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On the curing of linseed oil epoxidized methyl esters with different cyclic dicarboxylic anhydrides

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ABSTRACT

Methods for obtaining epoxidized linseed oil methyl esters and curing them with phthalic (PA), cis-1,2,3,6-tetrahydrophthalic (THPA) and cis-1,2-cyclohexanedicarboxylic (CH) anhydrides in the presence of 2-methylimidazole as initiator/catalyst are presented. The methodology employed for the characterization includes ^{1}H and ^{13}C NMR and FTIR spectroscopy. The curing processes were evaluated by non-isothermal differential scanning calorimetry (DSC) to evaluate the reaction mixture molar compositions and types of dicarboxylic anhydrides. The optimum conditions for curing were determined. The experimentally obtained enthalpies per epoxy group-equivalent are 37.9 kJ/ee for PA, 46.8 kJ/ee for THPA and 51 kJ/ee for CH. The average activation energies were obtained by using the Kissinger, Osawa, Samios and Barrett standard techniques.

1. Introduction

In the past few decades, natural and renewable sources have received a great amount of attention. Vegetable oils and their derivatives have received particular attention as raw materials due to their abundance, high purity, and especially their carboxyl and olefinic functionalities, which enable a variety of transformations. Vegetable oils are mixtures of triglycerides formed by different unsaturated fatty acids. Many of them include oleic ($C_{18\text{-}1}$), linoleic ($C_{18\text{-}2}$), and linolenic ($C_{18\text{-}3}$) acids containing carbon–carbon double bonds in unusual positions of the alkyl chain, as well as conjugated double bonds, which are very interesting from the chemical point of view [1–5].

Recent studies indicate that, among other processes, the epoxidation of vegetable oils with unsaturated fatty acids and the curing of the epoxy products obtained constitute a very important way to obtain thermoset materials [6–12]. Petzhold et al. [13] reported the mechanical and thermal properties of materials prepared by curing epoxidized soybean oil with various cyclic acid anhydrides in the presence of tertiary amines. The characteristics of the thermoset materials were shown to be dependent upon the type of anhydride, the anhydride/epoxy molar ratio, and the epoxy group content. Boquillon and Fringant [14], using differential scanning calorimetry (DSC), investigated the curing of networks obtained with a commercial epoxidized linseed oil (ELO). Various cyclic acid anhydrides, tertiary amines and imidazole catalysts were utilized. According to Boquillon, imidazole catalysts resulted in networks with higher stiffnesses and extents of anhydride conversion. The results showed that the use of imidazole catalysts was more convenient than using tertiary amines.

The final properties of the thermoset materials depend on the kinetics of the curing reaction. This knowledge is very important for the processing of composite materials. It is necessary in order to establish the relationships between processing and properties in the studied thermosetting systems and to find the optimum curing conditions [15]. Various experimental methods have been applied to the dynamics of the curing process [16–23], among them, the non-isothermal differential scanning calorimetric (DSC) technique [24–34], permitting us to evaluate the characteristics of the curing process in terms of the specific reaction enthalpy and obtain the kinetics parameters, including the activation energy (E) and pre-exponential factor (A).

Currently, according to our knowledge, there is no study on curing linseed oil epoxidized methyl esters. At least two important issues, namely, the possibility of using biodiesel as a basic upstream material and the scientific challenge of these studies, justify the present study. Instead using natural seed oil or other kinds of triglycerides, we proceed with the transesterification, and the methyl esters obtained were used after epoxidation. The differences in structure, viscosity and diffusion suggest that epoxidized

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fatty acid methyl esters would be more reactive than the respective epoxidized oils. The DSC technique was applied in the non-isothermal mode to investigate the curing kinetics of linseed oil epoxidized methyl esters (EME) with cyclic anhydrides phthalic (PA), cis-1,2,3,6-tetrahydrophthalic (THPA) and cis-l,2-cyclohexanedicarboxylic (CH), in the presence of 2-methylimidazole (2-MI) as the initiator. The aim of this work is to present a new family of thermosets obtained from biodiesel and to elucidate the kinetics of the different curing reactions by applying the multiple scanning-rate methods of Kissinger and Osawa, the half-width method proposed by Samios and coworkers [29], also known as the "Samios method", and the single rate method of Barrett, as discussed by deMiranda et al. [29,30].

2. Experimental

2.1. Methodology, materials and characterization techniques

The linseed oil was converted to methyl esters by transesterification using a specific procedure denominated TDSP-transesterification double step process, as described in section 2.2. The methyl esters obtained were epoxidized (section 2.3), and the epoxy products were cured using different dicarboxylic cyclic anhydrides, as described in section 2.4.

The linseed oil used in this study was obtained from Farmaquímica (Porto Alegre, Brazil). The fatty acid composition of linseed oil is dominated by C18 fatty acids and contains mainly up to 52% linolenic acid, 17% linoleic acid and 22% oleic acid [32]. On average, linseed oil has a molecular weight of about 890 g/mol and contains about 5.4 double bonds as determined by ^{1}H NMR [35]. The other reactants used were: methanol (99.9% P.A.), formic acid (85% P.A.) and hydrogen peroxide (30 wt%) provided from Synth (São Paulo, Brazil); potassium hydroxide (98% P.A.) – Nuclear (Diadema, Brazil); sulfuric acid (98% P.A.) and toluene (99.5% P.A.) – Merck (Darmstadt, Germany); $CDC1_3$ (99.8%) D with 0.03% (v/v) TMS, cis-l,2-cyclohexanedicarboxylic anhydride (CH-99%) and phthalic anhydride (PA-99%) – Aldrich Chemical (Milwaukee, WI – USA); and cis-1,2,3,6-tetrahydrophthalic anhydride (THPA-99%) and 2-methylimidazole (2-MI-99%) – Acros (Geel – Belgium). All materials were used as received.

Differential scanning calorimetry (DSC) was performed in the non-isothermal mode using a DSC 2920-TA Instruments. Dynamic DSC experiments were performed from 40 to 300 °C, with different heating rates (5, 10 and 20 °C/min) under dry N_2. The DSC was previously calibrated using an indium standard. The degree of thermal cure was followed by monitoring the DSC heat flow as a result of the curing reactions. The heat evolved during the cure reaction appears with an exothermic peak characterized by the temperature $T_{\min}$. The curing enthalpy (ΔH) was obtained by integrating the DSC exothermic peak area, using TA instrument software. The ^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova 300, 300 MHz, using $CDCI_3$ as the solvent and tetramethylsilane as the standard. The FTIR spectra were obtained with a Shimadzu FTIR spectrophotometer, model 8300, using KBr crystals, in a scanning range of 400–4000 cm^{-1} for 32 scans at a spectral resolution of 4 cm^{-1}.

2.2. The transesterification procedure

The preparation of methyl esters was performed in two consecutive steps in a transesterification process using the methodology of the transesterification double step process [36]. Initially, the alkali agent was dissolved in methanol (25 g KOH in 1 L methanol) at a temperature near 45 °C. Quantities of 40 mL of this solution and 100 mL of linseed oil, under vigorous and constant agitation, were introduced in a simple reactor equipped with a reflux device. The molar ratio alcohol/oil was 10, and the catalyst/alcohol ratio was 1.78×10^{-2}. The system remained in the reflux condition for approximately 1 h. After cooling, 60 mL of methanol and 1.5 mL of sulfuric acid (18 mol/L) were added, followed by soft heating. The heating of the system stabilized again in the reflux condition, remaining in this condition for 1 h. After this period, the system was cooled slowly to approximately 25 °C. At the end of this step, the formation of two phases occurred. The two phases were separated and processed further. The biodiesel phase was washed with cool water, and the residual alcohol was removed by evaporation under vacuum. The lower phase presents a pH of approximately 6 and was used for recuperation of the methanol excess, the glycerol, and other secondary products. The obtained biodiesel (fatty acids methyl esters) was analyzed by standard biodiesel techniques in addition to ^{1}H NMR.

Fig. 1a shows the ^{1}H NMR spectrum of the linseed oil. The complete transesterification of the linseed oil to methyl ester was

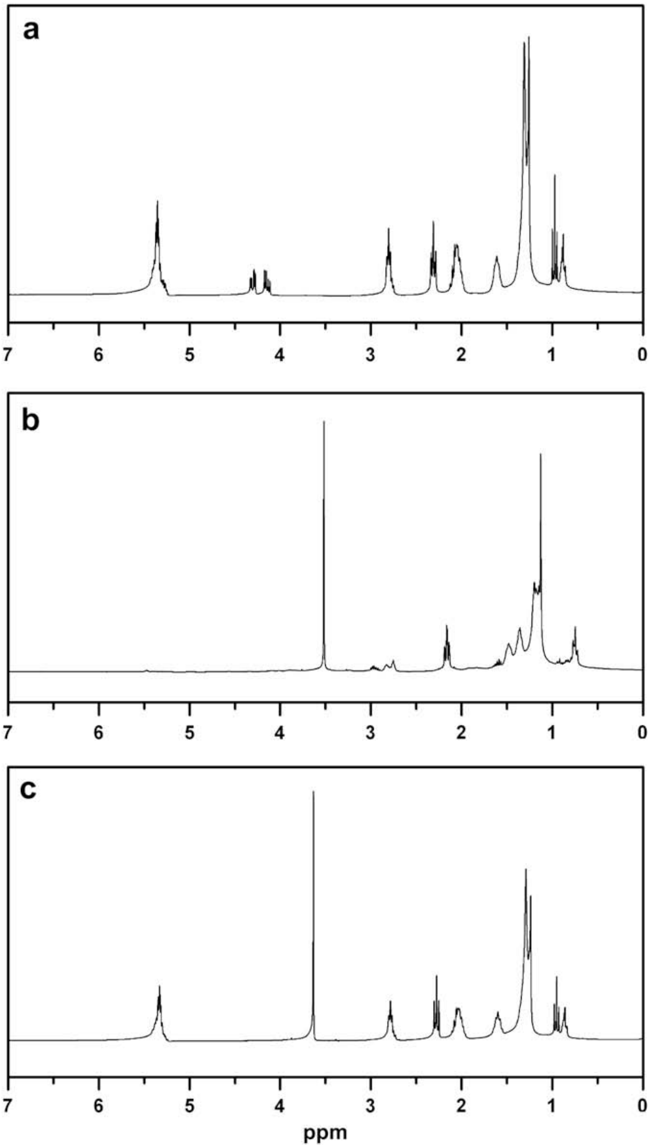

Fig. 1. ^{1}H NMR spectra of a) linseed oil, b) the methyl ester of linseed oil and c) linseed oil epoxidized methyl esters.

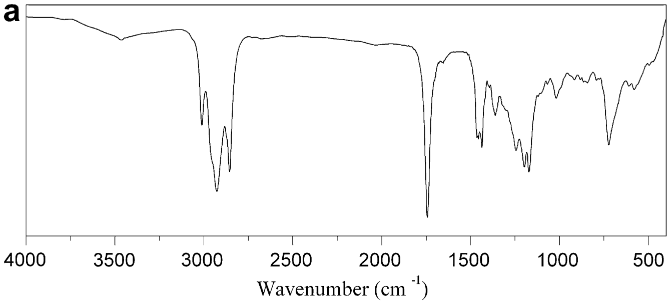

Fig. 2. FTRI spectra of the a) methyl ester of linseed oil and b) linseed oil epoxidized methyl esters.

confirmed from the emergence of the new signal at 3.6 ppm that proves the methyl ester formation, as shown in Fig. 1b. The transesterification procedure used in this study resulted in triglyceride conversions higher than 97%, corresponding to yields of 85%.

2.3. The linseed oil methyl esters' epoxidation procedure

The linseed oil epoxidized methyl esters (EME) were synthesized with performic acid generated *in situ*, using toluene to minimize ring opening [37,38]. The reaction was performed according to Gan et al. [37], using a molar ratio of hydrogen peroxide/formic acid/unsaturation (double bonds) of 20/2/1. In the experiment, 15 g of linseed oil methyl esters, 8 mL of formic acid and 100 mL of toluene were jointly placed into a round-bottom glass reactor, equipped with a reflux system, at room temperature, and stirred well. Then, 158 mL of hydrogen peroxide (30% v/v) was added dropwise. The reactor temperature was slowly raised to 80 °C to complete the reaction. This procedure requires about 7 h. After this time, the organic layer (containing the epoxide) was washed with water to remove residual H_2O_2. Anhydrous sodium sulfate was used to dry traces of water, and the epoxide was concentrated in a rotary evaporator. The conversion of the methyl esters to epoxy was confirmed by the complete disappearance of vinylic hydrogens at 5.3 ppm and the appearance of epoxy groups at 2.9–3.1 ppm region of the ^{1}H NMR [39] spectra, as shown in Fig. 1c, and the presence of signals at 53.4 and 55.9 ppm in the ^{13}C NMR spectra [40]. The degree of epoxidation was calculated by integrating the signals in the 2.9–3.1 ppm region of the ^{1}H NMR spectra, corresponding to the *cis* epoxy hydrogens [39]. The linseed oil epoxidized methyl esters were obtained with a yield above 90%. The average number of epoxy groups per fatty acid methyl ester obtained was 1.8. Additionally, the presence of functional groups was monitored using FTIR analysis. Fig. 2a shows the FTIR spectra of linseed oil methyl esters. The band at 3010 cm^{-1} was attributed to the C–H stretching of C=C–H; the band at 722 cm^{-1} was associated with methylene in-phase rocking, and that at 1745 cm^{-1} was associated with esters (aliphatic C=O stretch). The conversion of the methyl esters to epoxy was confirmed by the disappearance of the 3010 cm^{-1} band, and the appearance of two bands at 825 and 845 cm^{-1} indicates the presence of oxirane rings, as shown in Fig. 2b. The appearance of a large band around 3500 cm^{-1} in the FTIR spectra, attributed to OH stretching, suggests the occurrence of partial opening of the epoxy groups [41].

Table 1
Molar fractions of the reaction mixtures before the curing in terms of anhydride type, epoxy molar fraction x_{EME} under constant 2-MI molar fraction ($x_{2\text{-}MI} = 0.004$).

Sample number	Anhydride	x_{EME}
1	THPA	0.20
2	THPA	0.25
3	THPA	0.33
4	THPA	0.40
5	THPA	0.60
6	CH	0.33
7	PA	0.33

$Mw_{EME} = 322$ g/mol, $Mw_{THPA} = 152$ g/mol, $Mw_{CH} = 151$ g/mol, $Mw_{PA} = 148$ g/mol and $Mw_{2\text{-}MI} = 82$ g/mol.

2.4. The curing of fatty acid epoxidized methyl esters with cyclic dicarboxylic anhydrides

Non-isothermal differential scanning calorimetry was employed to study the cure process and to determine the kinetic parameters of the crosslinking reactions of linseed oil epoxidized methyl esters (EME) with three different cyclic dicarboxylic anhydrides, namely phthalic (PA), cis-l,2,3,6-tetrahydrophthalic (THPA) and cis-1,2-cyclohexanedicarboxylic (CH), in the presence of 2-methylimidazole (2-MI) as the initiator. The samples were prepared as follows: EME and anhydrides were mixed in different molar fractions and then heated to the melting points of the anhydrides. Next, the initiator 2-MI was added. The three components were

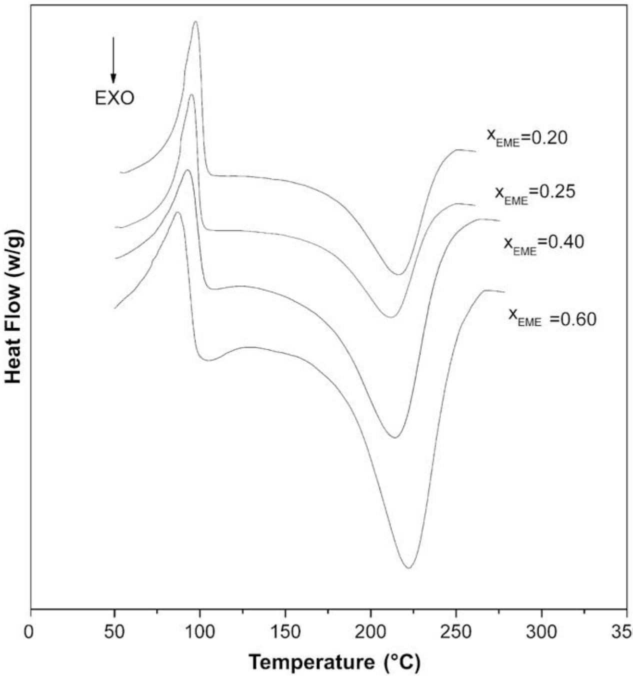

Fig. 3. DSC curves of EME/THPA/2-MI with different EME and THPA molar fractions and constant $x_{2\text{-}MI} = 0.004$. The heating rate was 10 °C/min.

Table 2
ΔH_{tot} and T_{min} obtained from the cure reactions of EME/THPA/2-MI with $x_{2\text{-MI}} = 0.004$ with heating rate 10 °C/min

Sample	x_{EME}	ΔH_{tot} (J/g)	T_{min} (°C)
1	0.20	153.8	219.2
2	0.25	193.8	221.0
3	0.33	233.0	220.3
4	0.40	213.5	223.0
5	0.60	140.0	220.1

$x_{2\text{-MI}} = 0.004$ (0.15% w/w).

continuously stirred while cooling for about 15 min. Subsequently, approximately 5–10 mg of the samples were accurately weighed onto DSC aluminum pans for cure experiments. Table 1 summarizes the molar fractions of the studied mixtures in terms of x_{EME}, where x_{EME} is the molar fraction of the linseed oil epoxidized methyl ester. First, five molar fractions of linseed oil epoxidized methyl esters were utilized to investigate the cure process with THPA and 2-MI, from $x_{EME} = 0.20$–0.60 (samples 1–5 – Table 1). Subsequently, the influence of different cyclic anhydrides on the cure reactions utilizing a constant molar fraction, $x_{EME} = 0.33$ (samples 3, 6 and 7 – Table 1), was investigated. All samples studied were synthesized with a constant 2-MI molar fraction, $x_{2\text{-MI}} = 0.004$.

3. Results and discussion

3.1. The variation of the curing mixture molar compositions

Fig. 3 shows thermograms of four curing reactions of EME with THPA and 2-MI with different molar compositions obtained using a heating rate of 10 °C/min. The only constant molar fraction was that of 2-MI, with $x_{2\text{-MI}} = 0.004$. The melting of the THPA was observed as an endothermic peak before the reaction exothermic peak. Total enthalpy values (ΔH_{tot}) and the T_{min} of the corresponding curing processes are given in Table 2.

Table 2 shows that the T_{min} values remained practically constant ($T_{min} = 220 \pm 2$ °C) with increasing EME molar fraction. The experimentally obtained ΔH_{tot} values, given in Table 2, are plotted together with the theoretically calculated values in Fig. 4. The largest experimental enthalpy value was 233.0 J/g, with $x_{EME} = 0.33$, suggesting that this molar fraction is near the stoichiometric one. Initially, the experimental values were fitted to a polynomial function in order to obtain the x_{EME} position (x_{EMEmax}) with the maximum enthalpy value (ΔH_{max}). The x_{EMEmax} reveals the “real stoichiometry” of the studied system and thus the average epoxy groups per molecule of the epoxidized fatty acid methyl esters.

Taking into account the ΔH_{max} and the mixture molar composition, the theoretical ΔH curve can be calculated for mixtures with anhydride excess (eq. (1)) and epoxy excess (eq. (2)), respectively [21,23]:

$$\Delta H_{(\text{anhydride excess})} = \frac{(x_{EME} \times n_{tot} \times \mathrm{Mw}_{EME})\Delta H_{max}}{x_{EME} \times n_{tot} \times \mathrm{Mw}_{EME} + x_{Anh} \times n_{tot} \times \mathrm{Mw}_{Anh} + x_{2-MI} \times n_{tot} \times \mathrm{Mw}_{2-MI}} \tag{1}$$

$$\Delta H_{(\text{epoxy excess})} = \frac{[(x_{Anh}/2) \times n_{tot} \times \mathrm{Mw}_{EME}]\Delta H_{max}}{x_{EME} \times n_{tot} \times \mathrm{Mw}_{EME} + x_{Anh} \times n_{tot} \times \mathrm{Mw}_{Anh} + x_{2-MI} \times n_{tot} \times \mathrm{Mw}_{2-MI}} \tag{2}$$

Here, n_{tot} is the total number of moles in the mixture. Mw_{EME}, Mw_{Anh} and $\mathrm{Mw}_{2\text{-MI}}$ are the respective molecular weights, and x_{EME}, x_{Anh} and $x_{2\text{-MI}}$ are the molar fractions of the components.

As shown in Fig. 4, the x_{EMEmax} obtained experimentally is approximately 0.33, which corresponds, on average, to two epoxy groups for every fatty acid ester. This value is in very good agreement with the one obtained in this paper through the NMR technique.

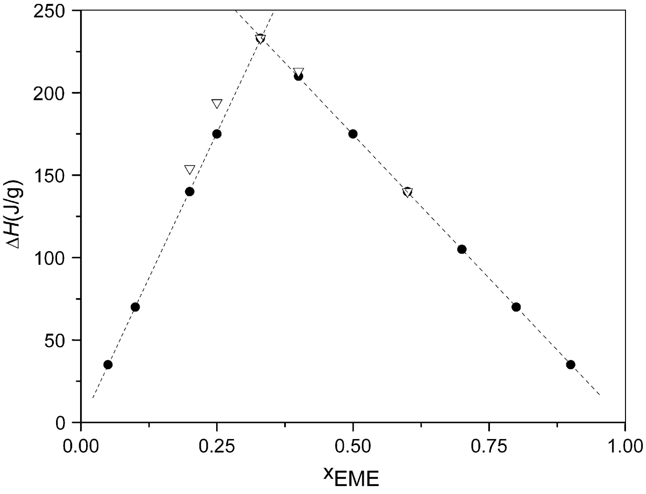

Fig. 4. The dependence of the curing enthalpy on the molar composition. Theoretical (●) and experimental (Δ) values of ΔH (J/g mixture) vs EME molar fraction ($x_{2\text{-MI}} = 0.004$ and a heating rate of 10 °C/min).

3.2. The curing of EME with different cyclic dicarboxylic anhydrides

The experiments were performed with three different cyclic anhydrides, namely, phthalic anhydride (PA), cis-l,2,3,6-tetrahydrophthalic anhydride (THPA) and cis-1,2-cyclohexanedicarboxylic anhydride (CH). Taking into account the previous result, shown in Fig. 4, the molar composition of the reaction mixtures was fixed to $x_{EME} = 0.33$, which corresponds to the stoichiometric composition. The 2-MI molar fraction was $x_{2\text{-MI}} = 0.004$. Figs. 5, 6 and 7 show the exothermic peaks characteristic of the curing reaction by EME with different anhydrides studied at the heating rates of 5, 10 and 20 °C/min. In the case of PA and THPA experiments, the melting of the anhydrides was observed as an endothermic peak before the reaction peak. The enthalpy values (ΔH_{tot}) and T_{min} of the cure reactions at different heating rates are shown in Table 3. The enthalpy values are expressed in kJ/g and, considering the presence of two epoxy groups per ester molecule, as discussed before, in kJ/ee, where ee is the EME epoxy equivalent.

Boquillon et al. [14] reported for the curing reaction of ELO with THPA anhydride, in the presence of 2-MI (0.5% w/w), the value of $\Delta H = 49.0$ kJ/ee, which is in very good agreement with the value obtained in this paper (Table 3). This means that the enthalpy per glycidyl equivalent is the same for epoxidized oil and epoxidized methyl ester. However, there is a significant difference between the curing enthalpies for the different cyclic anhydrides. The exothermic character of the reaction increased in the order $\Delta H_{PA} < \Delta H_{THPA} < \Delta H_{CH}$. Certainly this behavior is related to the molecular structure of the anhydrides, specifically the cyclic group adjacent to the anhydride group. In the anhydrides studied, the character of the adjacent cyclic group changes from

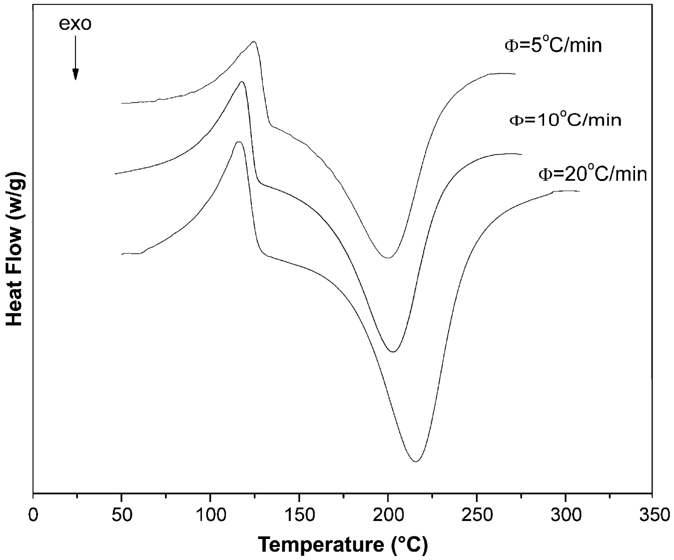

Fig. 5. DSC curves of EME/PA/2-MI at heating rates of 5, 10 and 20 °C/min.

the aromatic character of PA to the aliphatic character of the CH and the intermediate character of THPA.

As expected the $T_{\min}$ values increase with the scanning rate for all systems under investigation.

3.3. The evaluation of the curing kinetic parameters

The kinetic parameters of the crosslinking reactions by EME with different cyclic anhydrides in the presence of 2-MI were determined by applying the multiple scanning-rate methods of Kissinger, Osawa and Samios, as well as the single rate method of Barrett, as discussed by deMiranda et al. [29,30]. The basic equations for each method are collected in Table 4.

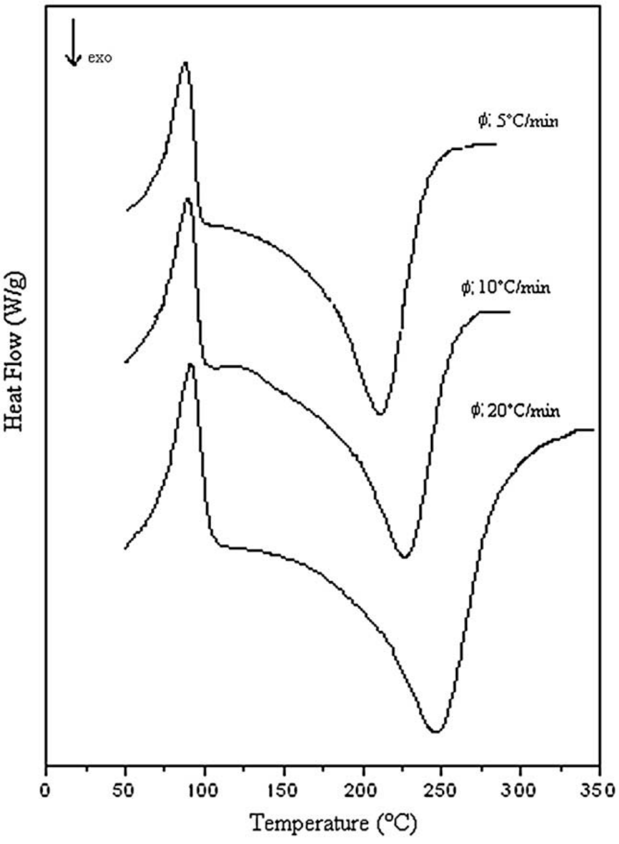

Fig. 6. DSC curves of EME/THPA/2-MI at heating rates of 5, 10 and 20 °C/min.

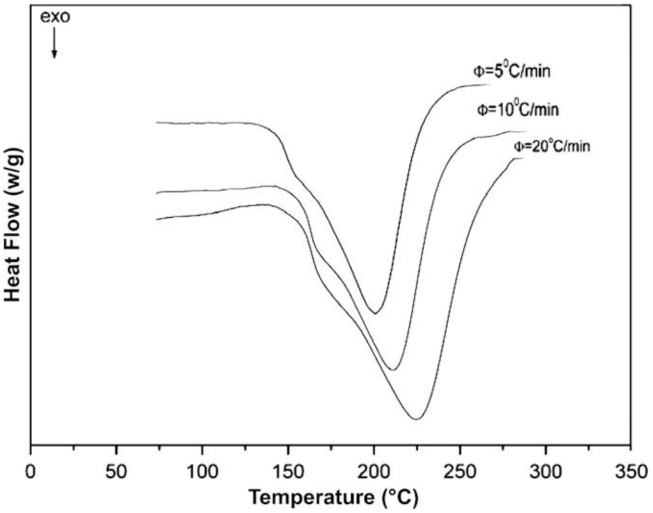

Fig. 7. DSC curves of EME/CH/2-MI at heating rates of 5, 10 and 20 °C/min.

The Kissinger, Osawa and Samios methods are based on linear relationships between ln $[\Phi/(T_{\min})^2]$, ln(Φ) and ln($t_{1/2}$), respectively, with the inverse temperature ($1/T_{\min}$) of the peak of the exothermic curing reaction. These three methods allow the determination of only the curing activation energy (E).

Fig. 8(a,b) shows an example of the plots for the determination of the activation energy using the Kissinger and Osawa (8a) and the Samios (8b) methods for EME/THPA/2-MI at various heating rates. The average values obtained for the activation energy (E) are given in Table 5.

Table 3
ΔH_{tot} and $T_{\min}$ of the cure reactions by EME with different anhydrides and heating rates of 5, 10 and 20 °C/min.

Anhydrides	Φ (°C/min)	ΔH (J/g)	ΔH (kJ/ee)	$T_{\min}$ (°C)
PA	5	184.5	37.7	184.1
	10	185.8	38.0	200.6
	20	185.6	37.9	216.1
		$<\Delta H> = 185.3 \pm 0.8$	$<\Delta H> = 37.9 \pm 0.01$	
THPA	5	233.8	47.0	211.9
	10	228.5	45.9	220.0
	20	236.8	47.6	247.1
		$<\Delta H> = 232.7 \pm 4.0$	$<\Delta H> = 46.8 \pm 0.8$	
CH	5	248.3	50.1	194.4
	10	247.9	50.0	207.9
	20	262.9	53.0	224.3
		$<\Delta H> = 253.0 \pm 4.0$	$<\Delta H> = 51.0 \pm 2.0$	

$Mw_{\text{EME}} = 322.0$ g/mol (1.8 epoxy groups per EME molecule), ee: EME equivalent = 161 g.

Table 4
Parameters plotted in the ordinate (y) and abscissa (x) axis and slope (m) of the straight line for different non-isothermal methods (linear plots: $y = mx + C$).

Method	y	x	Slope (m)	Intercept (C)
Kissinger	$\ln[\Phi/(T_{\min})^2]$	$1/T_{\min}$	$-E/R$	–
Osawa	$\ln(\Phi)$	$1/T_{\min}$	$-E/R$	–
Samios	$\ln(t_{1/2})$	$1/T_{\min}$	E/R	–
Barrett	$\ln(K)$	$1/T$	$-E/R$	ln(A)

$K = [d\alpha/dt/(1-\alpha)]$, $T_{\min}$: minimum peak temperature, T: absolute temperature, Φ: heating rate (°C/min), R: 8.314 J K^{-1} mol^{-1}, E: activation energy (kJ/mol), $t_{1/2}$: the half-width and (A) is the pre-exponential factor.

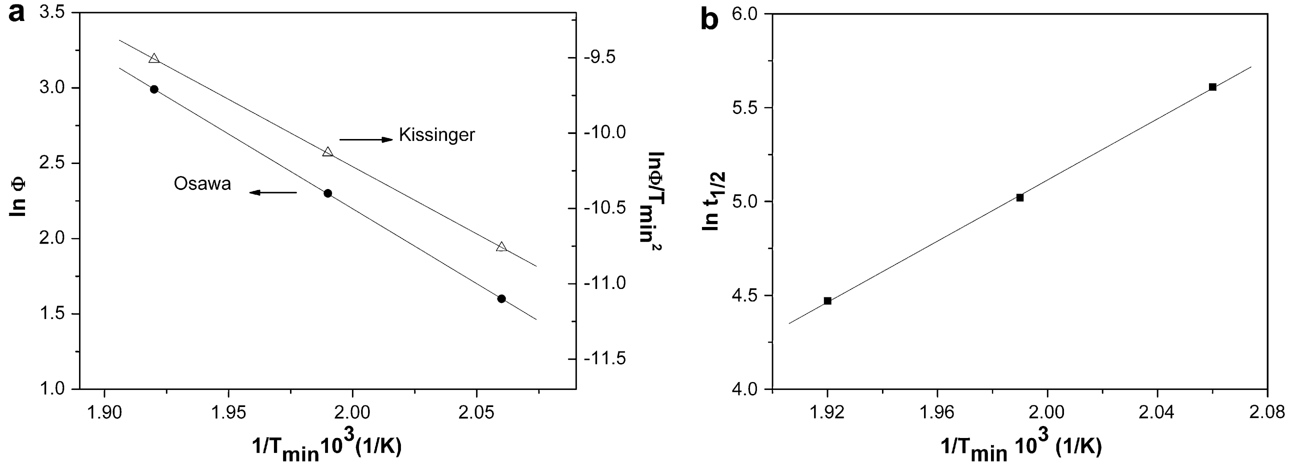

Fig. 8. Plots for the determination of the activation energy by the Kissinger and Osawa (a) and Samios (b) methods at heating rates of 5, 10 and 20 °C/min.

Table 5
Activation energies (E) of the curing reaction of EME with different cyclic anhydrides.

Anhydrides	E (kJ/mol) Kissinger	E (kJ/mol) Osawa	E (kJ/mol) Samios
PA	74.2	81.9	67.7
THPA	74.1	76.6	77.1
CH	79.7	82.5	67.0

The differences between the average activation energy values (Table 5) obtained by the three different methods are relatively small and can be related to each method's limitations, since the total time–temperature evolution of the overall curing process is not considered. Contrary to these simple methods, the classical kinetic Barrett method constitutes a useful way to investigate the curing process by considering the complete time–temperature evolution. Assuming that the overall curing process is composed of different first-order reactions, the linear plot between ln(K) vs 1/T can be produced, as indicated in Table 4. The Barrett method provides additional information on network formation, i.e., on initiation, gelation and vitrification processes [29]. In this work, the Barrett method was applied to determine the activation energies for the three epoxy-anhydride systems considering three different heating rates. Figs. 9, 10 and 11 show the graphic representations for PA, THPA and CH, respectively. In these figures, it can easily be seen that for the different heating rate experiments, there is a temperature range characterized by superposition. This range normally constitutes the central part of the curves, and it should be considered for the determination of the activation energy and the pre-exponential Arrhenius factor. The extremities of the curves are related to the initiation and the finishing of the crosslinking processes. Table 6 shows the average activation energies (E) and logarithm of the pre-exponential factor (ln A).

As shown in Table 6, the average Barrett values of the activation energy of the main curing processes lie in the range between 71.8 and 93.7 kJ/mol. When PA anhydride is used as the curing agent, the energy of activation is considerably higher than in the case of THPA or CH anhydride. One possible explanation could be linked to the molecular structure of the respective anhydrides. Boquillon et al. [14], using the Barrett method, reported for the curing of the linseed epoxidized oil with THPA in the presence of 2-MI (0.5%w/w) an E value of 97.6 kJ/mol. When EME and epoxidized linseed oil are compared, their E values are

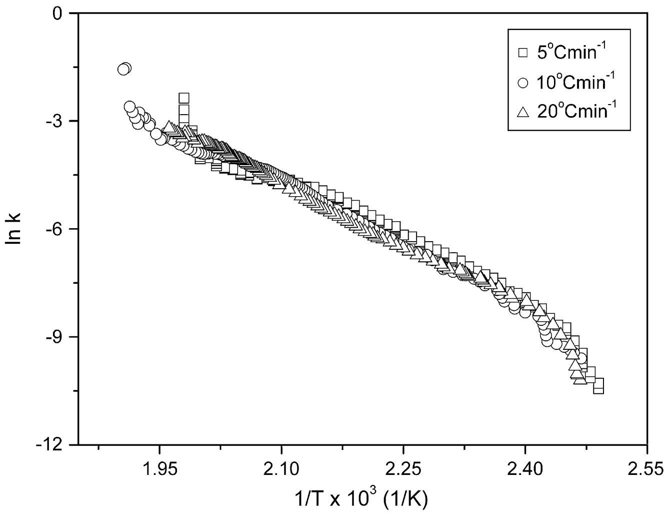

Fig. 9. Plot of ln(K) vs T^{-1} K^{-1} according to the Barrett method for EME cured with phthalic anhydride (PA), at heating rates of 5, 10 and 20 °C/min.

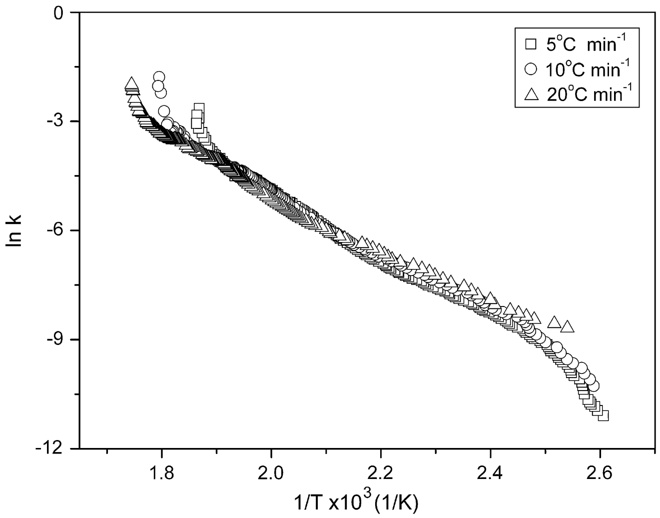

Fig. 10. Plot of ln(K) vs T^{-1} K^{-1} according to the Barrett method for EME cured with cis-1,2,3,6-tetrahydrophthalic anhydride (THPA) at heating rates of 5, 10 and 20 °C/min.

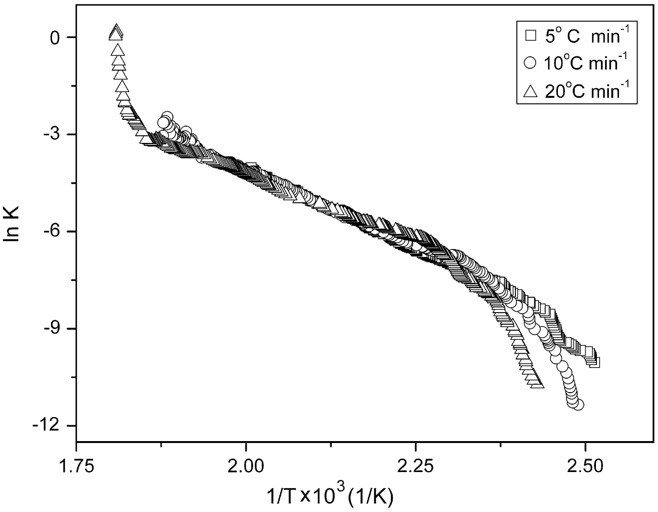

Fig. 11. Plot of ln(K) vs T^{-1} K^{-1} according to the Barrett method for EME cured with cis-1,2-cyclohexanedicarboxylic anhydride (CH) at heating rates of 5, 10 and 20 °C/min.

Table 6
Activation energies (E) and logarithm of the pre-exponential factor ($\ln A$) for the curing reactions of EME with different cyclic anhydrides determined by Barrett method.

	$\Phi = 5$ °C/min		$\Phi = 10$ °C/min		$\Phi = 20$ °C/min		Averages values	
	E (kJ/mol)	$\ln A$	E (kJ/mol)	$\ln A$	E (kJ/mol)	$\ln A$	E (kJ/mol)	$\ln A$
PA	83.2	18.87	97.4	19.83	101.0	20.76	93.7 ± 7.0	19.82
THPA	75.8	13.36	71.5	12.35	68.1	11.49	71.8 ± 4.0	12.4
CH	81.7	15.61	80.1	15.22	65.7	11.73	75.8 ± 9.0	14.2

shown to be similar. However, directly comparing the kinetic and thermodynamic results of the curing of THPA with epoxidized linseed oil [14], (ELO: $E = 97.6$ kJ/mol, $\ln A = 11.5$, $\Delta H = 49$ kJ/ee) and with EME ($E = 71.8$ kJ/mol, $\ln A = 12.4$, $\Delta H = 47$ kJ/ee), we can confirm that the processes are thermodynamically equivalent; however, the curing of the epoxidized methyl esters is favored kinematically.

4. Conclusion

This paper presents a new series of polyester-like materials produced using epoxidized linseed oil methyl esters cured with phthalic (PA), cis-1,2,3,6-tetrahydrophthalic (THPA) and cis-l,2-cyclohexanedicarboxylic (CH) anhydrides in the presence of 2-methylimidazole as initiator/catalyst. ^{1}H and ^{13}C NMR and FTIR spectroscopy permitted us to characterize the species involved in the synthesis of the fatty acid epoxidized methyl esters. The curing processes were evaluated by non-isothermal differential scanning calorimetry (DSC) with respect to reaction mixture molar composition and the type of dicarboxylic anhydride used. The optimum conditions for the curing were determined. The experimentally obtained DSC enthalpy values suggest that the reaction's stoichiometric composition must be 1 mol of EME over 2 mol anhydride; consequently, the EME molecule includes two epoxy group-equivalents. The value obtained by ^{1}H NMR was 1.8, which is very similar to that obtained by DSC. The experimentally obtained enthalpies per epoxy group-equivalent are 37.9 kJ/ee for PA, 46.8 kJ/ee for THPA and 51 kJ/ee for CH. Comparison of the curing of epoxidized linseed oil with THPA (14) and linseed oil epoxidized methyl esters with the same anhydride using 2-MI as initiator indicates that the curing of the epoxidized methyl esters is favored kinematically.

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