoxy group signal by FTIR-HATR is based on the analysis of two regions: the area between 765-854 cm^{-1}, and the net absorbance at 821 cm^{-1}. Both signals analysis showed high linear correlation coefficients corroborating that this methodology represents an easy, fast, and reliable technique in the quantification of epoxides in natural oils.

Keywords Linseed oil, Epoxidation, FTIR-HATR, ^{1}H-NMR

---

1. Introduction

Nowadays there is a great interest in epoxidized vegetable oils (EVOs) because they have a wide range of applications such as polyvinyl chloride (PVC) stabilizer [1], plasticizers [2,3], prepolymers [4–7], lubricants [8–10], as starting material to produce polyols [11–14], polyurethanes [15], as an intermediate in the fabrication of Non-isocyanate polyurethanes [16–23], etc. Usually, epoxides have been obtained from petroleum but this is a non-renewable source. However, vegetable oils are available in large quantities, they have a low cost and a non-toxic nature [20,24]. Two of the most important vegetable oils are soybean oil (SO) and linseed oil (LO) because of the large number of carbon double bonds present in their structure. Especially, LO has attracted attention due to has until 6.6 carbon double bonds. This characteristic is important due to the properties of the EVOs are affected by the number of epoxides [25,26]. Therefore, the greater the number of epoxides present in EVOs, the greater their reactivity.

There are several methods used to epoxidate vegetable oils [27–29] but the most common is the use of peracids to form the epoxy ring [8, 30–40]. Epoxidized linseed oil (ELO) has been used as raw material to produce bioresins [6,26,41,42] and cyclic carbonates [16,23,43] which are used in the fabrication of Non-isocyanate polyurethanes [20,22,23,43].

The epoxidation process can be monitored by chemical methods based on titrations [3,37,39,40,44,45]. These methods are usually accurate, however, they require the consumption of reagents, a large sample size as well as personnel and operating time and generate waste [44]. Also, problems in the determination of epoxide groups commonly arise in the presence of other functional groups or when simultaneous determinations are necessary [46]. ^{1}H-NMR [11,30,34,47–51], NARP-LC (Non-aqueous reversed-phase liquid chromatographic), and mass spectrometry [52] also have been used to quantify the number of epoxides and monitoring the epoxidation reaction of vegetable oils, however, these techniques are expensive and require a long waiting time to obtain the results.

On the other hand, mid-infrared spectroscopy has been widely using for the characterization of organic compounds. Both qualitative and quantitative information can be obtained by this technique [36,53,54]. The FTIR-HATR technique has many advantages such as small samples are required, no sample preparation is needing, and the course of the reaction can be followed easily and quickly.

The goal of this research was to quantify the number of epoxides per molecule in linseed oil with a high degree of epoxidation, by FTIR-HATR spectrometry as well as corroborating its reliability by ^{1}H-NMR.

---

* Corresponding author:
shernandezl@uaemex.mx (Susana Hernández López)
Received: Nov. 16, 2020; Accepted: Dec. 23, 2020; Published: Jan. 15, 2021

2. Material and Methods

2.1. Chemicals

The solvents toluene, ethyl acetate, and deuterated chloroform, chromatographic-grade α-Alumina, the catalyst Amberlite IR-120H (AIR-120H), hydrogen peroxide (30 and 50 wt.% solutions), and the reactive grade LO were supplied by Sigma-Aldrich, Co. The LO used has 6.5 double bonds and a molecular weight of 900.61 g/mol, both were determined by ^{1}H-NMR according to [11,43,47]. Acetic acid and anhydrous magnesium sulfate were acquired from Fermont. Sodium bicarbonate was purchased from J.T Baker. Whit the exception of LO, all the other reactants were used as they were received. LO was passed through a packed column of α-Alumina previous to use it, to eliminate the stabilizer.

2.2. Analytical Techniques

^{1}H-NMR spectra were recorded using a Varian spectrometer at 300 MHz with deuterated chloroform as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shift (δ) is quoted in ppm. The number of epoxides was calculated as described in [11,43,47].

FTIR-HATR spectra were acquired on an IRPrestige-21 SHIMADZU spectrometer equipped with a horizontal attenuated total reflectance (HATR) diamond crystal. The spectral window used was 4000-560 cm^{-1} with a resolution of 4 cm^{-1} and 64 scans.

2.3. Synthesis of Epoxidized Linseed Oil

The ELO samples with a different number of epoxides in their structure were obtained varying the temperature (65, 70, and 80°C), the concentration of hydrogen peroxide (30 and 50 wt.% solutions), the molar ratio of unsaturation to hydrogen peroxide (1:1 and 1:1.5) and the time of the reaction (40,50 and 120 min) keeping constant the values of the molar ratio of acetic acid to unsaturation (0.5:1.0), the quantity of toluene (44 wt.%) and Amberlite IR-120H (25 wt.%) respect to linseed oil weight. The epoxidized linseed oil was synthesized as described in [30]. The general procedure consisted of placing 10 g of LO with 6.5 double bonds in a two-neck reactor, 4.4 g of toluene as solvent, 2.5 g of Amberlite IR-120H as the catalyst, and 2.2 g of acetic acid. The mixture was kept under magnetic stirring for 15 min at 50°C. After that time, the addition of hydrogen peroxide (8.2 or 12.3 g at 30 wt.% solution or 4.9 or 7.4 at 50 wt.% solution) began by dripping. The temperature (50°C) was maintained constant using an oil bath to avoid the decomposition of hydrogen peroxide [55,56]. Once the addition of hydrogen peroxide was completed, the mixture was heated up until the temperature of the reaction was reached (65, 70, or 80°C). At the end of the reaction (40,50 or 120 min), the mixture was cooled to room temperature and 50 mL of acetyl acetate was added. The Amberlite IR-120H was separated by filtration and washed with ethyl acetate. The product of the reaction was washed with a saturated solution of sodium bicarbonate to neutralize. The oil phase was separated and the traces of moisture were eliminated using anhydrous magnesium sulfate. The solvents (toluene and ethyl acetate) were evaporated by vacuum distillation and the ELO samples were stored for 48 h in a vacuum desiccator to eliminate solvents traces. The ELO samples were analyzed by ^{1}H-NMR and FTIR-HATR techniques. Table 1 shows the epoxidation reaction conditions of the samples used.

Table 1. Epoxidation Reaction Conditions

Sample	LO (g)	Molar Ratio (Hydrogen Peroxide/ unsaturation)	T (°C)	Hydrogen Peroxide Solution (wt. %)	t (min)
ELO1	10	1.0	70	30	50
ELO2	10	1.0	80	30	50
ELO3	10	1.0	70	50	50
ELO4	10	1.0	80	50	50
ELO5	25	1.5	80	50	40
ELO6	10	1.5	65	50	120
ELO7	10	1.5	80	50	50
ELO8	10	1.5	80	50	50

t: Reaction time
LO: Linseed oil

3. Results and Discussion

The results of the evaluation of the variables used in the epoxidation reaction of linseed oil were discussed in detail in [30,43]. In the present work, we focus on the characterization and quantification of the epoxy groups by FTIR-HATR and ^{1}H-NMR techniques and their correlations.

3.1. ^{1}H-NMR Spectroscopy

Table 2. Signals Assignment of Partially Epoxidized Linseed Oil in the ^{1}H NMR Spectrum

Chemical Shift, δ (ppm)	Assignment
5.60	Olefinic hydrogens (-CH=CH-)
5.25	Central hydrogen in glycerol fraction (-CH_2-CH-CH_2-)
4.10-4.40	Four hydrogens in glycerol fraction (-CH_2-CH-CH_2-)
2.85-3.25	Epoxy group hydrogens (-CHOCH-)
2.15-2.45	Hydrogens of the methylene group alpha to carbonyl groups (-CH_2-CH_2-CO-O)
2.06-2.11	Allylic hydrogens (-CH_2-CH=CH-)
1.67-1.90	Hydrogens of the methylene group between two epoxy groups (-CHOCH-CH_2-CHOCH-)
1.54-1.67	Hydrogens of the methylene group beta to carbonyl groups (-CH_2-CH_2.-CO-)
1.40-1.54	Hydrogens of methylene groups adjacent to the epoxy group (-CH_2-CHOCH-CH_2-)
1.20-1.40	Hydrogens of the aliphatic methylene groups (-CH_2-)
0.76-1.13	Hydrogens of methyl groups (-CH_3)

^{1}H-NMR spectroscopy is a powerful technique used to characterize vegetable oils allowing quantify the number of unsaturation (carbon double bonds) and epoxides present in their structure [11,30,43,47,50,51,57]. Table 2 describes the assignment of all hydrogen signals of partially epoxidized linseed oil [30,43,47,49].

Figure 1 shows the ^{1}H-NMR spectrums of LO and ELO associated with the principal hydrogen signals of the theoretical structure of partially epoxidized linseed oil. These signals are used to monitor the epoxidation reaction of vegetable oils [30,43,47,48]. As the signal of the 4 hydrogens, that belong to methylene groups in the glycerol part (B, δ 4.1-4.4 ppm) remains without any change, it is possible to use it as an internal standard to quantify the area of all signals. Setting the value of this area to 4, the area of each signal is going to be proportional to the quantity of each equivalents hydrogens presents in the molecule.

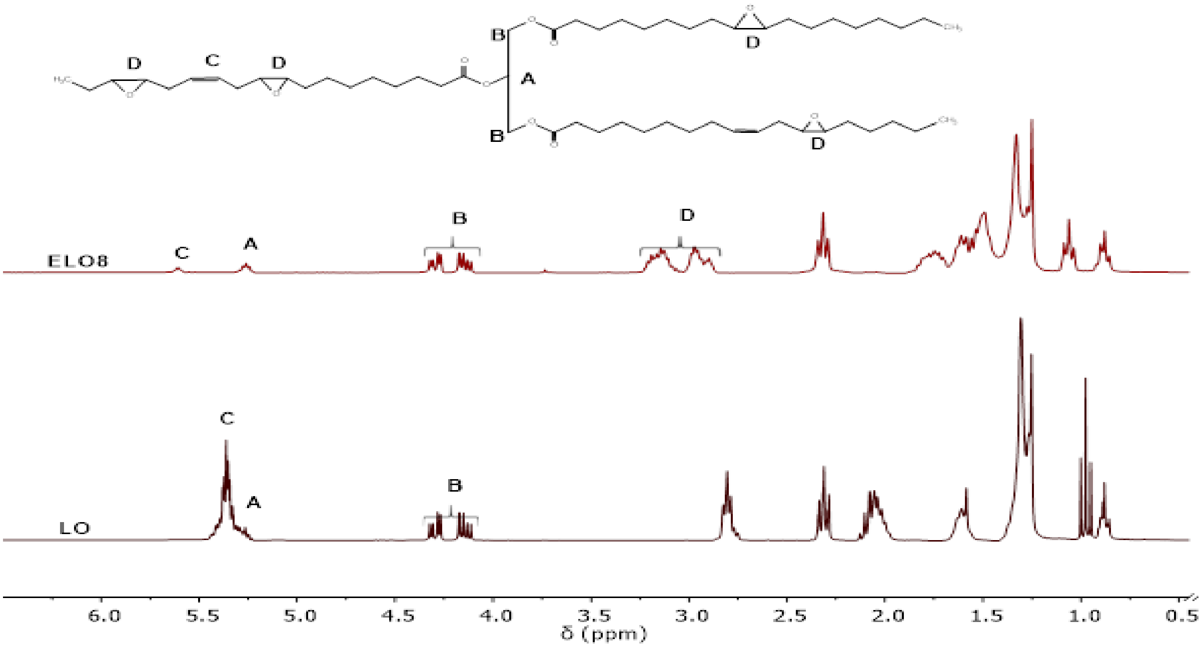

Figure 1. ^{1}H-NMR spectrums of linseed oil (LO) and partially epoxidized linseed oil (ELO)

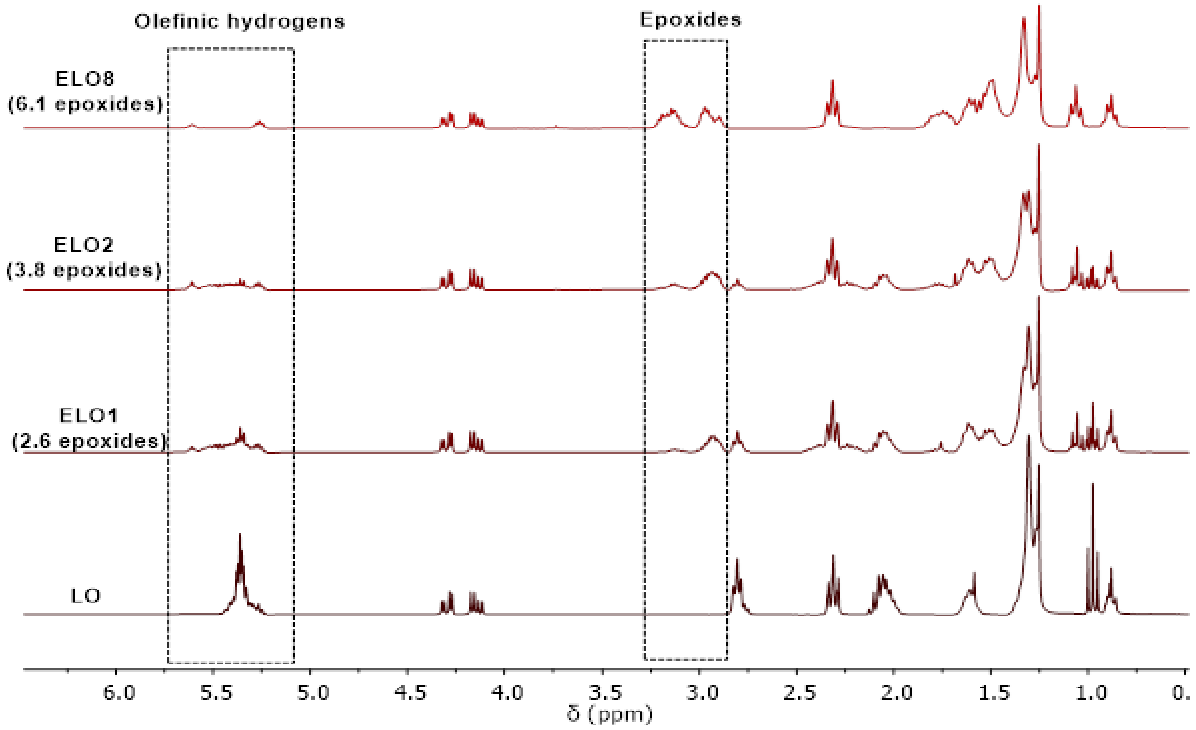

Figure 2. ^{1}H-NMR spectrums of samples of partially epoxidized linseed oil (ELO1, ELO2, and ELO8) and linseed oil (LO)

The signals of olefinic hydrogens (C, δ 5.6 ppm) and the hydrogen central of glycerol (A, δ 5.25 ppm) in the ELO spectrum are overlapped in the LO spectrum (centered in δ 5.35 ppm). However, this signal decreases as the double bonds react until being completely separated (Figure 2). Monitoring the olefinic hydrogen signal (C) is possible to quantify the number of carbon double bonds that remain in the structure allowing calculation of the conversion percentage of the reaction by Eq. (1). The hydrogens associated with epoxy groups (EG) (signal D, δ 2.85-3.25 ppm) are used to determine the number of epoxides in the molecule. As the number of epoxides present in the ELOs molecule grows the area of the hydrogen signals associated with the EG grows too (Figure 2). Relating the number of epoxides in the molecule with the initial carbon double bonds it is possible to calculate the percentage of epoxidation of the reaction by Eq. (2). The relation between the percentages of epoxidation to conversion is known as the selectivity percentage (Eq. (3)). These three parameters (conversion %, epoxidation %, and selectivity %) have been used to evaluate the epoxidation reaction of vegetable oils [30,43,47,48]. Table 3 shows the results obtained from the epoxidation reactions.

Table 3. Conversion, Epoxidation and Selectivity Percentages of the Epoxidation Reaction

Sample	Double Bonds	Epoxides	Conversion %	Epoxidation %	Selectivity %
ELO1	3.9	2.6	40.0	40.0	100.0
ELO2	2.7	3.8	58.5	58.5	100.0
ELO3	2.1	4.4	67.7	66.2	97.7
ELO4	1.9	4.5	70.8	69.2	97.8
ELO5	1.0	5.4	84.6	82.8	97.8
ELO6	0.1	5.5	86.5	84.3	97.5
ELO7	0.2	6.0	97.1	92.3	95.1
ELO8	0.1	6.1	98.5	93.8	95.3

$$\text{Conversion }\%=\left(\frac{\text{Initial double bonds-final double bonds}}{\text{Initial double bonds}}\right)*100 \quad (1)$$

$$\text{Epoxidation }\%=\left(\frac{\text{Epoxides}}{\text{Initial double bonds}}\right)*100 \quad (2)$$

$$\text{Selectivity }\%=\left(\frac{\text{Epoxidation }\%}{\text{Conversion }\%}\right)*100 \quad (3)$$

The highest number of epoxides in ELO (Samples ELO7 and ELO8) was obtained at 80℃, using a solution of hydrogen peroxide at 50 wt.% and the relation of 1.5 mol of hydrogen peroxide per unsaturation mol. Under the conditions used in the epoxidation reaction of LO, the hydrogen peroxide concentration was the most important factor to consider during the formation of the epoxides followed by the temperature [43]. The ELO samples obtained have an epoxidation percentage between 40% to 93.8%, which corresponds to 2.6 to 6.1 epoxides per molecule.

3.2. FTIR-HATR Spectroscopy

The infrared spectrum has been used to characterize organic compounds qualitatively because the different bonds present in the molecules vibrate at specific wavenumber (cm^{-1}). Also, it is possible to quantify functional groups, this is based on the Beer-Lambert law, in which the absorbance is proportional to the concentration of the functional group.

Evtushenko et al. 2003 and Nuñez et al. 2016 have related the growth of the epoxy signal in the IR spectrum with the concentration of epoxides obtained by chemical methods based on titrations.

On the other hand, Jebrane et al. 2017 related the areas of the epoxy groups from both the FTIR-ATR and ^{1}H-NMR spectrum for ELO with relative low epoxidation percentage (from 26.8% to 56.5%) and epoxidized soybean oil (ESO) with an epoxidation percentage from 28.9% to 69.0%. The epoxidation reactions were carried out by the formation of peracetic acid *in situ* using sulfuric acid as catalyst and low temperatures (30-50℃). According to the correlation coefficients obtained (0.96 and 0.99 for ELO and ESO, respectively), they propose the use of infrared spectroscopy to quantify the degree of epoxidation in vegetable oils.

The most important signals to follow the epoxidation reaction are the signals associated with the carbon double bonds (DB) and epoxy groups (EG). Figure 3 shows the FTIR-HATR spectrum regions of DB and EG respectively. These spectra were normalized with the signal of the carbonyl group of the ester at 1736 cm^{-1} (C=Ost) as an internal standard because its concentration was kept constant during the epoxidation reactions since the formation of the epoxide takes place between the peracetic acid formed *in situ* and the double bonds present in the LO [28,43,58]. Furthermore, the ELO hydrolysis reaction was ruled out, under the study conditions in the present work, due to the absence of hydroxyl group signals (OH-) in the FTIR-HATR spectra at 3100-3600 cm^{-1} region (Figure 3) and in the ^{1}H-NMR spectra at 3.3-4.1 ppm region (Figure 2) [43]. Also, the theoretical molecular weight of ELO samples was the same as the obtained by ^{1}H-NMR [43]. As shown in Figure 3, the signals of DB at 3009 cm^{-1} (=C-Hst) tend to disappear as the DB reacts. Contrary to the above, the epoxy group signals (765-864 cm^{-1}) tend to increase as the number of epoxy groups increase.

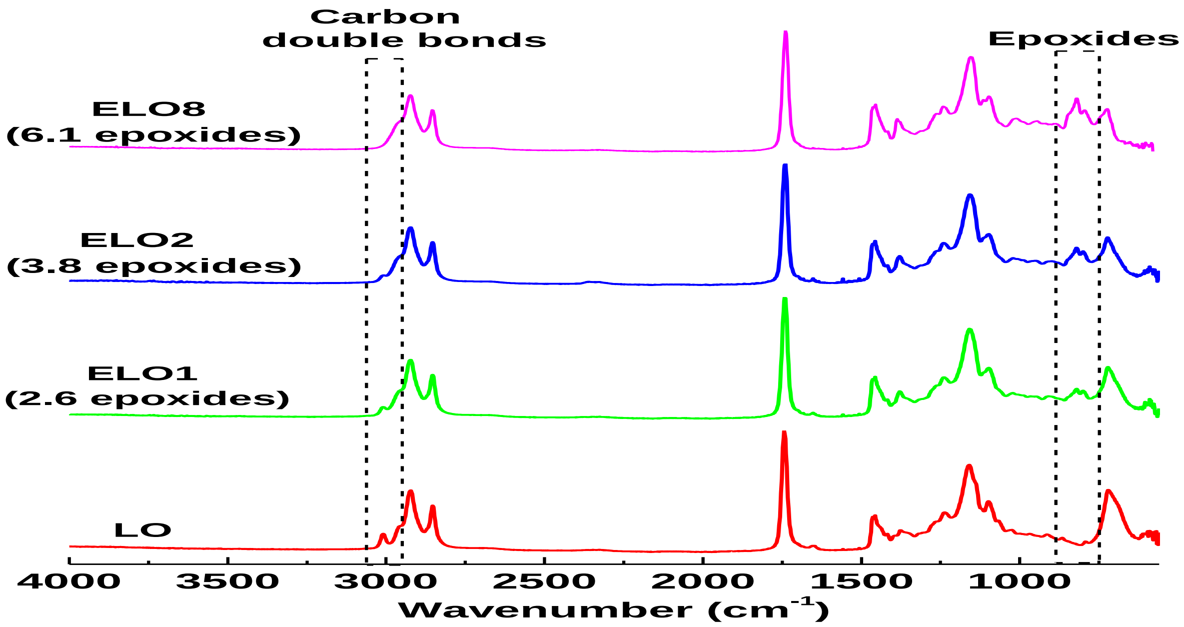

Figure 3. FTIR-HATR spectrum of linseed Oil (LO) and partially epoxidized linseed oil (ELO1, ELO2, and ELO8)

Measuring the area in the range at 765-864 cm^{-1} [36] and the net absorbance at 821 cm^{-1} of the EG signals by tracing a baseline (Figure 4) it is possible to relate these values with the number of epoxides obtained by ^{1}H-NMR. The wavenumber was chosen at 821 cm^{-1} because the EG signals present a maximum at this point.

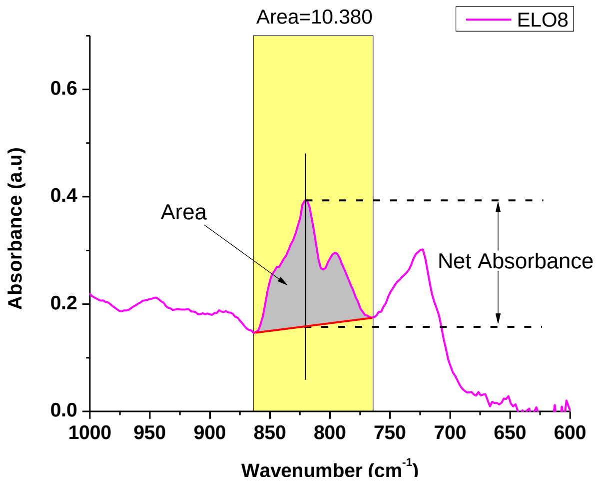

Figure 4. Measurement of the area (765-864 cm^{-1}) and the net absorbance (821 cm^{-1}) of the epoxy group signal of ELO in FTIR-HATR spectrum

Table 4 shows the number of epoxides per molecule obtained by ^{1}H-NMR, the area (765-864 cm^{-1}), and the net absorbance (821 cm^{-1}) obtained from FTIR-HATR spectrums of 8 samples of partially epoxidized linseed oil with different content of epoxides.

Table 4. Measurements of Areas and Net Absorbances of the Epoxy Group Signals of Partially Epoxidized Linseed Oil

Sample	Epoxides[a]	Area of Epoxy Group[b]	Net Absorbance of Epoxy Group[b]
ELO1	2.6	3.504	0.0910
ELO2	3.8	5.428	0.1355
ELO3	4.4	6.691	0.1619
ELO4	4.5	7.149	0.1703
ELO5	5.4	9.044	0.2131
ELO6	5.5	9.075	0.2154
ELO7	6.0	10.214	0.2306
ELO8	6.1	10.380	0.23259

a: Obtained by ^{1}H-NMR
b: Obtained from FTIR-HATR spectrums

The number of epoxides obtained by ^{1}H-NMR from the ELO samples was plotted as a function of the area (Figure 5) and the net absorbance (Figure 6). The linear correlation coefficients obtained were 0.9951 for the area method and 0.9953 for the net absorbance method. Both linear correlation coefficients were slightly higher than those reported by Jebrane et al. 2017 (R^2=0.96) for ELO. The high linear correlation coefficients obtained in this study and other works [36,46,54] corroborate that is possible to use FTIR-HATR spectroscopy for the quantification of the number of epoxides in epoxidized vegetable oils without taking into account the method used to epoxidize. This method also works to track the epoxidation reaction.

The mathematical models obtained from the linear fitting of the area and net absorbance methods (Figure 5 and Figure

6, respectively) were used to quantify the number of epoxides in partially epoxidized linseed oils obtaining good reproducibility with a maxima variation of 1.2% for the area and 1.9% for the net absorbance method. Also, if the number of initial double carbon bonds in vegetable oils is known is possible to report the epoxidation percentage of the reaction by Eq. (2) using the FTIR-HATR technique.

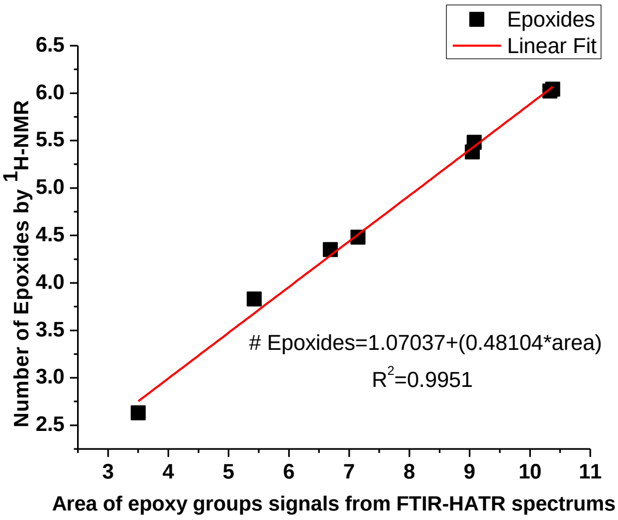

Figure 5. Correlation plot for area method

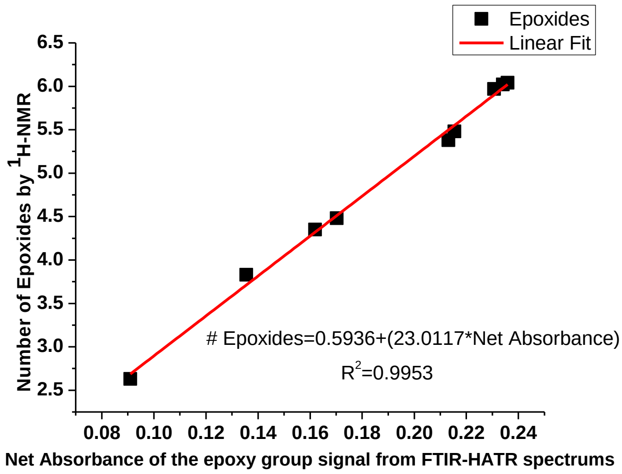

Figure 6. Correlation plot for net absorbance method

4. Conclusions

The high linear correlation coefficients obtained by the area (R^2=0.9951) and the net absorbance (R^2=0.9953) methods using FTIR-HATR spectroscopy corroborate that is feasible to use this technique to determine the number of epoxides per molecule on modified vegetable oils without taking into account the method of epoxidation used obtaining good accuracy.

ACKNOWLEDGEMENTS

The authors thank to project SIEA-UAEM 4965/2020CIB, CONACYT for the Master fellowship, and to M.C. María de las Nieves Zavala from CCIQS, UAEM-UNAM for her technical support in the ^{1}H-NMR analysis, through the intern project of the CCIQS SHL-2018.

REFERENCES

[1] P. Karmalm, T. Hjertberg, A. Jansson, and R. Dahl, “Thermal stability of poly(vinyl chloride) with epoxidised soybean oil as primary plasticizer,” *Polym. Degrad. Stab.*, vol. 94, no. 12, pp. 2275–2281, 2009.

[2] Y. B. Tee, R. A. Talib, K. Abdan, N. L. Chin, R. K. Basha, and K. F. Md Yunos, “Comparative study of chemical, mechanical, thermal, and barrier properties of poly(lactic acid) plasticized with epoxidized soybean oil and epoxidized palm oil,” *BioResources*, vol. 11, no. 1, pp. 1518–1540, 2016.

[3] D. Garcia-Garcia, A. Carbonell-Verdu, M. P. Arrieta, J. López-Martínez, and M. D. Samper, “Improvement of PLA film ductility by plasticization with epoxidized karanja oil,” *Polym. Degrad. Stab.*, vol. 179, p. 109259, Sep. 2020.

[4] E. A. Baroncini, S. Kumar Yadav, G. R. Palmese, and J. F. Stanzione III, “Recent advances in bio-based epoxy resins and bio-based epoxy curing agents,” *J. Appl. Polym. Sci.*, vol. 133, no. 45, pp. 1–19, Dec. 2016.

[5] Y. Chen, Z. Xi, and L. Zhao, “New bio-based polymeric thermosets synthesized by ring-opening polymerization of epoxidized soybean oil with a green curing agent,” *Eur. Polym. J.*, vol. 84, pp. 435–447, 2016.

[6] J. M. Pin, N. Sbirrazzuoli, and A. Mija, “From epoxidized linseed oil to bioresin: An overall approach of epoxy/anhydride cross-linking,” *ChemSusChem*, vol. 8, no. 7, pp. 1232–1243, 2015.

[7] Y. Y. Liu, J. He, Y. D. Li, X. L. Zhao, and J. B. Zeng, “Biobased, reprocessable and weldable epoxy vitrimers from epoxidized soybean oil,” *Ind. Crops Prod.*, vol. 153, no. May, p. 112576, 2020.

[8] A. Sammaiah, K. V. Padmaja, and R. B. N. Prasad, “Synthesis of epoxy jatropha oil and its evaluation for lubricant properties,” *J. Oleo Sci.*, vol. 63, no. 6, pp. 637–643, 2014.

[9] G. Gorla, S. M. Kour, K. V. Padmaja, M. S. L. Karuna, and R. B. N. Prasad, “Preparation and properties of lubricant base stocks from epoxidized karanja oil and its alkyl esters,” *Ind. Eng. Chem. Res.*, vol. 52, no. 47, pp. 16598–16605, 2013.

[10] R. Tesser, V. Russo, R. Turco, R. Vitiello, and M. Di Serio, “Bio-lubricants synthesis from the epoxidized oil promoted by clays: Kinetic modelling,” *Chem. Eng. Sci.*, vol. 214, p. 115445, 2020.

[11] E. Albarrán-Preza, D. Corona-Becerril, E. Vigueras-Santiago, and S. Hernández-López, “Sweet polymers: Synthesis and characterization of xylitol-based epoxidized linseed oil resins,” *Eur. Polym. J.*, vol. 75, pp. 539–551, 2016.

[12] P. Alagi, Y. J. Choi, J. Seog, and S. C. Hong, “Efficient and quantitative chemical transformation of vegetable oils to polyols through a thiol-ene reaction for thermoplastic polyurethanes,” *Ind. Crops Prod.*, vol. 87, pp. 78–88, 2016.

[13] P. Alagi, Y. J. Choi, and S. C. Hong, “Preparation of vegetable oil-based polyols with controlled hydroxyl functionalities for thermoplastic polyurethane,” *Eur. Polym. J.*, vol. 78, pp. 46–60, 2016.

[14] E. Sharmin, M. T. Kafyah, A. A. Alzaydi *et al.*, “Synthesis and characterization of polyvinyl alcohol/corn starch/linseed polyol-based hydrogel loaded with biosynthesized silver nanoparticles,” *Int. J. Biol. Macromol.*, vol. 163, pp. 2236–2247, Nov. 2020.

[15] Z. Dai, P. Jiang, W. Lou *et al.*, “Preparation of degradable vegetable oil-based waterborne polyurethane with tunable mechanical and thermal properties,” *Eur. Polym. J.*, vol. 139, no. September, p. 109994, 2020.

[16] D. Miloslavskiy, E. Gotlib, O. Figovsky, and D. Pashin, “Cyclic Carbonates Based on Vegetable Oils,” *Int. Lett. Chem. Phys. Astron.*, vol. 27, pp. 20–29, 2014.

[17] S. Doley and S. K. Dolui, “Solvent and catalyst-free synthesis of sunflower oil based polyurethane through non-isocyanate route and its coatings properties,” *Eur. Polym. J.*, vol. 102, pp. 161–168, 2018.

[18] B. Tamami, S. Sohn, and G. L. Wilkes, “Incorporation of Carbon Dioxide into Soybean Oil and Subsequent Preparation and Studies of Nonisocyanate Polyurethane Networks,” *J. Appl. Polym. Sci.*, vol. 92, pp. 883–891, 2004.

[19] I. Javni, D. P. Hong, and Z. S. Petrović, “Soy-based polyurethanes by nonisocyanate route,” *J. Appl. Polym. Sci.*, vol. 108, no. 6, pp. 3867–3875, Jun. 2008.

[20] A. R. Mahendran, N. Aust, G. Wuzella, U. Müller, and A. Kandelbauer, “Bio-Based Non-Isocyanate Urethane Derived from Plant Oil,” *J. Polym. Environ.*, vol. 20, no. 4, pp. 926–931, 2012.

[21] M. A. Sawpan, “Polyurethanes from vegetable oils and applications: a review,” *J. Polym. Res.*, vol. 25, no. 8, 2018.

[22] A. R. Mahendran, G. Wuzella, N. Aust, and U. Müller, “Synthesis, characterization, and properties of isocyanate-free urethane coatings from renewable resources,” *J. Coatings Technol. Res.*, vol. 11, no. 3, pp. 329–339, 2014.

[23] M. Bähr and R. Mülhaupt, “Linseed and soybean oil-based polyurethanes prepared via the non-isocyanate route and catalytic carbon dioxide conversion,” *Green Chem.*, vol. 14, no. 2, pp. 483–489, 2012.

[24] S. Miao, P. Wang, Z. Su, and S. Zhang, “Vegetable-oil-based polymers as future polymeric biomaterials,” *Acta Biomater.*, vol. 10, no. 4, pp. 1692–1704, 2014.

[25] S. J. Park, F. L. Jin, and J. R. Lee, “Synthesis and thermal properties of epoxidized vegetable oil,” *Macromol. Rapid Commun.*, vol. 25, no. 6, pp. 724–727, 2004.

[26] A. R. Mahendran, N. Aust, G. Wuzella, and A. Kandelbauer, “Synthesis and characterization of a bio-based resin from linseed oil,” *Macromol. Symp.*, vol. 311, no. 1, pp. 18–27, 2012.

[27] S. G. Tan and W. S. Chow, “Biobased epoxidized vegetable oils and its greener epoxy blends: A review,” *Polym. - Plast. Technol. Eng.*, vol. 49, no. 15, pp. 1581–1590, 2010.

[28] T. Saurabh, M. Patnaik, S. L. Bhagt, and V. C. Renge, “Epoxidation of vegetable oils: a review,” *Int. J. Adv. Eng. Technol*, vol. 2, no. Iv, pp. 491–501, 2011.

[29] B. M. Abdullah and J. Salimon, “Epoxidation of vegetable oils and fatty acids: Catalysts, methods and advantages,” *Journal of Applied Sciences*, vol. 10, no. 15. pp. 1545–1553, 2010.

[30] E. Dehonor Márquez, J. Nieto Alarcón, E. Vigueras Santiago, and S. Hernández López, “Effective and Fast Epoxidation Reaction of Linseed Oil Using 50 wt% Hydrogen Peroxyde,” *Am. J. Chem.*, vol. 8, no. 5, pp. 99–106, 2018.

[31] S. Dinda, A. V. Patwardhan, V. V. Goud, and N. C. Pradhan, “Epoxidation of cottonseed oil by aqueous hydrogen peroxide catalysed by liquid inorganic acids,” *Bioresour. Technol.*, vol. 99, no. 9, pp. 3737–3744, 2008.

[32] V. V. Goud, A. V. Patwardhan, and N. C. Pradhan, “Studies on the epoxidation of mahua oil (Madhumica indica) by hydrogen peroxide,” *Bioresour. Technol.*, vol. 97, no. 12, pp. 1365–1371, 2006.

[33] D. C. Webster, “Cyclic carbonate functional polymers and their applications,” *Prog. Org. Coatings*, vol. 47, no. 1, pp. 77–86, 2003.

[34] M. Musik and E. Milchert, “Selective epoxidation of sesame oil with peracetic acid,” *Mol. Catal.*, vol. 433, pp. 170–174, 2017.

[35] C. Cai, H. Dai, R. Chen *et al.*, “Studies on the kinetics of in situ epoxidation of vegetable oils,” *Eur. J. Lipid Sci. Technol.*, vol. 110, no. 4, pp. 341–346, Apr. 2008.

[36] M. Jebrane, S. Cai, C. Sandström, and N. Terziev, “The reactivity of linseed and soybean oil with different epoxidation degree towards vinyl acetate and impact of the resulting copolymer on the wood durability,” *Express Polym. Lett.*, vol. 11, no. 5, pp. 383–395, 2017.

[37] M. R. Janković, O. M. Govedarica, and S. V. Sinadinović-Fišer, “The epoxidation of linseed oil with in situ formed peracetic acid: A model with included influence of the oil fatty acid composition,” *Ind. Crops Prod.*, vol. 143, no. June 2019, 2020.

[38] A. F. Aguilera, P. Tolvanen, S. Heredia *et al.*, “Epoxidation of Fatty Acids and Vegetable Oils Assisted by Microwaves Catalyzed by a Cation Exchange Resin,” *Ind. Eng. Chem. Res.*, vol. 57, no. 11, pp. 3876–3886, 2018.

[39] A. B. Kousaalya, S. D. Beyene, V. Gopal, B. Ayalew, and S. Pilla, “Green epoxy synthesized from Perilla frutescens: A study on epoxidation and oxirane cleavage kinetics of high-linolenic oil,” *Ind. Crops Prod.*, vol. 123, no. June, pp. 25–34, 2018.

[40] M. Kurańska, H. Beneš, A. Prociak, O. Trhlíková, Z. Walterová, and W. Stochlińska, “Investigation of epoxidation of used cooking oils with homogeneous and heterogeneous catalysts,” *J. Clean. Prod.*, vol. 236, p. 117615, Nov. 2019.

[41] S. K. Sahoo, V. Khandelwal, and G. Manik, “Development of toughened bio-based epoxy with epoxidized linseed oil as reactive diluent and cured with bio-renewable crosslinker,” *Polym. Adv. Technol.*, vol. 29, no. 1, pp. 565–574, 2018.

[42] S. K. Sahoo, V. Khandelwal, and G. Manik, “Synthesis and characterization of low viscous and highly acrylated epoxidized methyl ester based green adhesives derived from linseed oil,” *Int. J. Adhes. Adhes.*, vol. 89, no. January, pp. 174–177, Mar. 2019.

[43] J. F. Nieto Alarcón, “Estudio de la reacción de carbonatación del aceite de linaza epoxidado,” Tesis de Maestría en Ciencia de Materiales. Facultad de Química. Universidad Autónoma del Estado de México, 2019.

[44] B. P. S. B. Dobbinsin, W. Hofmann, *The Determination of Epoxide Groups*, First. Pergamon Press, 1969.

[45] F. Gustone, *Rapessed and canola oil: production, processing, properties and uses*. Oxford: Blackwell Publishing, 2004.

[46] Y. M. Evtushenko, V. M. Ivanov, and B. E. Zaitsev, “Determination of Epoxide and Hydroxyl Groups in Epoxide Resins by IR Spectrometry,” *J. Anal. Chem.*, vol. 58, no. 4, pp. 347–350, 2003.

[47] G. L. Téllez, E. Vigueras-Santiago, and S. Hernández-López, “Characterization of linseed oil epoxidized at different percentages,” *Superf. y Vacío*, vol. 22, no. 1, pp. 5–10, 2009.

[48] M. Farias, M. Martinelli, and D. P. Bottega, “Epoxidation of soybean oil using a homogeneous catalytic system based on a molybdenum (VI) complex,” *Appl. Catal. A Gen.*, vol. 384, no. 1–2, pp. 213–219, 2010.

[49] W. Xia, S. M. Budge, and M. D. Lumsden, “1H-NMR Characterization of Epoxides Derived from Polyunsaturated Fatty Acids,” *JAOCS, J. Am. Oil Chem. Soc.*, vol. 93, no. 4, pp. 467–478, 2016.

[50] R. T. Alarcon, C. Gaglieri, K. J. Lamb, M. North, and G. Bannach, “Spectroscopic characterization and thermal behavior of baru nut and macaw palm vegetable oils and their epoxidized derivatives,” *Ind. Crops Prod.*, vol. 154, p. 112585, Oct. 2020.

[51] Y. Awoke, Y. Chebude, C. Márquez-Álvarez, and I. Díaz, “Solvent free epoxidation of vernonia oil using Ti-SBA-15 with tailor made particle morphology and pore size,” *Catal. Today*, vol. 345, no. September, pp. 190–200, Apr. 2019.

[52] S. T. Anuar, Y. Y. Zhao, S. M. Mugo, and J. M. Curtis, “Monitoring the epoxidation of canola oil by non-aqueous reversed phase liquid chromatography/mass spectrometry for process optimization and control,” *JAOCS, J. Am. Oil Chem. Soc.*, vol. 89, no. 11, pp. 1951–1960, 2012.

[53] M. González-González, J. C. Cabanelas, and J. Baselga, “Applications of FTIR on Epoxy Resins - Identification, Monitoring the Curing Process, Phase Separation and Water Uptake,” *Infrared Spectrosc. - Mater. Sci. Eng. Techology*, vol. 2, pp. 261–284, 2012.

[54] C. Núñez, E. Vergara, J. Lisperguer, and C. Droguett, “Fast and reliable method for monitoring epoxidation reaction in recycled vegetable oils (ERVO) using FTIR-ATR technique,” *J. Chil. Chem. Soc.*, vol. 61, no. 1, pp. 2763–2766, 2016.

[55] Z. A. Bakar, Z. Idris, A. Hazmi *et al.*, “Process control for epoxidation of rbd palm olein,” *J. Oil Palm Res.*, vol. 28, no. 2, pp. 228–233, 2016.

[56] P. D. Meshram, R. G. Puri, and H. V. Patil, “Epoxidation of wild safflower (Carthamus oxyacantha) oil with peroxy acid in presence of strongly acidic cation exchange resin IR-122 as catalyst,” *Int. J. ChemTech Res.*, vol. 3, no. 3, pp. 1152–1163, 2011.

[57] P. Joseph-Nathan and E. Díaz T., *Introducción a la Resonancia Magnética Nuclear*, Primera Re. México: Editorial Limusa, S.A., 1980.

[58] X. Zhao, T. Zhang, Y. Zhou, and D. Liu, “Preparation of peracetic acid from hydrogen peroxide. Part I: Kinetics for peracetic acid synthesis and hydrolysis,” *J. Mol. Catal. A Chem.*, vol. 271, no. 1–2, pp. 246–252, 2007.