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On the polymerisation of the epoxidised biodiesel: The importance of the epoxy rings position, the process and the products

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ABSTRACT

Polyesters were prepared using epoxidised methyl esters of oleic acid (EP_{OAME}) and epoxidised biodiesel (mixture of methyl esters) from sunflower oil (EP_{SOME}) and linseed oil (EP_{LOME}) with cis-1,2-cyclohexanedicarboxylic anhydride and triethylamine. The kinetic of partial processes involved in the polymerisation were elucidated and related to epoxy rings position in the fatty acid chain. The activation energies (E_a) for the epoxy ring opening by the catalyst are 298, 216 and 136 kJ/mol for EP_{OAME}, EP_{SOME} and EP_{LOME} respectively. The reactions of the epoxy rings in the positions C9–C10, C12–C13 and C15–C16 with anhydride require average activation energies of 116, 32 and 22 kJ/mol, respectively. The compensation effect between activation energy and pre-exponential factor is observed. The polymerisation enthalpy, molecular weight, glass transition temperature and electrical properties were determined. The polyesters studied show promising properties for use in various technological applications.

1. Introduction

Renewable resources, such as vegetable oils and animal fats, have great potential to substitute petrochemical derivatives. They tend to be biodegradable and therefore, less aggressive on the environment, less expensive and more diverse [1,2]. Vegetable oils are fatty acid triglycerides, which have different degrees of unsaturation. Fatty acids differ in the length of their carbon chain, the number and the position of double bonds. The unsaturated fatty acids with 18 carbons are the dominant constituents of vegetable oils (over 80%). Oleic acid (C18:1) presents only one unsaturation, which is located at C9–C10 position. Linoleic acid (C18:2) includes two unsaturated bonds at C9–C10 and C12–C13 positions, while linolenic acid (C18:3) has three unsaturations at C9–C10, C12–C13 and C15–C16 positions [1,2]. Depending on the double bonds distribution in the fatty acids, the materials produced from them have specific physical and chemical properties. A good knowledge in polymerisation of triglycerides was achieved in the last decades. Larock and co-authors [3] have produced polymers using the cationic copolymerisation of different vegetable oils. The chemical, physical, thermal and mechanical properties of the polymers were investigated as a function of the vegetable oil composition [3]. Polyurethane networks have been synthesised from polyols based on different vegetable oils [4–6].

From the other side, biodiesel polymerisation still counts with limited number of studies. Concerning synthesis and characterisation of polyesters obtained from biodiesel Martini et al. [7] investigated the reaction kinetics of epoxidised biodiesel from linseed oil with different cyclic anhydrides. Similarly, Reiznautt et al. [8] studied polyester formation using epoxidised sunflower biodiesel. Nicolau and co-authors reported the properties of linear polyesters produced from oleic acid and the respective

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methyl oleate in solution [9] and bulk [10]. Other important contributions in this area are given by Bunker and co-authors that produced high molecular weight polymers from methyl oleate [11].

To obtain polyesters from biodiesel, the respective vegetable oil has to be transesterified. The reactivity of monoalkyl esters, obtained as biodiesel, needs to be improved by the introduction of other functionalities to the molecules. Epoxidation has an important role in the functionalization of fatty acid derivatives [12–15]. Epoxides are very versatile structures in organic synthesis and are susceptible to a large number of nucleophilic, eletrophilic, acidic, alkaline, and reducing and oxidising agents. Because of this versatility, the epoxides are susceptible to polymerisation process when submitted to heat in the presence of reticulation agents, which are, generally, amines and anhydrides [16].

In the present work, epoxidised methyl esters of oleic acid, sunflower and linseed oils were used to synthesise polyesters. The polymerisation processes were evaluated in terms of the double bonds content and their position in the fatty acid chain. For first time, according to our knowledge, it was possible to determine the activation energy and the respective pre-exponential parameters of the epoxy rings located at different positions in the fatty acid chain. Nuclear magnetic resonance (^{1}H and ^{13}C NMR), infrared spectroscopy (FTIR), gel permeation chromatography (GPC), thermal analysis (DSC, TGA) and electric impedance spectroscopy (EIS) techniques contributed for the elucidation of the chemical process and the characterisation of the polyesters produced. Additionally, this study evaluates the relation of resistivity, capacitance and dielectric relaxation of the polyesters with the average number of epoxy rings in the fatty acid methyl esters. Assuming that the average number of epoxy rings, affects the structure of the obtained polyesters, through ramification or even crosslinking, it is to expect differences in the electrical properties. The properties of the studied polyesters are promising for different technological applications. These materials can be used as adhesives, plasticizers, thermal and electrical insulators, as well as intermediates for polyelectrolytes.

2. Experimental

2.1. Materials

Sunflower oil, linseed oil (Farmaquímica, Porto Alegre – Brazil) and oleic acid P.A (Synth, São Paulo – Brazil) were used as raw materials in this work. Table 1 summarises the fatty acid composition of the oils used. Other materials, including triethylamine 99%, cis-1,2 cyclohexanedicarboxylic anhydride 99%, 1,4-butanediol diglycidyl ether 95% and deuterated chloroform $CDCl_3$ 99.8% in deuterium with 0.03% w/w TMS (tetramethylsilane) were from Aldrich Chemical Co. Methanol 99.9%, potassium hydroxide (KOH) 85%, toluene 99.5% and formic acid 85% were from Synth (São Paulo – Brazil). Acetone 99.5%, sodium hydroxide (NaOH) 98.1% and hydrogen peroxide 29.0% w/w in water were from Nuclear (Diadema, Brazil). Sulphuric acid (H_2SO_4) 98% was obtained from Merck.

Table 1
Molar compositions of the mixtures in terms of X_{EPOAME}, X_{EPSOME}, X_{EPLOME}, X_{AN} and X_{TEA}, where X is the molar fraction of the components.

Sample	Molar fractions (X)		
(1)	$X_{EPOAME} = 0.5$	$X_{CH} = 0.5$	$X_{TEA} = 0.0085$
(2)	$X_{EPSOME} = 0.33$	$X_{CH} = 0.67$	$X_{TEA} = 0.0085$
(3)	$X_{EPLOME} = 0.33$	$X_{CH} = 0.67$	$X_{TEA} = 0.0085$

2.2. The epoxidation procedure

Sunflower (SO) and linseed (LO) oils used in this study were transesterified using the TDSP-transesterification double step process [17] to obtain biodiesel samples, namely sunflower (SOME) and linseed (LOME) oil methyl esters. The quality of biodiesel was tested using standard analysis [17]. Oleic acid (OA) was esterified with methanol using acidic catalysis to obtain oleic acid methyl ester (OAME) as reported in previous publications [9–10].

The samples OAME, SOME and LOME were epoxidised with performic acid generated in situ. The synthesis of the epoxides was carried out in a completely stirred tank reactor of 500 mL equipped with a reflux condenser. The molar ratio of hydrogen peroxide/formic acid/double bond was 20/2/1. For each 30 g of methyl ester, 100 mL of toluene was added. Hydrogen peroxide (H_2O_2, 30%) was added dropwise into the reaction mixture. The reactor temperature was slowly raised to 80 °C to complete the reaction. This procedure demanded about 3 h for OAME, 12 h for SOME and 15 h for LOME. Then the organic layer (containing the epoxide) was washed with water to remove residual hydrogen peroxide. Anhydrous sodium sulphate was used to dry traces of water, and the epoxy was concentrated on a rotary evaporator.

2.3. The characterisation techniques and the study of the polymerisation reaction by DSC

Three different families of polyesters were prepared using the EP_{OAME}, EP_{SOME} and EP_{LOME}. The curing agent for the polymerisation was cis-1,2-cyclohexanedicarboxylic anhydride (CH), and triethylamine (TEA) as catalyst. Table 2 summarises the molar compositions of the mixtures before the polymerisation reaction in terms of X_{EPOAME}, X_{EPSOME} and X_{EPLOME}, where x is the molar fraction of the components. The samples had a constant TEA molar fraction, $X_{TEA} = 0.0085$. The composition of the reaction

Table 2
The main fatty acids in oils used in this work.

	% Fatty acid		
	C18:1	C18:2	C18:3
Oleic acid[a]	>95		–
Sunflower oil[b]	18–24	64–67	<1
Linseed oil[b]	19–22	16–24	52–56

[a] According to the supplier.
[b] Taken from Refs. [1–3,5,6].

mixtures were chosen taking into account the average number of epoxy groups in the methyl esters.

To evaluate the evolution of the chemical reaction, differential scanning calorimetry experiments were performed on a DSC 2920-TA instrument. Samples of the uncured reaction mixtures (approximately 5 mg) were sealed in DSC pans, and the reaction was followed by DSC in the range between 40 and 280 °C.

For the isothermal curing, the mixtures were placed in sealed glass recipients, stirred and then heated in an oven at 165 °C for 3 h. The obtained materials were then stored in desiccators at room temperature.

The chemical structures of the materials involved and the synthesised polyesters were characterised using proton and carbon nuclear magnetic resonance (^{1}H and ^{13}C NMR) and Fourier transform infrared (FTIR) spectroscopy. The NMR spectra were acquired on a 300 MHz Varian instrument (model Innova). The NMR samples were prepared in $CDCl_3$ using tetramethylsilane as a reference. The FTIR spectra were recorded on a Shimadzu-FTIR-8300 using KBr cells.

The molecular weight measurements were performed with GPC Waters 510 gel permeation chromatography equipment. Four polystyrene/divinylbenzene Styragel Waters Millipore columns of different porosities (100, 1000, 10,000 Å and a mixed one) were connected to a refractive index detector (RI-410), and tetrahydrofuran was used as the solvent.

DSC and TGA were used to evaluate thermal properties of the products. For TGA analysis was used a TA-model 2050 thermogravimeter operating under an inert N_2 atmosphere.

Electrical impedance spectroscopy (EIS) experiments were carried out on a potentiostat with a frequency response analyser, AUTOLAB PGSTAT 30/FRA2, over the frequency range between 1 Hz and 1 MHz, as previously described elsewhere [18,19].

3. Results and discussion

3.1. Chemical structure of the biodiesel and epoxidised biodiesel

The chemical characterisation of the OAME, SOME and LOME by NMR was presented in previous publications [7,8,10]. The average number of double bonds ($\overline{DB}$) of these materials was obtained by ^{1}H NMR spectral analysis [20] using Eq. (1):

$$\overline{DB} = \frac{K}{2NF}, \tag{1}$$

where K is the area of the resonance signal of the double bonds at $\delta = 5.3$ ppm. NF (normalisation factor) is the area of a peak that does not change after the reaction divided by the number of corresponding protons. For this reason, we choose the signal at 2.31 ppm, which corresponds to the three methylene hydrogens adjacent to the ester group in oleic acid, sunflower oil and linseed oil. The results indicated that the $\overline{DB}$ of OAME, SOME and LOME were, respectively, 0.9, 1.3 and 1.9.The epoxidation reactions were confirmed by the disappearance of the signal at $\delta = 5.3$ ppm and the appearance of epoxide hydrogens at $\delta = 2.9$–3.1 ppm in the ^{1}H NMR spectra of EP_{OAME} (Fig. 1a), EP_{SOME} (Fig. 1b) and EP_{LOME} (Fig. 1c). In addition, the disappearance of the peak at $\delta = 2.02$ ppm (hydrogens adjacent to the double bond) and appearance of the peak at $\delta = 1.5$ ppm (hydrogens adjacent to the oxirane ring) also confirmed the epoxidation of these substrates. In the case of SOME and LOME, we also observed the disappearance of the peak at $\delta = 2.8$ ppm (hydrogens between double bonds) and the appearance of a peak at $\delta = 1.7$ ppm (hydrogens between oxirane rings) [20,21]. In these figures the singlet at $\delta = 3.67$ ppm corresponds to the methyl group of the ester function. The epoxidised methyl esters were obtained with a yield approximately 90% according to AOCS Cd 9-57.

3.2. Polymerisation reactions followed by DSC

In this step of the work the polymerisation reactions were studied in terms of kinetic and thermodynamics. The characteristic exothermic peak of the epoxy-anhydride reaction was observed (Fig. 2). The polymerisation enthalpy (ΔH) is obtained through the integration. The ΔH_{tot} of the reactions prepared with EP_{OAME}, EP_{SOME} and EP_{LOME} were, respectively, $\Delta H_{EPOAME} = 90$ J/g, $\Delta H_{EPSOME} = 125$ and $\Delta H_{EPLOME} = 215$ J/g. Considering the composition of the samples, the epoxy equivalent values $EE_{EPOAME} = 346$, $EE_{EPSOME} = 243$, $EE_{EPLOME} = 171$ and the selectivity of approximately 90% in the epoxidation reaction, the corresponding enthalpies expressed in terms of epoxy equivalent are $\Delta H_{EPOAME} = 56$, $\Delta H_{EPSOME} = 69$ and $\Delta H_{EPLOME} = 82$ kJ/EE. These results, expressed in terms of reactivity, demonstrated that ΔH is related not only to the total number of epoxy rings per molecule, but depends on the epoxy ring position.The combination of the biodiesels used in this study (Table 2) permitted to differentiate the reactions according to the epoxy ring positions. In the case of oleic acid methyl ester the predominant position is the C9–C10. In the sunflower biodiesel the positions are C9–C10 and C12–C13 and finally in the linseed biodiesel the positions C9–C10, C12–C13 and C15–C16 are presented. The effect on the reactivity of the epoxy rings, according to their position in the fatty acid methyl esters was elucidated. The Barrett method [7,22–24] was used to evaluate the kinetic parameters of the reactions.The extent of the reaction (α) is related to the enthalpy of the reaction by Eq. (2):

$$\alpha = \frac{\Delta H}{\Delta H_{TOT}} \tag{2}$$

where ΔH is the partial enthalpy of the reaction and ΔH_{TOT} is the total enthalpy.

The general kinetic rate Eq. (3) is given by:

$$\frac{d\alpha}{dt} = k(T).f(\alpha) \tag{3}$$

Considering only one process, characterised by one activation energy (E_a) and one frequency factor (A), the Eq. (3) can be transformed in the Eq. (4):

$$\frac{d\alpha}{dt} = A\exp(-E/RT).f(\alpha) \tag{4}$$

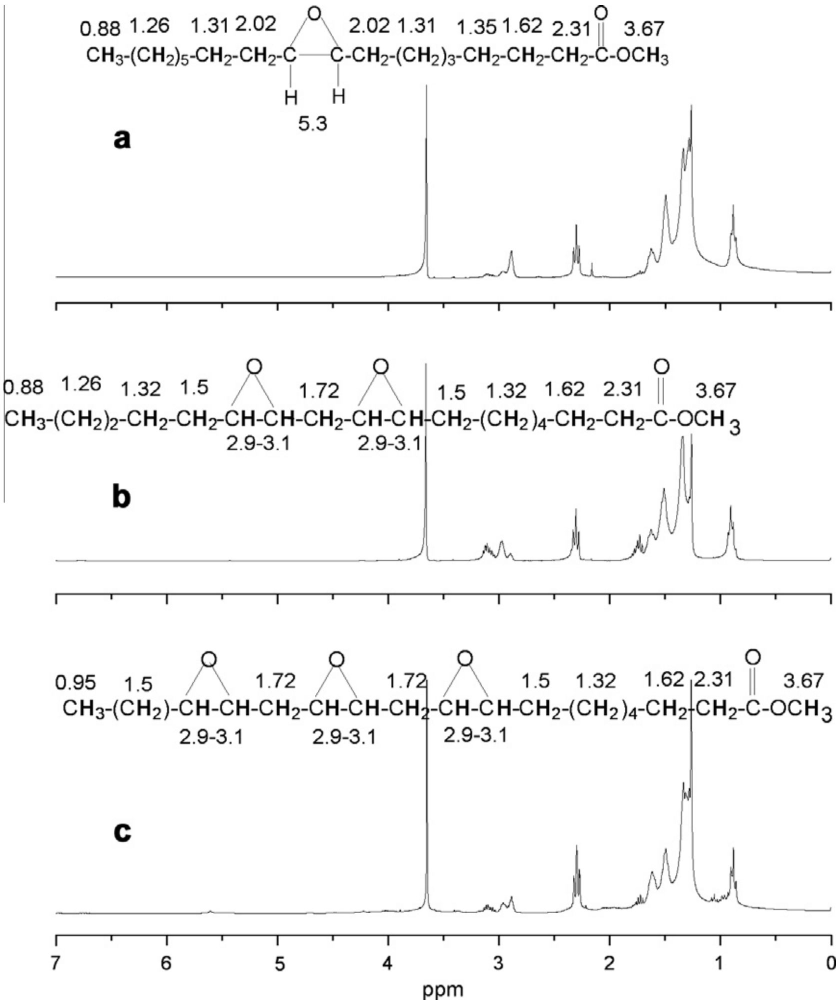

Fig. 1. The ^{1}H NMR spectra of the (a) EP_{OAME} (b) EP_{SOME} and (c) EP_{LOME}.

In the dynamic DSC measurements the relation between time, temperature and the extent of the reaction (α) is given by Eq. (5) where ϕ is the instrumental heating rate :

$$\frac{d\alpha}{dt} = \frac{d\alpha}{dt}\frac{dt}{dT} = \frac{1}{\Phi}\frac{d\alpha}{dt} \tag{5}$$

Substituting Eqs. (5)–(12), Eq. (6) is obtained:

$$\frac{d\alpha}{dT} = \frac{A}{\Phi}\exp(-E/RT).f(\alpha) \tag{6}$$

Assuming that: (i) the process is a first order one and (ii) the extent of the reaction α is proportional to the partial enthalpy of the reaction. The Eq. (6) can be written as:

$$\frac{d\alpha}{dT} = \frac{A}{\Phi}\exp(-E/RT).(1-\alpha)^n \quad \text{where n} = 1 \tag{7}$$

The respective logarithmic form is :

$$\begin{aligned} lnK &= \ln\left(\frac{d\alpha}{dT}\right) - n\ln(1-\alpha) + \ln\Phi \\ &= \ln A - \left(\frac{E}{RT}\right) \quad \text{where n} = 1 \end{aligned} \tag{8}$$

Eq. (8) includes the experimental information: (i) temperature derivative of α, (ii) the values of α as defined in Eq. (1), (iii) the heating rate of the experiment and (iv) the temperature variation. The graph of lnK versus 1/T is providing the pre-exponential factor (A) and the respective activation energy of the process. However, in cases with different processes the linear parts of the Eq. (8) would provide the pre-exponential factors and activation energies of the corresponding processes. Fig. 3 demonstrates the graph of ln k versus 1/T for the reactions of EP_{OAME}/AN/TEA, EP_{SOME}/AN/TEA and EP_{LOME}/AN/TEA. The EP_{OAME} curve was shifted by a factor +4, the EP_{LOME} by a factor −4 in order to visualise better the respective curves. It is observed that all of these curves are composed by different linear parts. The first linear part of these curves must correspond to the epoxy ring opening by the initiator and consequently followed by the consecutive reactions of the other epoxy rings with anhydride [25]. The evaluation of these linear parts is capable to provide the kinetic parameters of the respective processes. Table 3 shows that epoxy ring opening for EP_{OAME} occurs in temperature below 195 °C with E_a approximately 298 kJ/mol. In the case of EP_{SOME}

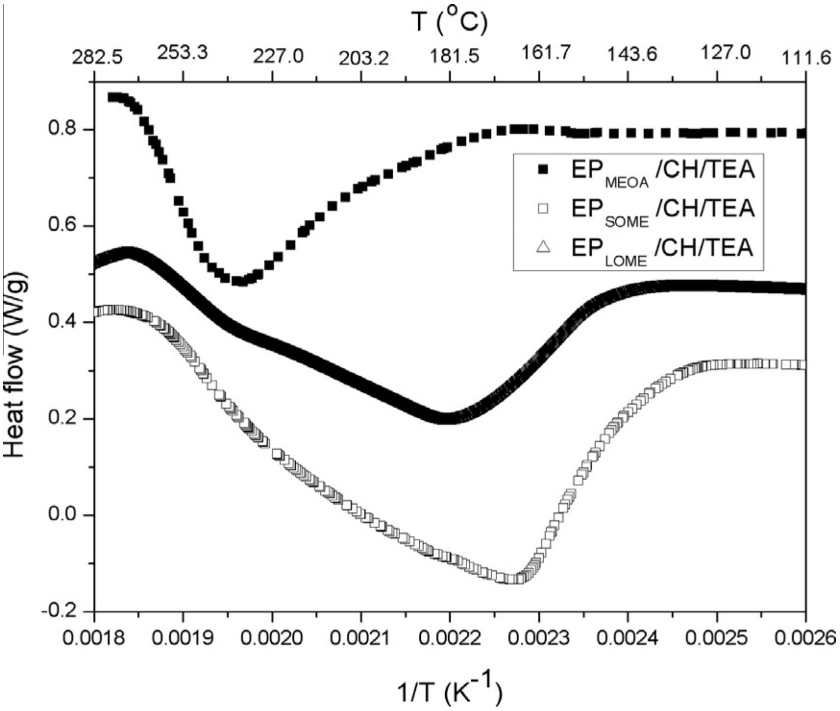

Fig. 2. DSC thermograms of the reaction mixtures based on EPOAME/AN/TEA, EP$_{SOME}$/AN/TEA and EP$_{LOME}$/AN/TEA.

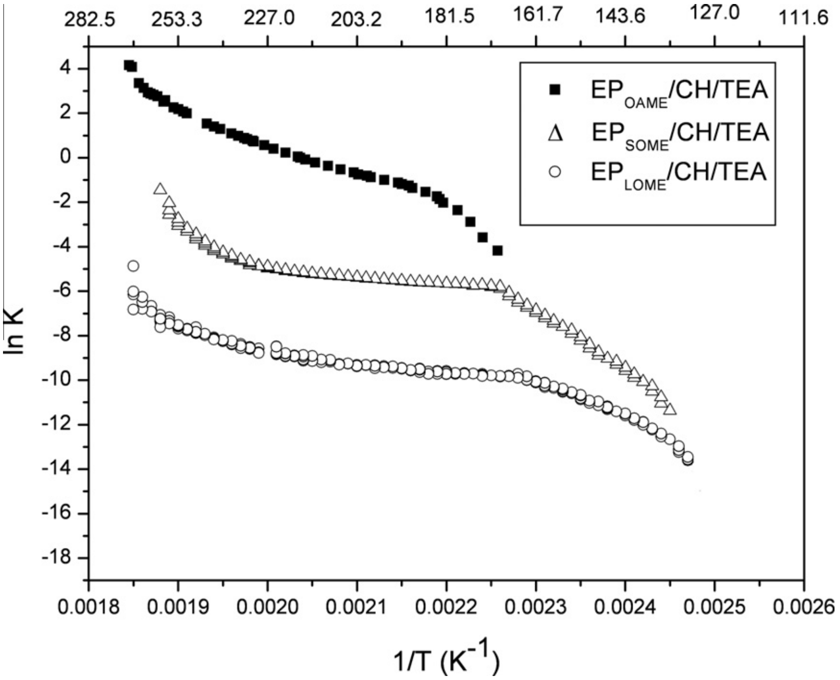

Fig. 3. The graph ln *k* versus 1/T of the reaction mixtures based on EPOAME/AN/TEA, EP$_{SOME}$/AN/TEA and EP$_{LOME}$/AN/TEA.

and EP$_{LOME}$ the epoxy ring opening occurs below 170 °C with E_a approximately 216 and 136 kJ/mol, respectively. The reaction main process of the EP$_{OAME}$ is obtained in the range between 195 and 260 °C, with E_a of 107 kJ/mol. As it can be seen in Table 3 similar activation energies 130 kJ/mol (210–260 °C) and 112 kJ/mol (230–260 °C) were obtained, respectively for the sunflower and linseed epoxidised biodiesels. A detailed evaluation of the Fig. 3

Table 3
Activation energy (E_a) and preexponential factor (ln*A*) involved in the polymerisation of the samples EP_{OAME}/AN/TEA, EP_{SOME}/AN/TEA and EP_{LOME}/AN/TEA.

	Epoxy ring opening	15–16 epoxy ring reaction	12–13 epoxy ring reaction	9–10 epoxy ring reaction
EP_{OAME}/CH/TEA	T.R = below 195 °C Ea = 298 KJ/mol lnA = 74.5	–	–	T.R = 195–260 °C Ea = 107 KJ/mol lnA = 22.4
EP_{SOME}/CH/TEA	T.R = below 170 °C Ea = 216 KJ/mol lnA = 53.1	–	T.R = 210–260 °C Ea = 28 KJ/mol lnA = 1.07	T.R = 170–210 °C Ea = 130 KJ/mol lnA = 30.1
EP_{LOME}/CH/TEA	T.R = below 166 °C Ea = 136 KJ/mol lnA = 31.9	T.R = 166–183 °C Ea = 22 KJ/mol lnA = 0.33	T.R = 183–230 °C Ea = 37 KJ/mol lnA = 4.7	T.R = 230–260 °C Ea = 112 KJ/mol lnA = 24.8

TR = temperature range.

indicates that in the case of EP_{SOME} the reaction of the 12–13 epoxy rings occurs in the range between 170 and 210 °C and with activation energy of approximately 28 kJ/mol. In the case of EP_{LOME} the reaction of the rings in the position 15–16 occurs in the range between 166 and 183 °C, with E_a of 22 kJ/mol, while the 12–13 occurs between 183 and 230 °C characterised by E_a approximately 37 kJ/mol. Apparently the epoxy rings in position 12–13 and 15–16 do not possesses very difference E_a. This observation leads to the conclusion that the epoxy ring in 9–10 position reacts with the highest E_a. The E_a is being decreased with the proximity of the oxirane ring to the end of the chain.

In order to evaluate the compensation effect, the values of E_a versus lnA were plotted in Fig. 4. A good linear correlation is obtained between these parameters. Considering the complexity of the studied systems, this linearity confirms the compensation effect. The three different epoxy rings behave similarly, conferring to the reaction mixtures similar kinetic conditions. However, the linear correlation between E_a and lnA has to be further studied for other similar polymerisation reactions.

3.3. The chemical structure of the polyesters

In order to elucidate the steps of transformation from biodiesel to polyesters we present a systematic series of FT-IR spectra in Fig. 5. This figure includes the infrared spectra of the SOME, EP_{SOME}, cis-1,2-ciclohexanedicarboxylic anhydride, the reaction mixture (EP_{SOME} + anhydride + TEA) before reaction and the product of the reaction. In the SOME spectrum, the bands at 3009 and 1655 cm^{-1} are due to the axial deformation in C–H of sp^2 carbons and C=C respectively. The disappearance of these bands in the EP_{SOME} and the appearance of the bands at 824 and 843 cm^{-1} indicates the conversion of the double bonds to oxirane rings. In the FTIR spectrum of the reaction mixture the band at 1736 cm^{-1} characterises the C=O stretching of the $EP_{SOME,}$ while the bands at 1855 and 1786 cm^{-1} are related to the carbonyl stretching of the anhydride. The substitution of these three bands by a new one at 1736 cm^{-1} in the polyester spectrum indicates the anhydride ring opening and the disappearance of the bands at 827 and 843 cm^{-1} are related to the opening of the epoxy

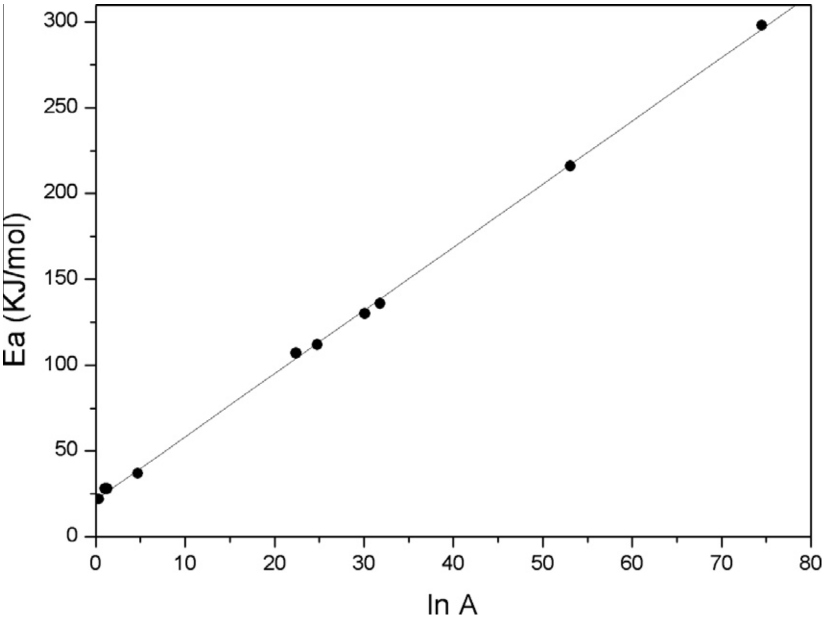

Fig. 4. Activation energy (E_a) versus preexponential factor logarithm (ln*A*).

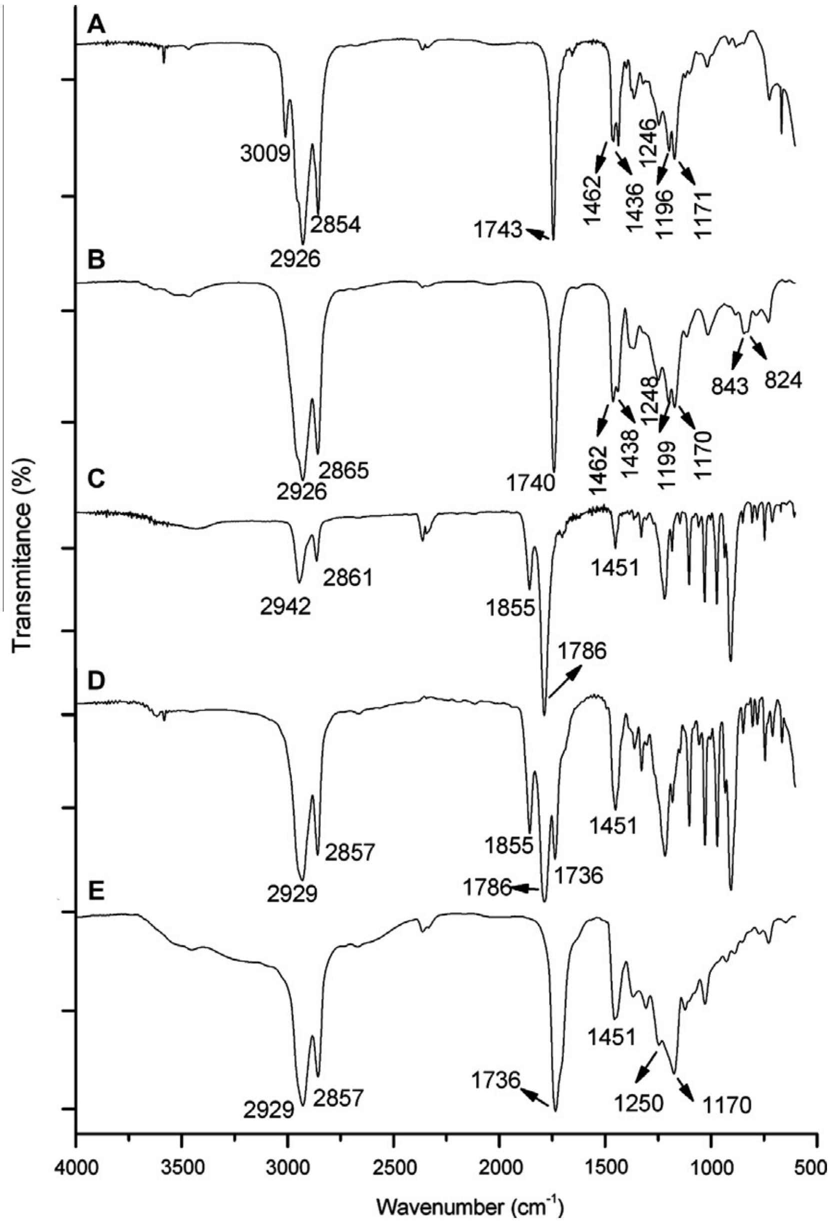

Fig. 5. The infrared spectra of the (A) SOME, (B) EP_{SOME}, (C) cis-1,2-ciclohexane anhydride, (D) the reaction mixture (EP_{SOME} + anhydride + TEA) before reaction and (E) the respective polyester.

ring. The infrared spectra of the polymers obtained from all epoxidised methyl esters were similar. This indicates that the obtained products contained mainly the same functional groups. The spectra of the products showed a strong band at 1736 cm^{-1}, which characterises the stretching of the C═O in the carboxylic group. The bands at 1250 and 1170 cm^{-1} indicate C–O–C ester linkages.

The ^{1}H and ^{13}C NMR spectra of the polymers presented similar peaks. The ^{1}H and ^{13}C spectra are illustrated in Figs. 6a and 6b, respectively, for the polymer obtained from EP_{LOME}. The appearance of a resonance at $\delta = 4.98$ ppm indicates incorporation of the anhydride, creating an internal ester linkage [8,26]. In addition, peaks observed at $\delta = 1.79$, $\delta = 2.06$, $\delta = 2.60$ and $\delta = 2.86$ ppm, are related to the hydrogens of the cyclohexane ring of the anhydride. Additionally, the disappearance of the peak at $\delta = 0.95$ ppm, characteristic of the EP_{LOME}, confirms ones more the opening of the respective oxirane ring. The new ester linkage was also confirmed by ^{13}C NMR due to the appearance of a signal at $\delta = 73.7$ ppm [8,26]. The peaks at $\delta = 42.2$ and $\delta = 44.5$ ppm were attributed to the tertiary carbons of the cyclohexane ring of the anhydride.

A comparison of the spectroscopic data indicated that the polymers produced from different biodiesel samples were polyesters. Size exclusion chromatography (SEC) measurements indicated that the average molecular

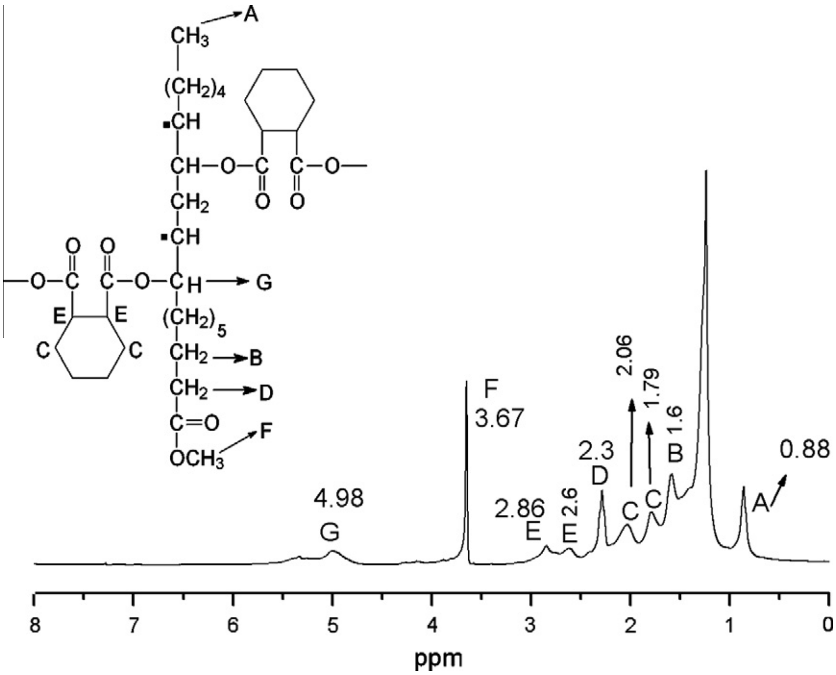

Fig. 6a. ^{1}H NMR of the polyester based on EP_{LOME}/AN/TEA.

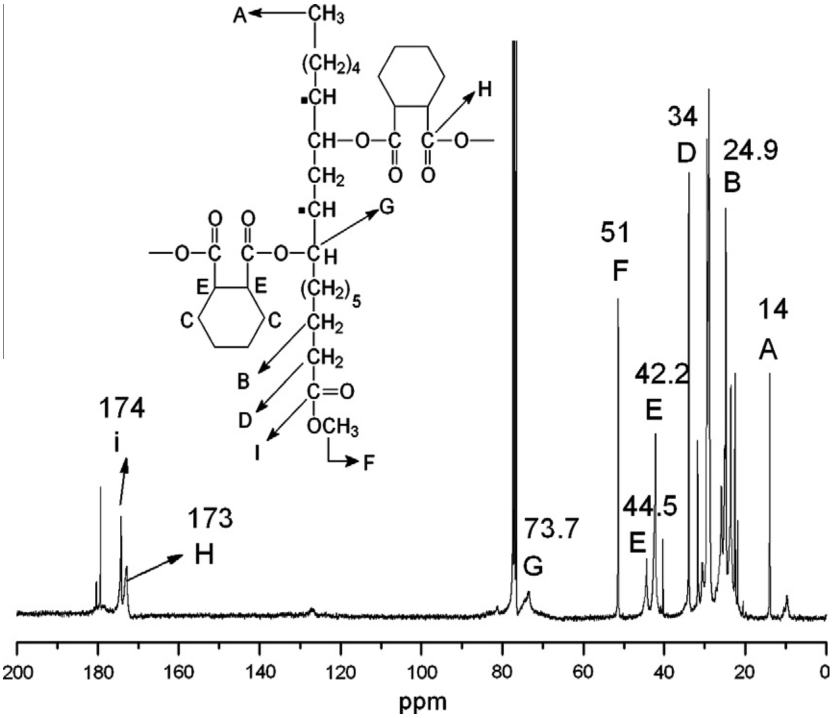

Fig. 6b. ^{13}C NMR of the polyester based on EP_{LOME}/AN/TEA.

weight (M_w) increased with the average number of double bonds of the starting oil. The M_w obtained for polymers synthesised with oleic acid, sunflower oil and linseed oil were, respectively, 2.5×10^3, 5.3×10^3 and 14×10^3 g/mol.

3.4. Thermal and electrical properties

Fig. 7 presents the thermograms of the polyesters obtained by DSC technique after isothermal curing. The glass transition temperature (T_g) of the product obtained using

EP_{OAME} is approximately −59 °C. This T_g value is comparable to those reported for acrylated methyl oleate polymers [11]. The polymers based on EP_{SOME} and EP_{LOME} exhibited T_g values of −11 and −6 °C, respectively. Therefore, the T_g seemed to depend on M_w and average number $\overline{DB}$. Glass transition temperature values lower than room temperature, such as the ones of the materials prepared in this study, are required for pressure-sensitive adhesive application [11].

Thermogravimetric analysis indicated that the products, without any treatment, obtained from the different biodiesels were thermally stable in air below 200 °C. The thermogram of all samples showed a two-stage thermal degradation process above this temperature, as can been seen in Fig. 8. Two-step degradation has also been observed for other polymers obtained from vegetable oils [6]. The first step degradation was attributed to the decomposition of unreacted components, as well as the saturated methyl esters and oligomers with lower molecular weights. The second stage corresponds to the degradation of the polymer structure. The maximum thermal degradation temperatures for each step (T_{max1} and T_{max2}) were approximately 230 and 370 °C for each polymer.

The electrical impedance spectroscopy was performed to evaluate the resistance and capacitance of the polyesters obtained. Models of dielectric behaviour are based on series and/or parallel combinations of resistance (R) and capacitance (C) that can account for the contribution of all active mechanisms to the overall dielectric polarisation [18,19,27,28]. An R–C parallel circuit represents an adequate model of the dielectric response of the studied material. The impedance, Z, is represented in terms of its real (Z') and imaginary (Z'') components:

$$Z = Z' - jZ'' \tag{9}$$

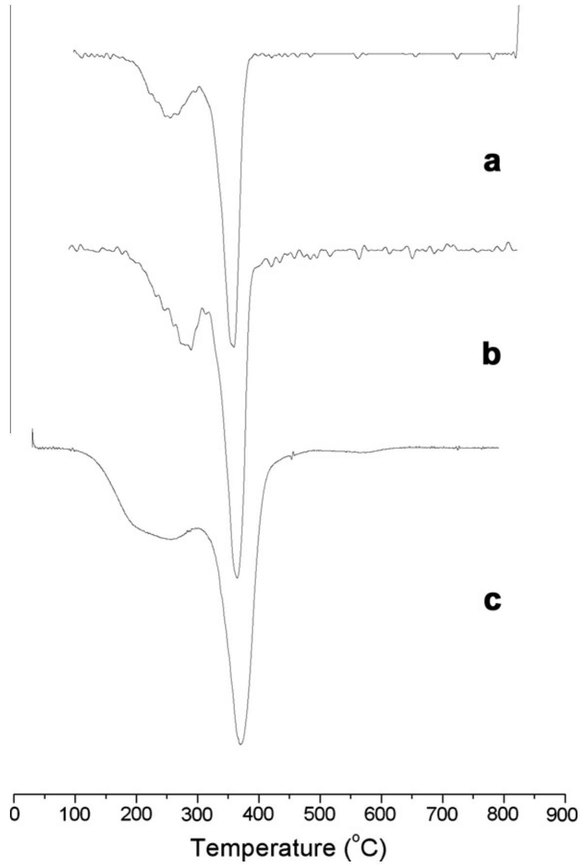

Fig. 8. Derivative TGA curves of polyesters based on (a) EP_{OAME}/AN/TEA, (b)EP_{SOME}/AN/TEA and (c) EP_{LOME}/AN/TEA.

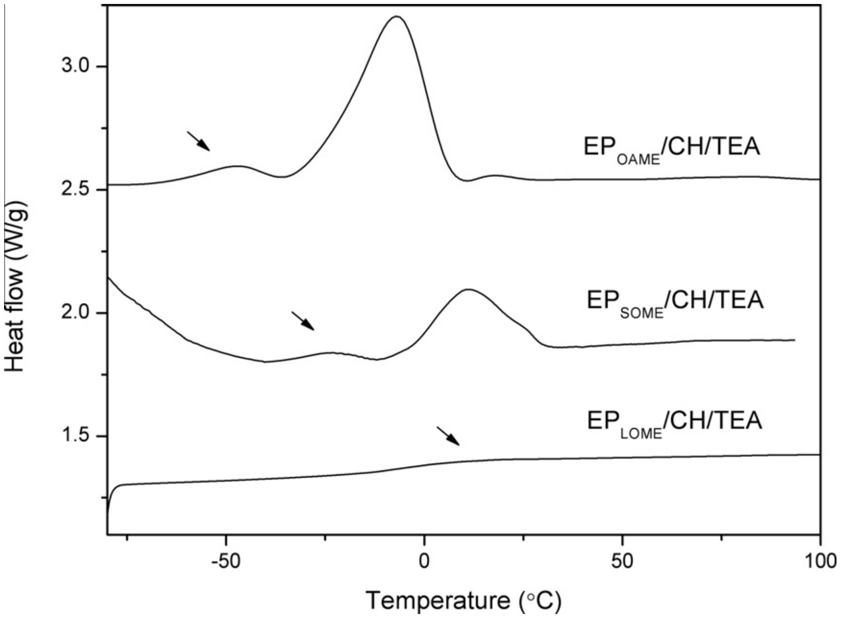

Fig. 7. Thermograms of the polyesters obtained by DSC technique after isothermal curing.

$$Z' = \frac{R}{1 + \omega^2 C^2 R^2}$$

$$Z'' = \frac{\omega C R^2}{1 + \omega^2 C^2 R^2},$$

where $\omega = 2\pi f$ and $j = -1$.

Quantitative evaluation of the R and C can be carried out by different representations of the impedance as Nyquist and Bode diagrams. In the case of Nyquist plot, the value of the resistance is obtained from the intersection of the semicircle and the Z' axis. The value of the capacitance is determined from the Nyquist plot using Eq. (10):

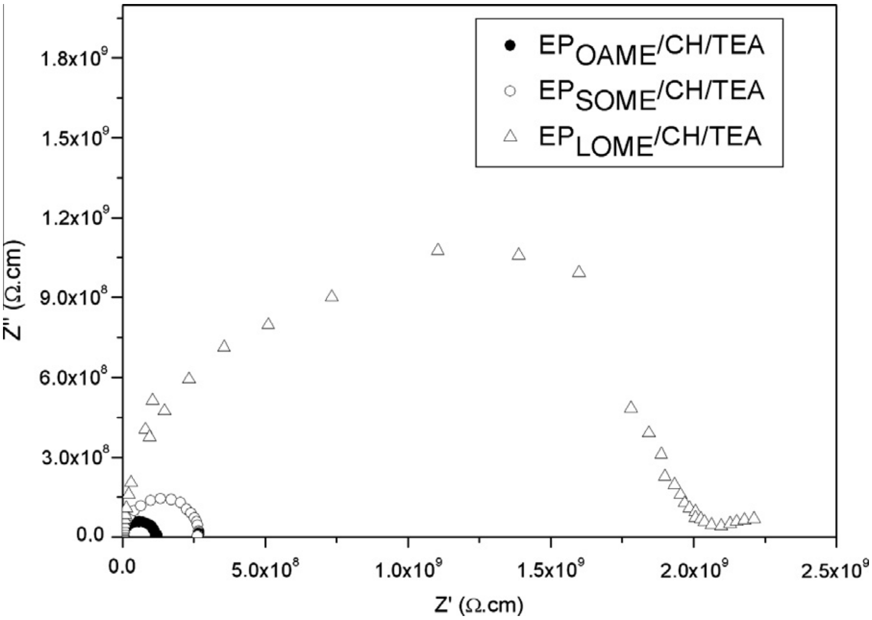

Fig. 9. Nyquist diagrams obtained by electric impedance spectroscopy for polyesters based on (a) EP$_{OAME}$/AN/TEA, (b) EP$_{SOME}$/AN/TEA and (c) EP$_{LOME}$/AN/TEA.

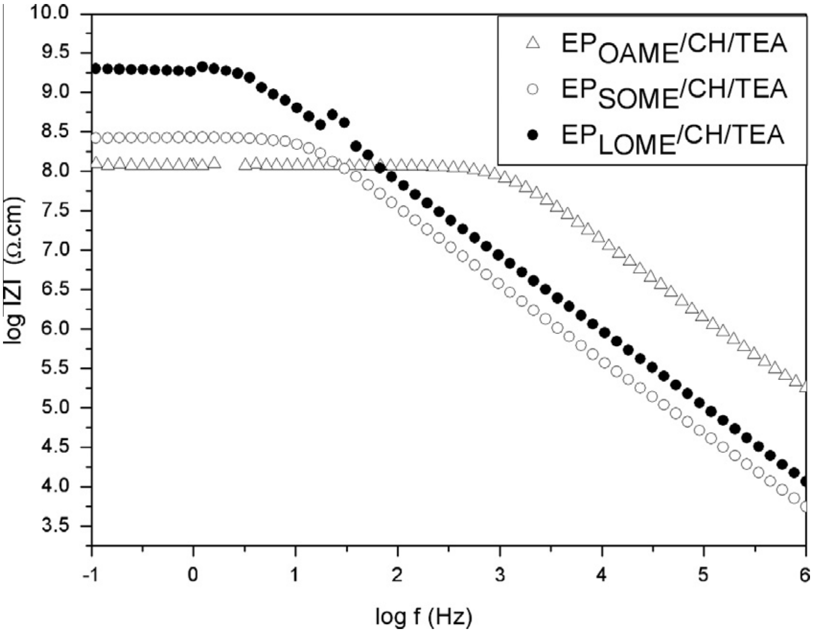

Fig. 10. Bode diagrams obtained by electric impedance spectroscopy for polyesters based on (a) EP$_{OAME}$/AN/TEA, (b) EP$_{SOME}$/AN/TEA and (c) EP$_{LOME}$/AN/TEA.

$$C = \frac{1}{2\pi f_{Z''_{\max}} R} \qquad (10)$$

Fig. 9 shows the Nyquist plots for the three studied systems. This figure shows well-defined Nyquist semicircles; in other words, these samples present resistive and capacitive properties. The increase in the average number of carbon–carbon double bonds of the biodiesel caused an increase in the resistivity value, which was indicated by an increase in the semicircle diameter.

Bode diagrams are based on a representation of the modulus value of complex impedance, |Z|, where [Z]=[Z'^{2} + Z''^{2}] by plotting log |Z| as a function of the logarithm of the frequency (Fig. 10). The value of the resistance is obtained from the intersection of the frequency-independent horizontal line and the log |Z| axis. The value of the capacitance is calculated from Eq. (11):

$$C = \frac{1}{2\pi Z} \qquad (11)$$

where the impedance, Z, is obtained by extrapolating the straight line with a slope -1 to the point where log f = 0. These plots allow representation of the impedance as an explicit function of frequency. According to Fig. 10, the polymers prepared from EP$_{OAME}$, EP$_{SOME}$ and EP$_{LOME}$ were

Table 4

Average number of the carbon–carbon double bonds ($\overline{DB}$), molecular weight (M_w), resistivity (ρ), capacitance (C) and time constant (τ) of the polyesters.

Sample	$\overline{DB}$	M_w (g/mol)	${}^a\rho_{Nyquist} \times 10^8$ (Ω cm)	${}^a\rho_{Bode} \times 10^8$ (Ω cm)	${}^bC_{Nyquist}$ (pF/cm)	${}^bC_{Bode}$ (pF/cm)	τ (ms)
X$_{EPOAME}$/CH/TEA	0.9	2.5×10^3	1.18	1.20	1.20	1.70	0.19
X$_{EPSOME}$/CH/TEA	1.3	5.3×10^3	2.67	2.70	0.35	0.51	11.7
X$_{EPLOME}$/CH/TEA	1.9	14×10^3	17.3	16.8	0.25	0.36	44.8

X_{TEA} = 0.0085 for all samples.

[a] $\rho = R \times K$, where K is the cell constant (K = S/L), S is the electrode area and L is the sample thickness.

[b] Capacitance values (C) normalised by cell constant K.

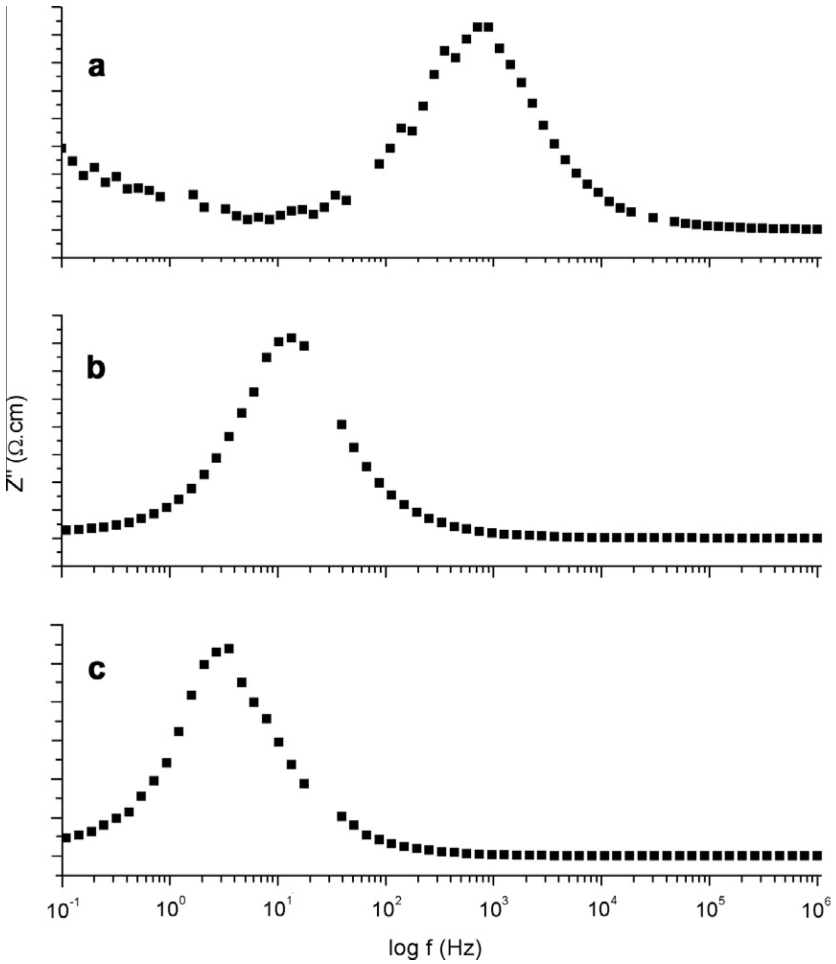

Fig. 11. Z'' versus log f diagrams for polyesters based on (a) EP$_{OAME}$/AN/TEA, (b) EP$_{SOME}$/AN/TEA and (c) EP$_{LOME}$/AN/TEA.

characterised by a resistive behaviour at high frequencies and a capacitive behaviour at low frequencies. The EP_{OAME} product showed a resistive behaviour until approximately 1124 Hz, and then it became capacitive. The same pattern was observed for products from EP_{SOME} and EP_{LOME} until 11.8 and 2.7 Hz, respectively. Therefore, the increase in double bond number shifted the beginning of the resistive plateau from 1124 Hz to 2.7 Hz, indicating that relaxation processes occur with higher time constants [17,18]. The values of the resistance and capacitance as calculated using Nyquist and Bode diagrams are presented in Table 4. A tendency to increase the resistivity and decrease the capacitance with increasing $\overline{DB}$ is observed. However this relation between $\overline{DB}$ and electrical properties is not conclusive because the molecular weight (Table 4) is increasing too. In order to elucidate this question further experimental work is necessary. The polymers produced in this work are characterised by high resistivity and low capacitance, making them insulator materials.

Imaginary impedance as a function of frequency was used to evaluate the relaxation dielectric processes of the studied systems (Fig. 11). The frequency position of the maximum Z'' relaxation curve was shifted to lower frequencies and the corresponding time constant (τ) was increased. Using the frequencies f_p where Z'' reaches the maximum, the time constant according to Eq. (12) was calculated. The τ values are shown in Table 4.

$$\tau = \frac{1}{2\pi f_p} \tag{12}$$

The results indicated that the utilisation of biodiesel obtained from polyunsaturated vegetable oils, such as sunflower and linseed oil, allowed the production of polymers with chemical structures that were more complex than those prepared with oleic acid, which is monounsaturated. It is expected that the relaxation processes are related to dipolar polarisation, which can be detected at frequencies lower than 10^9 Hz [17,18,27,28].

4. Conclusions

Polyesters were produced using the methyl ester of oleic acid (OAME) and biodiesel of sunflower (SOME) and linseed (LOME) oils. The OAME, SOME and LOME were epoxidised and polymerised with cis-1,2-cyclohexanedicarboxylic anhydride in the presence of triethylamine. The polymerisation reaction studied by DSC indicated that the reaction enthalpy is related not only to the total number of epoxy rings per molecule, but depends on the epoxy ring position.

The studied EP_{OAME}, EP_{SOME} and EP_{LOME} permitted the elucidation of the processes involved in the polymerisation. The activation energy and pre-exponential factors for the epoxy ring opening by the catalyst and main polymerisation reactions were obtained. The E_a values for the ring opening by the catalyst are 298, 216 and 136 kJ/mol for EP_{OAME}, EP_{SOME} and EP_{LOME} respectively. The reaction of the epoxy rings requires average activation energies 116, 32 and 22 kJ/mol for the positions C9–C10, C12–C13 and C15–C16 respectively. The studied polymerisation reactions demonstrated that the kinetics of this system abbeys to the compensation principle between activation energy and pre-exponential factor. The chemical structures of the polyesters were elucidated using NMR and FTIR techniques. The average molecular weights of the polyesters prepared with EP_{OAME}, EP_{SOME} and EP_{LOME} were, respectively, 2.5×10^3, 5.3×10^3 and 14×10^3 g/mol. The polyesters presented glass transition at -59 °C for EP_{OAME}, -11 °C for EP_{SOME} and -6 °C for EP_{LOME}. The produced polyesters were thermally stable until approximately 200 °C, and all of them showed a two-stage thermal degradation. The resistivity and capacitance values of the polymers prepared from EP_{OAME}, EP_{SOME} and EP_{LOME} were $1.20 \times 10^8\ \Omega$ cm and 1.70 pF/cm, $2.70 \times 10^8\ \Omega$ cm and 0.51 pF/cm and $16.8 \times 10^8\ \Omega$ cm and $0.36 \times$ pF/cm, respectively. These polyesters are a promising field of materials research because of the applicability of them for use as adhesives, thermal and electrical insulators, polyelectrolytes, plasticisers and other applications.

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