Characterization of linseed oil epoxidized at different percentages

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Several degree-epoxidized linseed oils (8, 20, 35, 40, 47 and 54%) were prepared for changing different reaction parameters such as temperature, amount of peroxide and enzyme of the well studied chemoenzymatic epoxidation method. The epoxidation reaction following was carried out by Infrared spectroscopy (FTIR) and Proton Nuclear Magnetic Resonance (H^1NMR) which are the most usual spectroscopes for this propose. However, microRaman spectroscopy and Differential Scanning Calorimetry (DSC) characterization were used in this work as complementary techniques. Particularly, DSC permitted to correlate the epoxy-aperture energy to each epoxidation percentage making it another optional technique for quantify epoxidation levels in triglycerides.

Keywords: Linseed oil; Enthalpic heat; Epoxy aperture; Chemoenzymatic reaction

1. Introduction

Due to the recent concerns about contaminants and their effects in nature, there has been an increased interest in producing environmentally friendly products that substitute the oleo-chemical derived ones. Hardly biodegradable natural oils that come from renewable resources are a good choice as raw materials for producing a variety of products such a coatings, paints, lubricants, soaps [1], inks [2], among others [3,4]. For more complex molecules such polymers, copolymers and their composites, the oils have to be chemically modified. One of the most interesting functional group for this purpose is the epoxy ring. Epoxidation consists on the formation of an oxirane (epoxy) group by the reaction of peroxyacids (peracids) and olefinic double bonds. In general, peracetic or performic acids are used in epoxidation process for oxygen transfer to the double bonds [5]. The use of these acids is prone to loss of yield and side reactions as hydrolysis of the ester groups. A better method has been presented by Rusch gen, et al. [6,7] and consists on using an immobilized enzyme, the lipase B of *Candida antarctica* as catalyst. This process is selective and takes place under mild conditions, giving high epoxidation yields suppressing completely the undesirable ring opening. The reaction system consists of an aqueous phase containing the hydrogen peroxide, an organic phase containing usually toluene as solvent, the oil, and free fatty acid and immobilized enzyme as solid phase readily separable [8]. Epoxies are valuable commercial products and specifically epoxidized triglycerides have been used as diluents [9], lubricants [10], coatings [11] and stabilizers in PVC. They are known as phthalate-free, non-volatile, extraction and migration resistant plasticizers [12] and have been prepared from linseed, rapeseed, olive, corn, and sunflower, mainly. However, those epoxidized triglycerides can be used also as polymer building blocks [13,14], for producing more interesting materials as polyester resins [15], blends [16], nanocomposites [17], thermal and oxidative stable compounds [18]. Acrylate-epoxidized oils had been very studied derivates for obtaining polymer and composites with important mechanical [19,20], thermal [21], and electrical properties [22,23] comparable to those of the petrochemical-derivated materials. In this last topic, composites based on acrylate-epoxidized soybean oil (AESO), poly(butylmethacrylate) and carbon black, have shown very low percolation concentration (less than 2% w/w CB) [23] than those composites based on oil-polymers.

The synthesis and characterization of epoxidized linseed oil is analyzed in this work with special focus on the characterization of the desired product. Usually, the following of epoxidation reaction and its products are qualitative or semi quantitative characterized by spectroscopic techniques such as Nuclear Magnetic Resonance (NMR) [3], Infrared Spectroscopy (FTIR) [3,9,25], mass spectrometry, chromatography [6,9,25,27], and Near Infrared spectroscopy (NIR) [24]. However, they are usually quantitative supported by analytical methods as iodo index, oxirane index [9,24,25,26] and viscosity [9], mainly. In this work, epoxidized products at different percentages were additionally to Infrared spectroscopy (IR) and Proton Nuclear Magnetic Resonance (H^{1-}NMR) also characterized by MicroRaman spectroscopy and Differential Scanning Calorimetry (DSC). Double bonds number and then epoxidation conversion were calculated by H^1NMR based on the well accepted and reliable method described by Diaz and Joseph-Nattan [28]. On the other hand, DSC renders information of the heat changes in a sample by heating or cooling it. The changes could be physical, chemical even biological. Due to the oxirane aperture is a chemical exothermic process, we suggest the possibility of establish a relationship between the released

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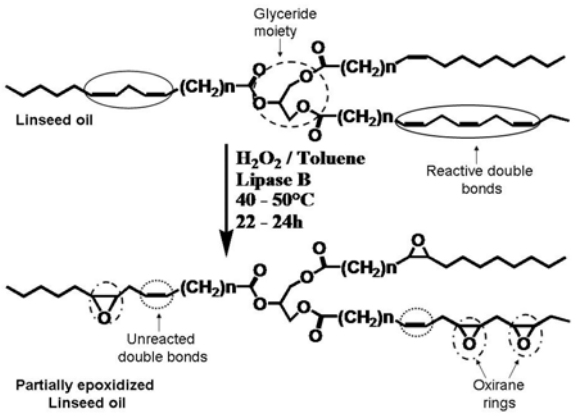

Figure 1. Epoxidation reaction of linseed oil.

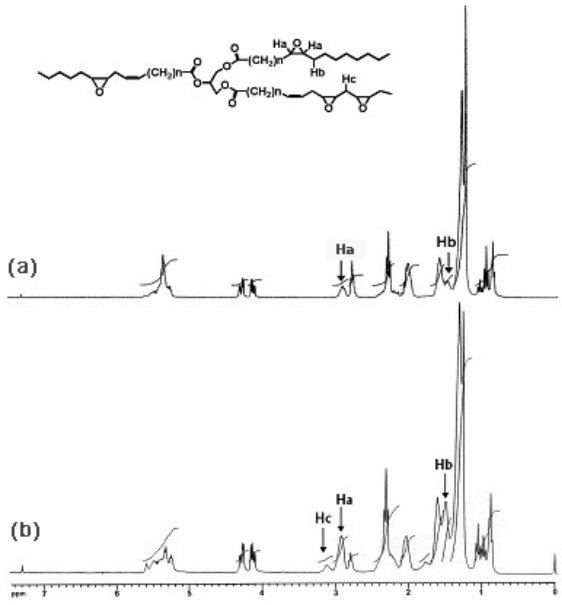

Figure 2. H^1RMN spectra of (a) ELO_2 epoxidized 20%, and (b) ELO_6 epoxidized 54%.

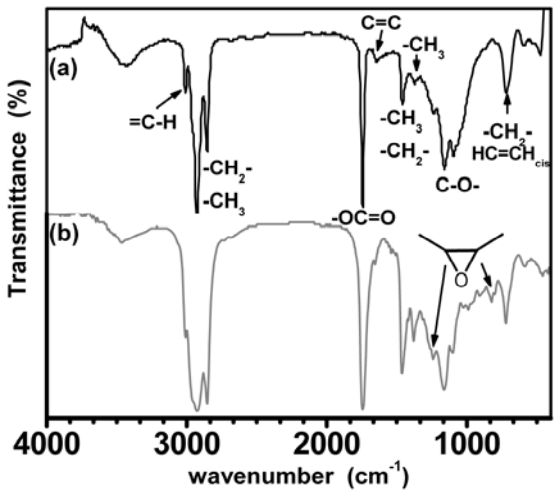

Figure 3. FTIR spectra of (a) LO and (b) ELO_6 .

heat of the oxirane rings from the oils with the epoxidized degree which is proportional to the oxirane amount.

2. Materials and methods

2.1. Reactants

Reactive grade Linseed oil, Novozyme 435 (immobilized *Candida antarctica* lipase B) oleic acids (99%), toluene (analytic grade), deutered chloroform ($CDCl_3$), chromatographic grade alumina and spectrum grade potassium bromide (KBr) were purchased from Sigma-Aldrich, Co. and used without any treatment. Hydrogen peroxide 30% and 50% v/v aqueous solution were purchased from Fermont, sodium bicarbonate (analytic grade) and anhydrous magnesium sulfate.

2.2. Equipment

The FTIR spectra were measured on an Avatar 360 FTIR spectrometer into the range of 4000 to 400 $cm^{-1.}$ Absorbance spectra were acquired at 4 cm^{-1} resolution and signal averaged over 32 scans. Samples were prepared as follow: A film of liquid and oily samples (linseed oil (LO) and epoxidized linseed oil (ELO)), was distributed on the surface of KBr disk. The H^1 NMR spectra were recorded on a Bruker Avance 300 MHz Nuclear Magnetic Resonance, solving the samples in $CDCl_3$. MicroRaman spectra were recorded on a Jobin Yvon-Horiba Labram 800 spectrometer, with a He-Ne laser at a wavelength of 632.8 nm. The samples were introduced into a capillary and measured directly on the top of it. Measurements of the ring aperture heat were made on a coupled heat-flux DSC-TGA, SDT Q-600 modulus from TA Instruments previously calibrated with zinc. A heating rate of 20 °C/min from 30 to 600°C under nitrogen atmosphere (100 mL/min) and platinum pans were the conditions used for the ramp. The aperture reaction heat in Joules per gram (J/g) was obtained for integrating (Thermal Advantage software) the area under the curve of the corresponding exothermic transition in the DSC curve.

3. Experimental

Synthesis of epoxidized linseed oil (ELO)

Epoxidized linseed oil (ELO) was synthesized using the chemoenzymatic method described in the cited journals [6-8]. Many conditions were changed in order to obtain several epoxidation degrees [25]. A general procedure (Figure 1) is described and the specific conditions are showed in Table 1 (synthesis columns). All of them are referenced to 5 g of linseed oil (LO) which contains 6.4 double bonds number and 887.4 g/mol of molecular weight (both determined by H^1 NMR) [29]. LO was solved in 10.6 mol of Toluene, then 0.105 g of oleic acid and the given amount of lipase B (Table 1) were added and mixed. Finally, hydrogen peroxide at 30 or 50% was dropped in 5

Table 1. Reaction conditions for the epoxy reaction of Linseed Oil, and some characterization.

Sample	Synthesis			H^1NMR characterization		DSC evaluation	
Epoxide	**Temperature** (°C)	**Peroxide** (g)	**Lipase B** (g)	**Epoxidation percentage**	**Number of epoxy groups per molecule**	**Energy** (J/g)	**Peak Temperature** (°C)
LO	-	-	-	0	0	0	397.0[c]
ELO_1	44-46	0.70[a]	0.10	8	0.5	186	395
ELO_2	48-50	1.2[b]	0.14	20	1.3	192	380
ELO_3	44 46	1.2[b]	0.14	35	1.9	359	371
ELO_4	40-42	0.8[ba]	0.14	40	2.5	410	344
ELO_5	44-46	1.0[a]	0.14	47	3.0	417	330
ELO_6	44-46	1.2[b]	0.30	54	3.4	478	321

[a] Peroxide aqueous solution at 50%
[b] Peroxide aqueous solution at 30%
[c] This temperature corresponds to T_{10}, that means the temperature at which LO has lost 10% of its original weight.

min. Temperature was increased and led to reach the established one (Table 1) and the reaction was mechanically stirred for 22 h. The mixture was allowed to cool to room temperature and 5 mL of toluene were added followed by filtering the lipase B using a Buchner funnel and vacuum. The enzyme was left to dry and was stored for further reactions. The filtered liquid was transferred to a separator funnel and washed 2 times each with 50 mL of a 2% sodium bicarbonate aqueous solution. Organic layer was dried with $MgSO_4$ anhydrous and filtered. Toluene was evaporated under vacuum to give the epoxidized oil in 85% yield. The methodology described in this work was carried out several times (at least three) for obtaining a good reproducibility.

4. Results and discussion

Since the objective of this work was to obtain different percentages of epoxy rings, some reaction conditions were modified in order to get them (Table 1). The epoxidation percentages obtained according to the reactions conditions established here are shown in Table 1 (H^1NMR characterization columns), being 54% [29] the maximum conversion. The epoxidation percentage was reproduced very well (± 2%) but the yield was some different each time, between 83-86%. Many conditions and their influence on the epoxidation conversion and yield had been studied for other authors [25, 26]: the hydrogen peroxide concentration, solvents, temperature, moles of enzyme and the addition and quantity of a carboxylic acid ester or fatty acid [7]. Many authors have reported epoxidation percentages up to 85% by increasing the amount of enzyme up to 20% mol respect to the oil [25].

The corresponding assignment of the signals for LO, has been reported in other works [2, 3]. The signals and the corresponding integrals for linseed oil used in this work are given as follow: the signal at 0.75 ppm corresponds to the hydrogens of the ending methyl groups ($C\mathbf{H}_3$-$(CH_2)_n$-); the peak at 1.0 ppm is due to the hydrogens of the ending methyl groups of linolenic acid ($C\mathbf{H}_3$-CH_2CH=CH-), the integral (I) for these both peaks was 4.853. Peaks at 1.2-1.4 ppm (I = 19.051) originate from aliphatic methylene hydrogens (-$C\mathbf{H}_2$-); hydrogens beta to the carbonyl group (-$C\mathbf{H}_2$-CH_2-C(O)-O-) are detected at 1.7 ppm (I = 3.216); the peak at 2.05 ppm (I = 5.307) corresponds to the allyl hydrogens (-$C\mathbf{H}_2$-CH=CH-); the methylene hydrogens alpha to carbonyl groups (-$C\mathbf{H}_2$-C(O)-O-) appear at 2.35 ppm (I = 3.009); peak at 2.7 ppm (I = 3.654) originates from hydrogen between two double bonds (-CH=CH-$C\mathbf{H}_2$-CH=CH-); at 4.1-4.4 ppm (I = 2.944) methylene hydrogens from the glyceride moiety (-CH-$\mathbf{CH}_2$-O-) appear; finally vinyl hydrogens (-C**H**=C**H**-) and methyne hydrogen from glyceride group (-C**H**-O-C(O)-) is detected at 5.35 ppm (I = 6.767). The number of double bonds (6.4) and molecular weight (887.4 g/mol) for LO were calculated from the H^1NMR-integrals according to the relationship discussed and used in other works [28, 29].

Figure 2a and 2b correspond to ELO epoxidized at 20% (ELO_2) and 54% (ELO_6), respectively. The percentages were calculated from the integrals of double bonds and epoxy ring hydrogen signals [29]. The signals associated to the epoxy group are: -CH- hydrogens (H_a) which are sited at 2.9 ppm with integrals of 1.08 and 2.258 for ELO_2 and ELO_6, respectively. -CH- hydrogens adjacent to epoxy groups (H_b) appears at 1.45 ppm with 2.073 and 4.004 integrals, respectively. -CH- hydrogens between two epoxy groups (H_c) are sited at 3.1 ppm, with a no detectable integral for ELO_2 while it was 0.536 for ELO_6. Comparing the Integrals of the hydrogens at 5.4 ppm, it decreases from 6.767 for LO to 4.847 and 2.998 for ELO_2 and ELO_6, respectively. That decreasing was attributed to an upfield shift of those vinyl hydrogens due to the hybridization change of the carbons. They were originally bonded to sp^2 carbons and these changed to sp^3 carbons after they were transformed in oxirane ring. Some similar behavior was produced in allyl hydrogens originally sited between two double bonds (2.0 ppm), after epoxidation they are shifted to 1.45 ppm.

The FT-IR spectroscopy was used for monitoring the reaction by qualitative identification of the main signals corresponding to epoxy group mainly. In order to show it, only two spectra are analyzed: the raw oil, LO and ELO_6 (Figures 3a and 3b, respectively). For LO the signals at 3020 cm^{-1}, 1650 and 719 cm^{-1} correspond to the stretching

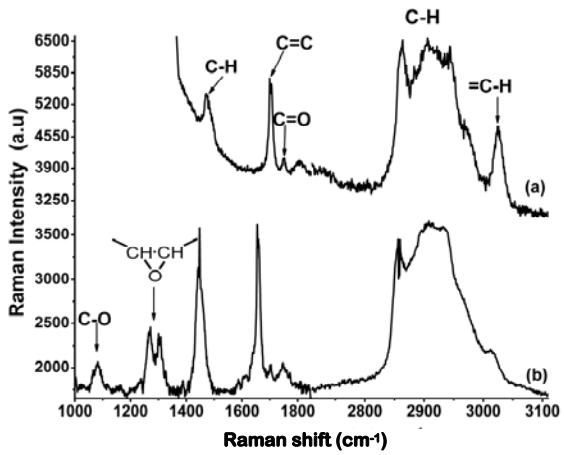

Figure 4. Raman spectra of (a) LO and (b) ELO_6.

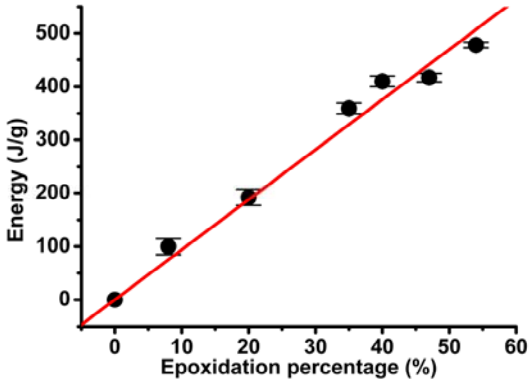

Figure 5. Curve showing a linear correlation between calculated epoxidized degree and epoxy aperture energy.

vibration of the double bonds: =C-H, C=C, *cis*-CH=CH, respectively. In the FTIR spectrum of ELO_6 (Figure 3b), these signals decreased but no completely due to the epoxidation conversion was not 100%. C-O-C stretching from oxirane vibration (Figure 2b) appears at 1250 cm^{-1} and 830-850 cm^{-1}. The signal at 1250 cm^{-1} usually overlay with other as the C-O ester one in these kinds of oils [30]. The most representative signal that evidences the oxirane group is the small intensity one sited at 830 cm^{-1} [3, 25]. The identification of this signal and the diminishing mainly of the 3020cm^{-1} double bonds band, are the complementary evidence of the epoxidation reaction is taking place. This was always supported by H^1NMR and complemented by Raman spectroscopy. Otherwise, it is well known that the main side reaction in the epoxidation process in oils is the hydrolysis of the ester group. However, in the course of the reaction no evidence of the carbonyl from carboxylic acid group signal was observed. This band usually is very intense (even at low carboxylic group concentration,) and is sited at 1650 cm^{-1} [29], near but differentiable of the ester carbonyl in the glyceride moiety at 1741 cm^{-1}.

In the same way as FTIR, microRaman was useful as a monitoring qualitative technique of signals involved in the chemical reaction. The advantage of it is that double bonds signals in Raman are very useful due to they are more intense than in FTIR spectroscopy. This advantage allows reliable changes followings in that functional group. Considering that no reports about the use of this spectroscopic technique for characterize epoxidized oils, all the signals are assigned for LO and ELO_6 in this work. A Raman spectrum for LO is showed in Figure 4a. The region (1300-1900 cm^{-1}) could be assigned to the next vibrations modes: bending C-H at 1450 cm^{-1}, stretching C=C at 1660 cm^{-1}, stretching C=O at 1707 cm-^{1}. In the next region (1900-3250 cm^{-1}), we could appreciate the stretching C-H vibration from methyl and methylene groups into the range from 2800 to 3000cm^{-1} and the strong vinyl stretch vibration =C-H at 3025 cm^{-1}. The region from 400 to 1000 cm^{-1} (out of range in the figure 3a) evidenced some fluorescence effect which could be attributed to some residual lead naphtene stabilizer even it was removed passing the oil through a chromatographic alumina column twice. This compound is part of the formulation for avoiding the oxidation of linseed oil. However, is well documented that this type of salts in ppm [30, 31] is enough to produce that effect in a strong way.

Raman signals for the epoxy ring were identified in Figure 4b by the doublet at 1280 a 1260 cm^{-1} which correspond to symmetric stretching vibrations. Other bands are those sited at 1500-1490 cm^{-1} and 2800-3000 cm^{-1} which are typical for the bending and stretching C-H vibration, respectively from methyl, methylene and methyne groups. Signal at 1650 cm-^{1} corresponds to unreacted C=C groups. Carbonyl group from glyceride moiety is observed as a weak signal at 1700 cm^{-1}. Finally there is a very weak signal (a shoulder) around 3090–3010 cm^{-1} corresponding to the =C-H stretching vibration from double bonds. Due to its important intensity decreasing in comparison with the unreacted oil, is a very reliable support of its chemical transformation in this case, to an oxirane ring. Using this spectroscopy is difficult to detect if some side reaction were carried out on the ester carbonyls. In case of hydrolysis, an carboxylic acid functional group is formed and according to some references [32] this carbonyl group doesn't show a Raman signal.

Oxirane ring posses a high potential energy due to its strain angular in such a way that the ring-opening reaction is an exergenic one giving the evolution of thermal energy (heat).The opening of the epoxy groups have much higher energy differences than other reactions and the amount of heat evolved corresponds to the number of epoxy group reacting and to the rate of the reaction [34]. The dominant effect is the enthalpy change although structural changes results in significant entropy change [34]. Those enthalpy changes are usually and quantitatively studied by calorimetry, conventionally by Differential Scanning Calorimetry since the heat flow during a constant pressure reaction is defined as the change of enthalpy of the system, obtained form the area under the exotherm peak [33,34,36].

Initially the reaction kinetics is controlled by the chemical reactivity of the functional groups, but later on becomes controlled diffusion and the degree of the conversion levels offs and tends to a limiting value [14,33].

The enthalpic information for LO and the synthesized epoxidized linseed oils is registered in Table 1 (DSC columns). It can be seen that as epoxidation percentage (calculated by H^1NMR) or number of epoxy group per linseed molecule increases, the exothermic cure energy increases too (from 180°C for ELO_1 to 417°C for ELO_6) and the peak temperature (end of the reaction) decreases (from 395 for ELO_1 to 330°C for ELO_6) . This last effect on the peak temperature could be explained as follow: when an epoxy ring is opened, it reacts with another epoxy group simultaneously bonding to another fatty chain. As a low number of epoxy rings there is a low probability of reaction among epoxy groups in such a way that it is enhanced with an increasing of temperature and of the chains mobility. At a higher number of oxirane groups, that probability of reaction increases needed lower temperatures for reacting.

The energies on Table 1 (DSC columns), were correlated to calculated epoxidation percentage giving a linear correlation of 0.9915 (Figure 5). Considering that epoxidation percentages were calculated from H^1NMR spectra, this method could be considered as a good alternative for quantify the epoxidation levels in natural oils. In order to make it a reliable and reproducible method, it will be necessary to quantify the epoxidation percentage using quantitative direct methods as oxirane and, iodo index, viscosity, chromatography, as mentioned before.

Kinetic studies through DSC, DSCS, DMA, had been done in simple epoxy resins compounds [33, 34, 35] in presence or absent of cross linkers molecules, but not in epoxidized triglycerides surely due to their more complex structure. However we have started a kinetic study on epoxidized linseed oil and the results will be published in a future.

Conclusions

The chemoenzymatic method for epoxidation of linseed oil is an efficient way to avoid side reactions and to obtain a wide range of conversion percentages. The reaction was supported by FTIR and Raman spectroscopes, the epoxy signals were well identified and intensity of the signals due to the double bonds vibrations and not any side reactions were evidenced by the spectroscopic techniques used. H^1NMR was a powerful tool for evidence the reaction. It permitted to obtain the number of double bonds (unsaturations) which was used to correlate it with the epoxy number and epoxidation percentage of the oils. Finally, the exothermic process of epoxy aperture rendered good information and correlation with the epoxidation level in linseed oil and it is proposed as a quantification and characterization alternative for evaluating epoxidized natural oils.

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