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Anionic copolymerization of DGEBA with two bicyclic bis(γ-lactone) derivatives using tertiary amines as initiators

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ABSTRACT

The anionic copolymerization, to form thermosets, of diglycidylether of bisphenol A (DGEBA) with two condensed bis(γ-lactone)s (bisMe and bisPhe) using 4-(*N*,*N*-dimethylamino)pyridine (DMAP), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and 1-methylimidazole (1MI) as initiators was studied by differential scanning calorimetry (DSC). The kinetics was evaluated by isoconversional procedures. The evolution of the typical functional groups that form or disappear during curing was followed by Fourier transform infrared in the attenuated-total-reflection mode (FTIR/ATR) to clarify the reactive processes that takes place. Unexpected processes, which lead to the formation of five-membered lactones, were detected when non-stoichiometric proportions of monomers were used. The stoichiometric DGEBA/bislactone ratio produces the expected alternate poly(ester–ketone) network. The thermal degradability of the materials obtained was evaluated by TGA, and their reworkable character was confirmed. Materials obtained from stoichiometric mixtures were completely soluble in ethanolic KOH.

1. Introduction

Ring opening is a polymerization mechanism that has the advantage of allowing the copolymerization of monomers with different reactive groups, such as lactones and epoxides. The polymerization of lactones leads to polyesters and the polymerization of epoxides leads to polyethers. Thus, the copolymerization of these two monomers can produce poly(ether–ester) structures with a relative proportion of structural units that depend on the feed ratio. This copolymerization can be initiated by both anionic and cationic species. Cationic initiators conduce to a rather complex mechanism, with four reactive processes, one of them being the formation of an intermediate spiroorthoester. On the other hand, anionic copolymerization takes place directly by the attack of the initiator to one of the monomers and the subsequent alternant addition of the others to the final reactive chain end.

Five-membered lactones are difficult to homopolymerize or copolymerize with epoxides because their ring closing is much more favourable than their ring opening. Therefore, it is necessary to suppress ring closing by the accurate selection of the lactone structure. It has been described that bis(γ-lactone)s copolymerize with epoxides to rend the copolymer, which contains poly(ester–ether–ketone) moieties, being the ketone group produced by an isomerization of the bislactone, which takes place during their opening [1–4].

Several authors reported the alternant character of the anionic copolymerization of epoxides with condensed [3,5] or spiranic [6] bis(γ-lactone)s. Among anionic initiators, strong bases such as *t*-butoxide, methyl lithium and hydroxides have been used in the linear copolymerization of epoxides with bis(γ-lactone)s [3]. However, from a technological point of view, these initiators are not suitable to obtain thermosets from diepoxides and bis(γ-lactone)s because their use requires solvent and/or inert atmosphere. For this reason we propose the use of tertiary amines as initiators in the preparation of new thermosets from mixtures of diglycidylether of bisphenol A (DGEBA) and two different condensed bis(γ-lactone)s, 1-methyl-2,8-dioxabicyclo[3.3.0] octane-3,7-dione (bisMe) and 1-phenyl-2,8-dioxabicyclo[3.3.0]octane-3,7-dione (bisPhe). As tertiary amines, we selected 4-(*N*,*N*-dimethylamino)pyridine (DMAP), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1-methylimidazole (1MI). Tertiary amines were previously reported to be active in the ring opening homopolymerization of epoxides [7–9].

The structure of monomers and initiators are represented in Scheme 1. The poly(ether–ester–ketone) three-dimensional structures obtained in this way should be more thermally degradable than the thermosets obtained from pure DGEBA, due to the presence of ester linkages. The introduction of ester groups in thermosetting materials has been used as one of the most fruitful

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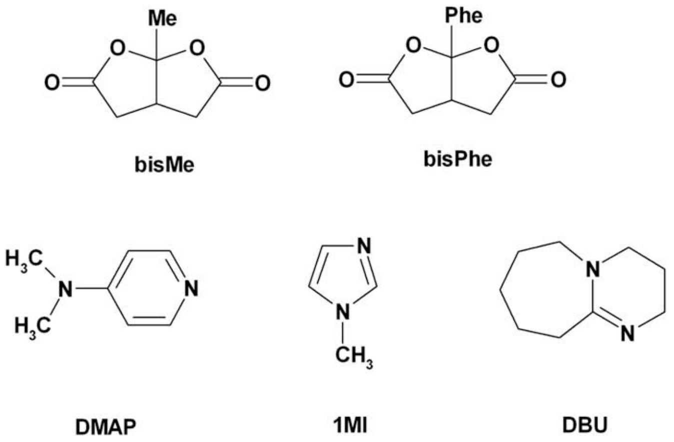


Scheme 1.

strategies to improve the reworkability of the thermosets. The concept of reworkable thermoset is defined as the ability to break down the network under controlled conditions to remove it from a substrate. However, this term does not mean that the polymeric material can be reused or recycled but only that the partially degraded material can be removed by solvents or by brushing from the surface where it is applied. Rework enables the straightforward repair, replacement or recycling of electronic devices assembled with such materials. Among the research groups that followed this strategy it should be considered the works reported by Ober [10,11] Shirai [12,13] and Wong [14,15].

In addition to the thermal degradability, we expect to reach an improvement in the chemical degradation by saponification of the ester groups, as we showed in a previous paper [16] based in the anionic copolymerization of DGEBA with spiranic bis(γ-lactone)s, due to the alternant character of the copolymeric network that we obtained.

2. Experimental part

2.1. Materials

Diglycidylether of bisphenol A (DGEBA) EPIKOTE RESIN 827 from Shell Chemicals (Epoxy Equiv. = 182.08 g/eq.).

Tricarballylic acid, acetic anhydride, benzoic anhydride, 4-(*N*,*N*-dimethylaminopyridine) (DMAP), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1-methylimidazole (1MI) and phenylglycidylether (PGE) (from ALDRICH) were used as-received.

The solvents were purified by standard methods.

2.2. Monomer synthesis

2.2.1. 1-Methyl-2,8-dioxabicyclo[3.3.0]octane-3,7-dione (bisMe) (Scheme 2)

A mixture of tricarballylic acid (6 g, 33 mmol), acetic anhydride (50 mL, 508 mmol) and DMAP (0.9 g, 7.36 mmol) was refluxed with stirring for 3 h under argon. After elimination of acetic acid in vacuum the product was precipitated in ethanol, being the remaining anhydride soluble in this solvent. After filtration, the solid product was dissolved in acetone and the solution was treated with active charcoal. After filtration and evaporation of the solvent a white solid was obtained. The product was recrystallized in ethanol affording a white crystalline solid. Yield: 40%. m.p.: 101-2 °C. (lit.[3] 98–99 °C).

FTIR/ATR (cm^{-1}): 1782, 1264, 1134, 1074, 1051, 922.

^1H NMR (400 MHz $CDCl_3$): δ (ppm) 3.0–3.2 (2dd, 3H), 2.6 (dd, 2H), 1.8 (s, 3H). ^{13}C NMR (75.4 MHz $CDCl_3$): δ (ppm) 172.5, 113.2, 39.2, 35.6, 24.1.

2.2.2. 1-Phenyl-2,8-dioxabicyclo[3.3.0]octane-3,7-dione (bisPhe) (Scheme 2)

It was similarly synthesized using benzoic anhydride instead of acetic anhydride and using xylene as the solvent. Benzoic acid and anhydride were soluble in ethanol but the bislactone precipitated. Yield: 55%. m.p.: 139–140 °C (lit. [17] 122 °C, lit. [4] 138–139 °C).

FTIR/ATR (cm^{-1}): 1791, 1450, 1241, 1189, 1149, 1092, 992, 972, 859, 761.

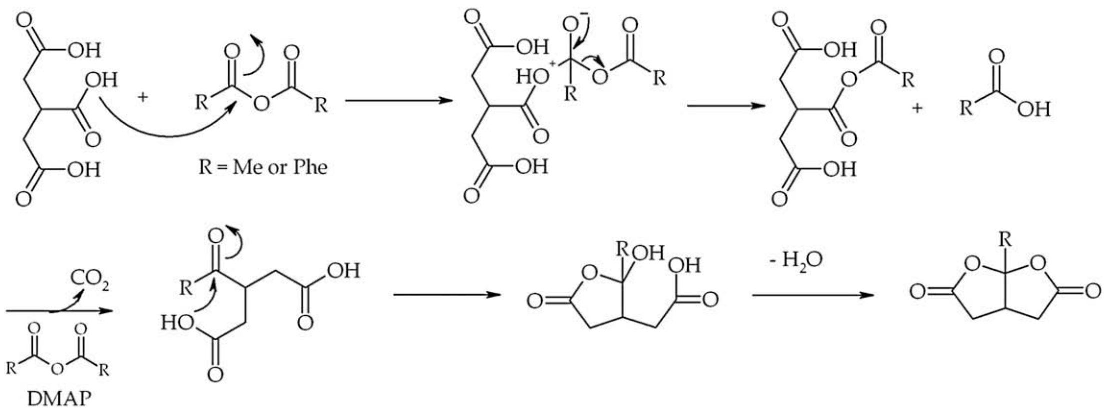
^1H NMR (400 MHz $CDCl_3$): δ (ppm) 7.5 (s, 5H), 3.4–3.3 (broad m, 1H), 3.2–3.1 (dd, 2H), 2.7–2.6 (dd, 2H). ^{13}C NMR (75.4 MHz $CDCl_3$): δ (ppm) 172.9, 136.6, 130.8, 129.6, 125.4, 113.7, 42.0, 35.8.

2.3. Preparation of the curing mixtures

The samples were prepared by mixing the selected quantity of initiator with the corresponding amount of bislactone and DGEBA with manual stirring in a mortar. The prepared mixtures were kept at −18 °C before use.

2.4. Characterization and measurements

Calorimetric studies were carried out on a Mettler DSC-821e thermal analyzer in covered Al pans under N_2 at 10 °C/min. To determine kinetic parameters, the curves were registered at 2, 5, 10 and 15 °C/min. The calorimeter was calibrated using an indium standard (heat flow calibration) and an indium–lead–zinc standard (temperature calibration). The samples weighed approximately 7–9 mg.



Scheme 2.

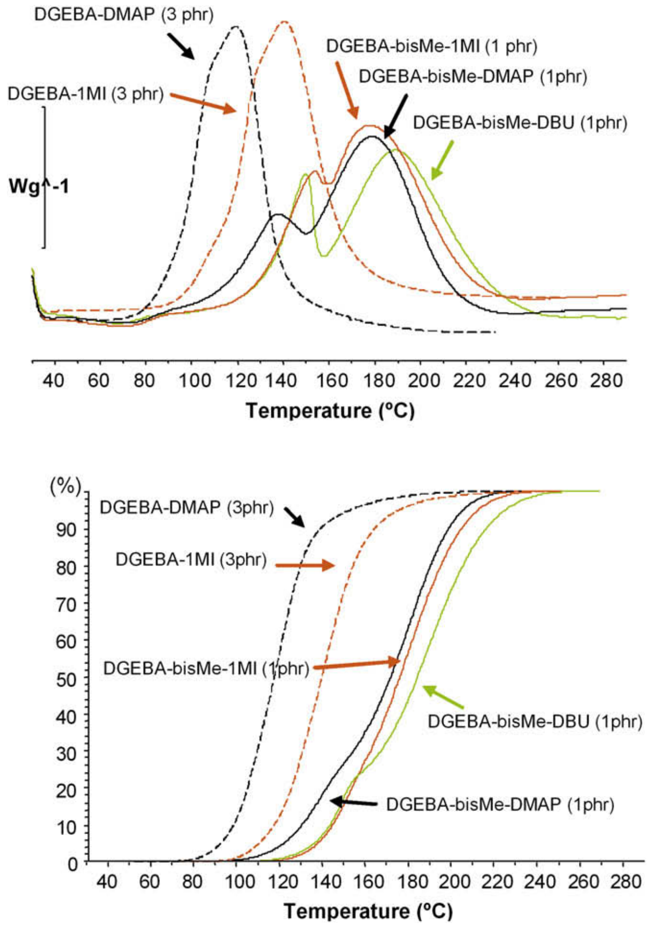


Fig. 1. DSC scanning and conversion curves versus temperature of DGEBA initiated by 3 phr of 1MI and DMAP and DGEBA/bisMe 2:1 (mol/mol) mixture initiated by 1 phr of DMAP, MI and DBU at a heating rate of 10 °C/min.

In the dynamic curing process the degree of conversion by DSC (α_{DSC}) was calculated as follows:

$$\alpha_{\text{DSC}} = \frac{\Delta H_T}{\Delta H_{\text{dyn}}} \tag{1}$$

where ΔH_T is the heat released up to a temperature T, obtained by integration of the calorimetric signal up to this temperature, and ΔH_{dyn} is the total reaction heat associated with the complete conversion of all reactive groups.

The glass transition temperatures (T_gs) were calculated, after complete curing by means of a second scan, as the temperature of the half-way point of the jump in the heat capacity when the material changed from the glassy to the rubbery state under N_2 atmosphere.

The isothermal curing process at 160 °C was monitored with an FTIR spectrophotometer FTIR-680PLUS from JASCO with a resolution of 4 cm^{-1} in the absorbance mode. An attenuated-total-reflection accessory with thermal control and a diamond crystal (Golden Gate heated single-reflection diamond ATR, Specac-Teknokroma) was used to determine FTIR spectra.

Thermogravimetric analyses (TGAs) were carried out with a Mettler TGA/SDTA 851e thermobalance. Cured samples with an approximate mass of 7 mg were degraded between 30 and 600 °C at a heating rate of 10 °C/min in N_2 (100 cm^3/min measured in normal conditions).

2.5. *Kinetic analysis*

Integral isoconversional non-isothermal kinetic analysis named Kissinger–Akahira–Sunose procedure was used to determine the kinetic parameters of the curing process [18–20].

2.6. *Chemical degradation*

The chemical degradation via saponification was performed at reflux in 1 M ethanolic KOH (ethanol/water 90/10 v/v).

3. Results and discussion

In a previous work [6] we studied the curing of mixtures of DGEBA epoxy resin with 1,6-dioxaspiro [4.4]nonan-2,7-dione s(γ-BL) using DMAP, 1MI and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), a homologous of DBU. The evolution of the reactive groups was monitored by FTIR. By this technique and DSC, it was proved that the pure bislactone cannot homopolymerize with none of the initiators tested and, therefore, the reactivity ratio of the spiranic bislactone tends to zero. Epoxy groups can homopolymerize in the presence of the anionic initiator when s(γ-BL) is run out. To get a completely alternant copolymer a DGEBA/s(γ-BL) 1:2 (mol/mol) formulation is needed, since the functionality of DGEBA is four and the functionality of the bislactone is two. Thus, this formulation contains one bislactone per four epoxide groups. When epoxy

Table 1
Calorimetric data of the formulations studied.

Entry	Formulation (mol/mol)	Proportion of initiator (phr)	Initiator	Moles initiator/ eq. epoxy	T_g (°C)	ΔH (J/g)	ΔH^a (kJ/ee)	$T_{\text{màx}}$ (°C)
1	DGEBA	3	DMAP	0.044711	145	473	86	119
2	DGEBA/bisMe 2:1	1	DMAP	0.018100	95	449	99	138/179
3	DGEBA/bisMe 2:1	2	DMAP	0.036201	106	473	105	129/165
4	DGEBA/bisMe 2:1	3	DMAP	0.054301	105	469	104	132/156
5	DGEBA/bisMe 1:1	1	DMAP	0.021297	80	361	94	152/186
6	DGEBA/bisMe 1:1	2	DMAP	0.042595	85	381	99	140/170
7	DGEBA/bisMe 1:2	1	DMAP	0.027682	69	272	92	160
8	DGEBA/bisMe 1:2	2	DMAP	0.055363	69	270	91	152
9	DGEBA/bisPhe 2:1	2	DMAP	0.038741	106	432	102	126/162
10	DGEBA/bisPhe 1:1	2	DMAP	0.047677	96	315	92	133/164
11	DGEBA/bisPhe 1:2	2	DMAP	0.065540	89	221	88	143
12	DGEBA	3	1MI	0.066533	141	490	89	141
13	DGEBA/bisMe 2:1	1	1MI	0.026934	94	446	99	154/178
14	DGEBA/bisMe 2:1	2	1MI	0.053869	105	474	105	145/164
15	DGEBA	3	DBU	0.035880	–	–	–	–
16	DGEBA/bisMe 2:1	1	DBU	0.014525	98	451	100	150/190
17	DGEBA/bisMe 2:1	2	DBU	0.029050	105	475	105	140/175

[a] Enthalpy release by epoxy equivalent.

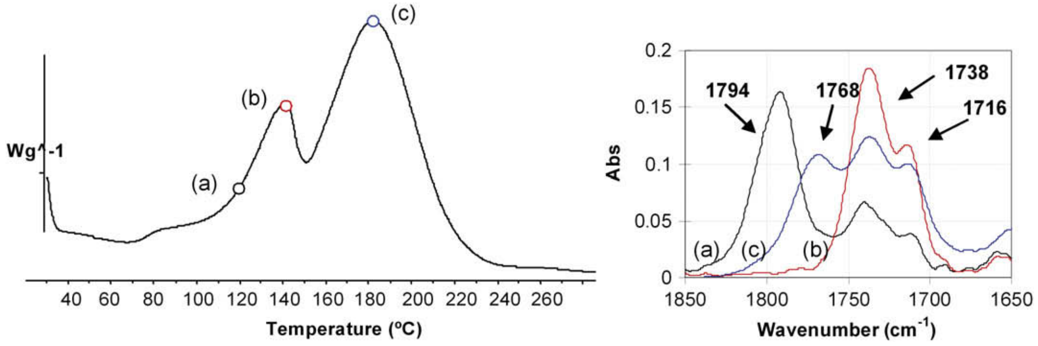
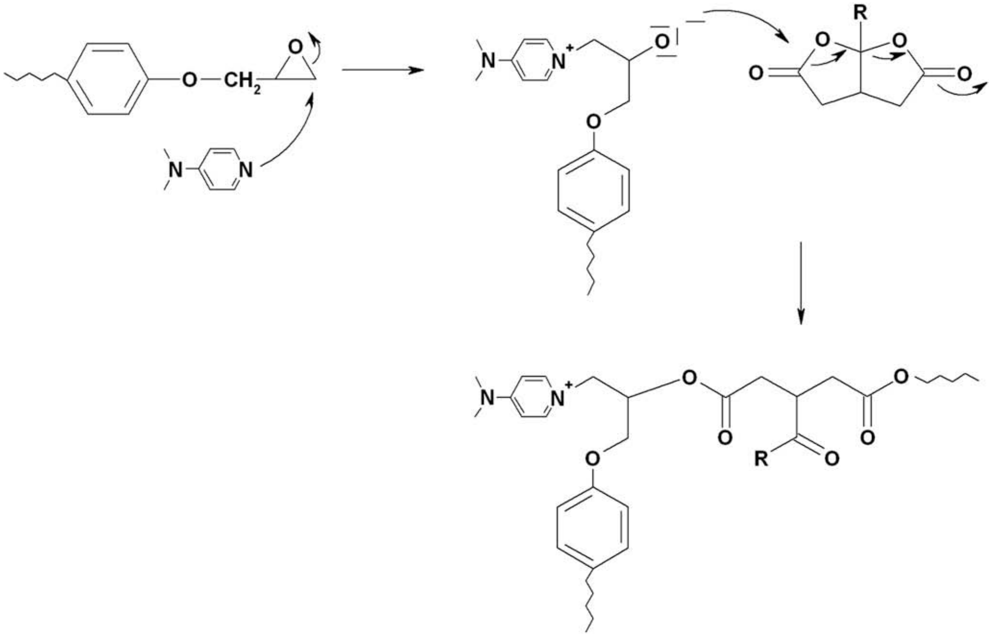


Fig. 2. DSC curing exotherm with the detail of the thermal treatment of the samples investigated by FTIR and carbonylic region of the FTIR spectra of samples partially cured in the DSC from a DGEBA/bisMe 2:1 (mol/mol) formulation with 1 phr DMAP (a) before the 1st maximum (in black), (b) in 1st maximum (in red) and (c) in the 2nd maximum (in blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

groups were in excess in the formulation their homopolymerization also occurred. By DSC we saw that the addition of the spirobislactone to DGEBA produced an acceleration of the curing process and that DMAP, among the amines tested, was the most active. However, the efficiency of these initiators is related not only with the intrinsic activity of their tertiary nitrogens but also to the chance of undergoing termination reactions, which allow to refresh the initiator and keep a sufficient amount of active species [8] in the reaction medium. It was determined that a complete curing could be achieved with a small amount of any of the initiators tested, in contrast to the higher amount of initiator needed for the homopolymerization of pure DGEBA.

In the present study we copolymerized DGEBA with the condensed bis(γ-lactone)s shown in Scheme 1. Similar systems were previously studied by other authors with mono or bifunctional epoxides using hydroxides, alkoxides or organometallics as initiators [3,5,21,22]. Because we used different initiators (DMAP, 1MI and DBU) we firstly studied by DSC the curing evolution of DGEBA/bisMe 2:1 (mol/mol) mixtures with 1–3 phr of each initiator. It should be said that in this reaction DGEBA acts as a tetrafunctional monomer and bis(γ-lactone) as bifunctional and therefore homopolymerization of epoxide can be expected because it is in excess. The calorimetric curves are shown in Fig. 1, which includes the curves for pure DGEBA curing in order to compare. Table 1 collects the main calorimetric data. In these studies we observed that 3 phr of DMAP or 1MI were necessary to completely cure pure DGEBA and that DBU was not able to cure DGEBA even in this proportion. The heat released per epoxy equivalent during DGEBA curing with 3 phr of DMAP or 1MI agrees with the values previously described [6]. In contrast, bislactone/DGEBA mixtures can cure with only 1–2 phr of initiator. As can be seen in the figure, DGEBA shows unimodal curves whereas the mixtures show bimodal shape, which indicates the occurrence of different reactive processes. To know the reaction responsible of each exotherm, we registered the FTIR/ATR spectra of partially cured samples using DMAP at some selected curing temperatures: at the beginning of the first exotherm and in the maxima of the two exotherms (Fig. 2). The most significant absorptions that indicate which process takes place during curing are the bands corresponding to the initial lactone at 1794 cm^{-1}, the linear ester formed at 1738 cm^{-1} and the epoxy absorption at 915 cm^{-1}. In the first spectrum (a, black line), registered at the beginning of the first exotherm, we can observe the lactone band and the expected linear ester and the ketone (at 1738 and 1716 cm^{-1} respectively) that begin to form by opening of



Scheme 3.

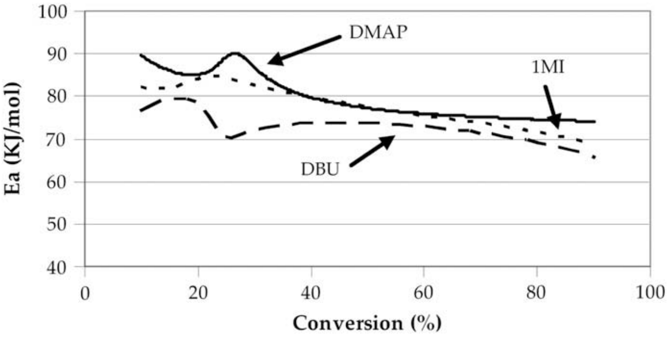


Fig. 3. Dependence of the activation energy on the degree of conversion for the curing of DGEBA/bisMe 2:1 (mol/mol) mixture initiated by 1 phr of DMAP, 1MI and DBU.

the bislactone with isomerization (Scheme 3). In the spectrum registered in the first maximum (b, red line), the band of the lactone has disappeared and the absorptions at 1738 and 1716 cm^{-1} have increased. Moreover, the intensity of the epoxy band (not represented in the figure) has decreased. This indicates that the first exotherm corresponds to the copolymerization of epoxide and lactone. In the spectrum registered in the second maximum (c, blue line) the carbonyl bands previously formed have diminished and, surprisingly, a new absorption at 1768 cm^{-1} appears. Moreover, the intensity of the epoxy band diminishes. These observations indicate that, in addition to the homopolymerization of epoxide, this second exotherm includes other reactive processes, which were not described before by Endo's group [3–5,21,22]. This second exotherm, corresponding to the homopolymerization of epoxide, which includes these unexpected processes lead to a greater enthalpy than that observed in a previous work on the copolymerization of a spiranic bis(γ-lactone), which did not experiment unexpected reactions [6]. With both spiranic and condensed bislactones the copolymerization occurs before the homopolymerization of epoxide. If we recall Fig. 1, we can see that DMAP seems to be the most active initiator in both processes, while DBU is the less active. For this reason we selected DMAP to follow this study.

Fig. 3 shows the evolution of the activation energies during curing. As we can see, the curves reflect two different parts. The first one, up to a conversion of about 25% corresponds to the copolymerization process of bislactone and epoxide. From this conversion, the predominant process is the homopolymerization of epoxide, which is accompanied by the unexpected processes before mentioned. The activation energy of the copolymerization is higher than that of the homopolymerization, as we reported previously [6].

Fig. 4 shows the calorimetric curves and conversions obtained in dynamic scans for the different DGEBA/bisMe formulations studied using 2 phr of DMAP as initiator. Before discussing these results, it should be commented that the main heat is released by the opening of the epoxide, because the enthalpy released in the opening of a γ-lactone is reported to be 5–10 kJ/mol [23]. The stoichiometric mixture 1:2 (mol/mol) shows an endotherm due to the melting of the solid bislactone and a unimodal exotherm, which seems to indicate that an only process occurs. In contrast, the other two formulations present a bimodal exotherm, the first one corresponding to the ester formation and the second to the epoxide homopolymerization plus the unexpected processes, increasing the second one with the proportion of epoxide (2:1 formulation). The conversion curves against temperature show that until a conversion of 25% the three formulations coincide and from this point formulation 2:1 slows down. Up to a conversion of about 50% formulations 1:1 and 1:2 also coincide and then the former begins to delay, being from this conversion the stoichiometric formulation the fastest. This can be attributed to the fact that the copolymerization takes place at the beginning of the curing process, until the lactone is run out, and that it is faster than the homopolymerization of epoxide. These results are in accordance with those obtained for analogous anionic copolymerization of DGEBA/spirobislactones [6].

If we look at the T_gs of the materials and the enthalpy per epoxy equivalent (Table 1) we can see that the use of 2 phr of each initiator allows the complete curing of the DGEBA/bislactone mixtures (entries 2–4) and even 1 phr was enough when the ratio epoxy/bislactone was stoichiometric (entries 7 and 8). Due to the flexibility introduced by the copolymerization with the bislactone and the greater distance between crosslinks, the T_gs of the materials are reduced in comparison to pure DGEBA and their values decrease on increasing the proportion of lactone. The three initiators lead to similar T_gs and curing enthalpies but DMAP has a higher catalytic activity (entries 2, 3, 13, 14, 16 and 17).

We also studied the effect of changing methyl by phenyl group in the bislactone in the evolution of the curing process (entries 9–11). It can be seen that when the proportion of bisPhe is low the T_gs are similar (entries 3 and 9), but when the proportion is high (entries 6 and 10, and 8 and 11) the values increase in reference to bisMe. The presence of the phenyl substituent slightly decreases the temperature of the maximum of the exotherms.

To go deeply in the reaction mechanism followed in the preparation of the thermosets, we registered the FTIR spectra during curing to see the evolution of the different absorptions. Fig. 5 collects the FTIR spectra of the curing of a DGEBA/bisMe 2:1 (mol/mol) formulation with 2 phr of DMAP obtained at 160 °C in the ATR

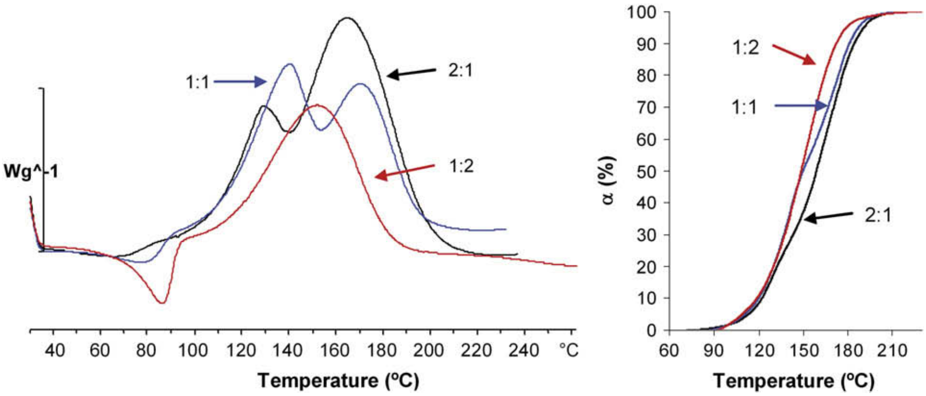


Fig. 4. DSC scanning and conversion curves versus temperature of DGEBA/bisMe mixtures in molar ratios of 2:1, 1:1 and 1:2 (mol/mol) initiated by 2 phr of DMAP at a heating rate of 10 °C/min.

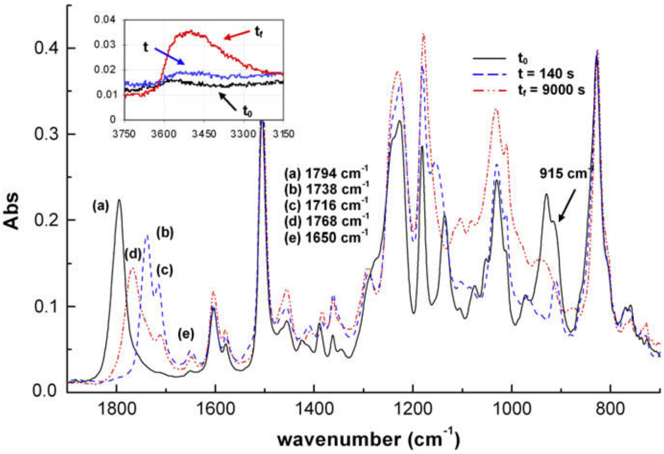


Fig. 5. FTIR–ATR spectra taken at different curing times of a DGEBA/bisMe 2:1 (mol/mol) mixture with 2 phr of DMAP at 160 °C.

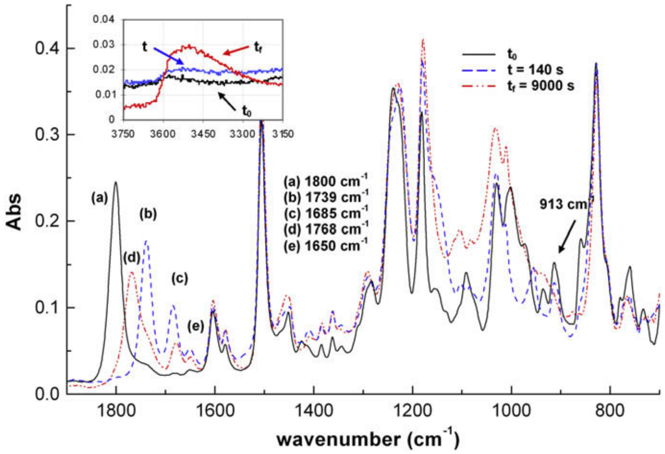


Fig. 7. FTIR–ATR spectra taken at different curing times of a mixture of DGEBA/bisPhe in a molar ratio of 2:1 with 2 phr of DMAP at 160 °C.

before and after curing and at an intermediate stage. As we can see, the initial lactone band at 1794 cm^{-1} has completely disappeared in the spectrum taken at 140 s, whereas the expected linear ester absorption at 1738 cm^{-1} and the ketone absorption at 1716 cm^{-1} can be clearly appreciated. At this curing time a little peak at 1650 cm^{-1} can be also observed. This peak can be attributed to the formation of the pyridinium salt from the initiator, because it increases proportionally with the amount of DMAP added and it is not present when 1MI was used. As expected, the epoxy absorption at 915 cm^{-1} decreases and the ether absorptions increase during curing indicating the homopolymerization of epoxide. In the spectrum of the final material the intensity of linear ester and the ketone bands decrease, and a new carbonyl absorption at 1768 cm^{-1} appears. This seems to indicate that larger reaction times lead to unexpected processes in which linear ester and ketone groups are involved. In the inset of the figure the hydroxylic absorption is also included, where we can see that this signal increases during curing.

To investigate if these unexpected processes take also place with other formulations, we registered their FTIR spectra during curing. Fig. 6 shows the carbonyl zone of the cured materials obtained from formulations DGEBA/bisMe 2:1, 1:1 and 1:2 (mol/mol) using 2 phr of DMAP as initiator at 160 °C. Whereas an excess of epoxide leads to the formation of the band at 1768 cm^{-1}, the stoichiometric proportion (formulation 1:2) only produces the expected poly(ether–ester–ketone). Moreover, in the hydroxylic region we can see how the signal increases as the proportion of epoxide increases. From these results we can infer that the excess of epoxide and the subsequent formation of alkoxides could be responsible of these unexpected processes. The substitution of DMAP by 1MI or DBU leads to similar results.

In the carbonyl zone of the FTIR spectra of the DGEBA/bisPhe 2:1 (mol/mol) formulation (Fig. 7), although the ketone appears at a different wavenumber (1685 cm^{-1} for bisPhe and 1716 cm^{-1} for bisMe) because of the conjugation with phenyl group in the former, the unexpected carbonyl band in both final materials appear at the same wavenumber (at 1768 cm^{-1}). Again, in the spectrum of the material obtained from DGEBA/bisPhe 1:2 formulation, we could only observe the expected signals of poly(ether–ester–ketone).

Taking into account all these results, we can propose some plausible mechanisms, which are depicted in Scheme 4. At the first part of the curing, the alternant copolymerization takes place and, when the lactone is run out, the alkoxide groups can initiate the homopolymerization and other parallel reactions. At this point, the material has enough mobility because of the lactone moiety introduces flexibility and increases the distance between crosslinks.

The alkoxide, acting as a base, can extract the acidic α-carbonyl protons (Scheme 4a–c) or, as nucleophile, can directly attack the ketone (Scheme 4d). In all these proposed reaction pathways, final thermodynamically stable five-membered lactones are formed: in a, an unsaturated γ-lactone; in b and d, saturated γ-lactones and in c, a condensed lactone fused with an unsaturated five-membered ring. The first three processes are aldolic-like reactions and therefore there are equilibrium processes. The mechanism d, after the first attack of alkoxide to the ketone, consists in a transesterification. By mechanisms a–c, hydroxylic groups are formed,

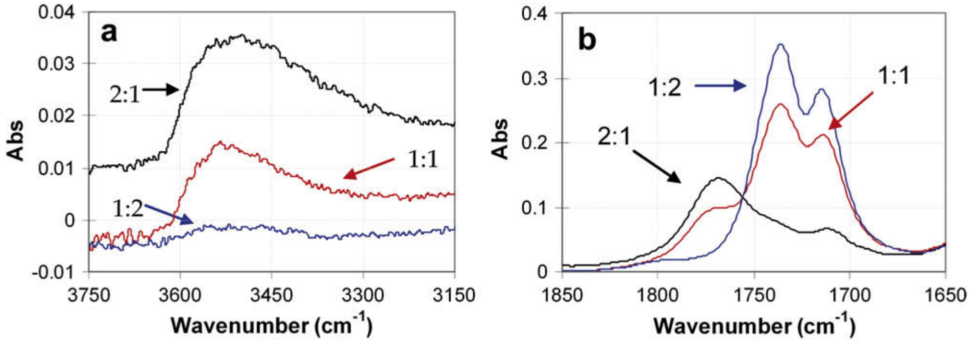
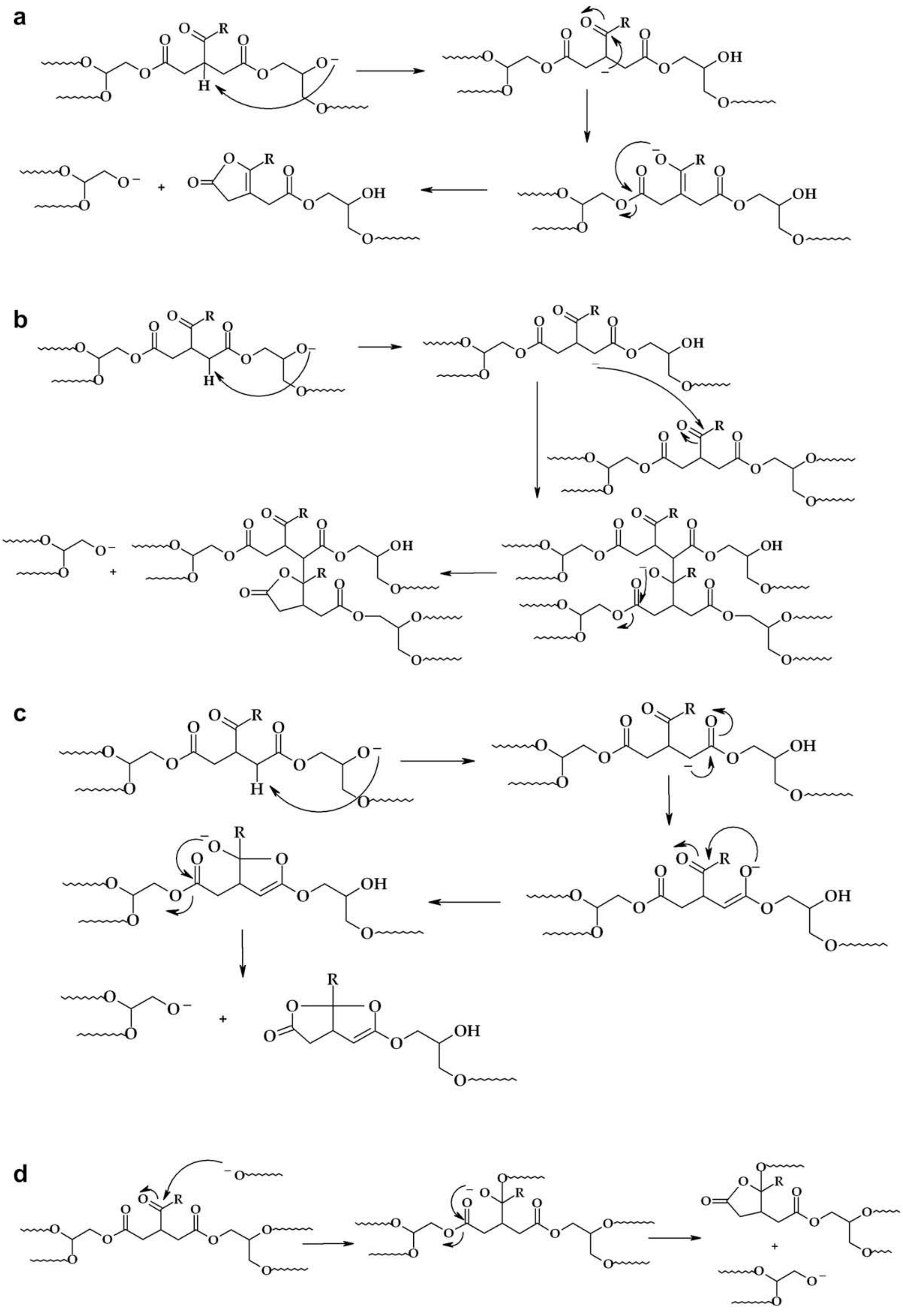


Fig. 6. FTIR–ATR spectra of (a) hydroxyl and (b) carbonyl zone of DGEBA/bisMe 2:1, 1:1 and 1:2 (mol/mol) formulations initiated by 2 phr of DMAP.



Scheme 4.

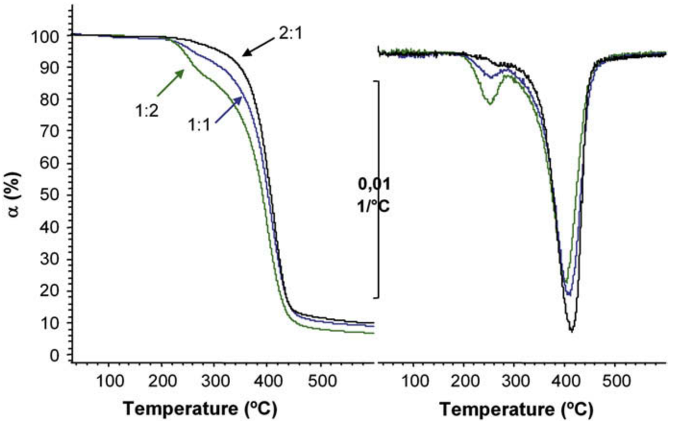


Fig. 8. Thermogravimetric and DTG curves under N_2 atmosphere registered at 10 °C/min of the materials obtained from DGEBA/bisPhe (mol/mol) formulations initiated by 2 phr of DMAP varying the proportion of bislactone.

whereas none is formed by mechanism d. By FTIR we could see a significant increase of the hydroxylic absorption and therefore a–c mechanisms seem to be the most probable. Among these mechanisms, we can discard the mechanism a because we cannot observe in the FTIR spectra any difference in the wavenumber of the carbonyl absorption on changing methyl by phenyl in the final lactone; these absorptions should be different in bisPhe, because of the phenyl group is conjugated with the double bond. Moreover, the unsaturated lactone should produce a new absorption at about 1680 cm^{-1} that cannot be observed either.

The mechanism b can be an inter- or intramolecular process, being the latter highly improbable by enthropic and steric reasons. However, Zhang and colleagues [24] observed by MALDI-TOF the formation of cyclic oligomers in the copolymerization of stoichiometric bisMe/PGE formulations using potassium *t*-butoxide as initiator. The formation of the analogous cyclic oligomers is more difficult in our case because of the three-dimensional character and the absence of solvent. The mechanism c is intramolecular and lead to a condensed structure with a certain similarity with the initial lactone.

In the mechanisms a, b and d when one alkoxide attacks, one ketone and one linear ester disappear but one linear ester remains unreacted. In these mechanisms one lactone ring is formed for each alkoxide that react. Therefore, it seems that these mechanisms should lead to similar absorption intensities for lactone and final ester groups. In mechanism c the attack of the alkoxide leads to the disappearance of one ketone and two linear ester groups at the same time and, therefore, the linear ester absorptions should be lower than that of the lactone formed. If we look at the intensities of the carbonyl signals in the final spectra (Figs. 5 and 7) we can observe that a little proportion of ketone and ester groups remains unreacted, but the size of the lactone absorption is much bigger than that of linear ester. Pathway c, in which one ketone and two ester groups disappear, seems to be the mechanism that better explains the relative intensities of the carbonyl absorptions, and therefore it could be the predominant pathway that follows this unexpected process.

The different evolution of the stoichiometric and non-stoichiometric DGEBA/bislactone formulations can be rationalized by the alternant character of the polymerization mechanism. In stoichiometric mixtures the initiators firstly attack to the epoxide and then the alkoxide formed opens the lactone, leading to final carboxylate groups. The lower basicity and nucleophilicity of these groups in comparison to alkoxides prevent the initial attack in the mechanism represented in Scheme 4. When epoxide is in excess in the formulation, the chain ends are mainly alkoxides, which are capable of initiating the unexpected processes.

Although the use of model compounds to investigate reaction mechanisms cannot always be applied to crosslinked materials, we studied the copolymerization in bulk of a monofunctional epoxide compound (PGE) with bisMe in different proportions using DMAP, to clarify the mechanisms implied. The stoichiometric proportion showed, by FTIR and ^{13}C NMR spectroscopy, the formation of the expected poly(ether–ester–ketone) as Endo et al. reported [3]. However, when epoxide was in excess in the initial mixture, the FTIR spectrum after reaction showed the band at 1768 cm^{-1} of a five-membered lactone, and the ^{13}C NMR spectrum showed a complex pattern with several carbonyl signals in the zone of 175–177 ppm and also a great number of signals in the aliphatic region. All the expected signals of the condensed lactone formed by mechanism c were present in the ^{13}C NMR spectrum, but its complexity did not allow the total exclusion of the other structures formed by other side-reactions.

On the basis of these results, we can conclude that to obtain poly(ether–ester–ketone) networks the stoichiometric proportion DGEBA/condensed bis(γ-lactones) is required.

The thermosets, obtained using DMAP as initiator, were studied by thermogravimetry in order to test their thermal degradability. Fig. 8 shows the TGA and DTG curves of the materials obtained from bisPhe. We can see how, on increasing the proportion of lactone in the formulation, the temperature of the initial weight loss decreases and the rate of initial thermal degradation increases. However, the composition of the formulation has no great influence on the temperature of the maximum rate of degradation. This fact can be rationalized by the ester rupture, which takes place at lower temperature, whereas the rupture of ether bonds occurs at higher temperature. It should be said, that the degradability of reworkable materials is usually associated to the temperature at which a low percentage of weight is lost (i.e. 5%) because the loss of mechanical characteristics takes place at this low percentage, independently of the temperature at which the maximum weight loss occurs.

Table 2 collects the thermogravimetric data of the materials prepared. In general, the introduction of ester groups noteworthy increases the degradability in reference to pure DGEBA. The T_{max} are similar for the materials obtained from both lactones but all of them are lower than the T_{max} of the pure DGEBA. However, the nature of the substituent (Me or Phe) affects the temperature of 5% weight loss, which can be explained by the higher weight of the lost fragment in the case of phenyl substituent. On increasing the proportion of bislactone in the formulation, the chair yield is reduced, as expected.

The breakage of the ester groups decreases the density of crosslinking and therefore the T_g of the material will be reduced on

Table 2
Thermogravimetric data evaluated in N_2 atmosphere of the materials prepared.

Entry	Formulation (mol/mol)	Prop. of Initiator (phr)	Initiator	Mol initiator/ eq. epoxy	T (5%)[a] (°C)	$T_{màx}$[b] (°C)	Chair yield (%)
1	DGEBA	3	DMAP	0.044711	396	435	13.2
3	DGEBA/ bisMe 2:1	2	DMAP	0.036201	323	414	10.7
6	DGEBA/ bisMe 1:1	2	DMAP	0.042595	278	405	8.7
8	DGEBA/ bisMe 1:2	2	DMAP	0.055363	275	402	6.3
9	DGEBA/ bisPhe 2:1	2	DMAP	0.038741	308	413	9.6
10	DGEBA/ bisPhe 1:1	2	DMAP	0.047677	256	410	8.7
11	DGEBA/ bisPhe 1:2	2	DMAP	0.065540	241	403	6.4

[a] Temperature at which a 5% of weight loss occurs.
[b] Temperature of the maximum degradation rate.

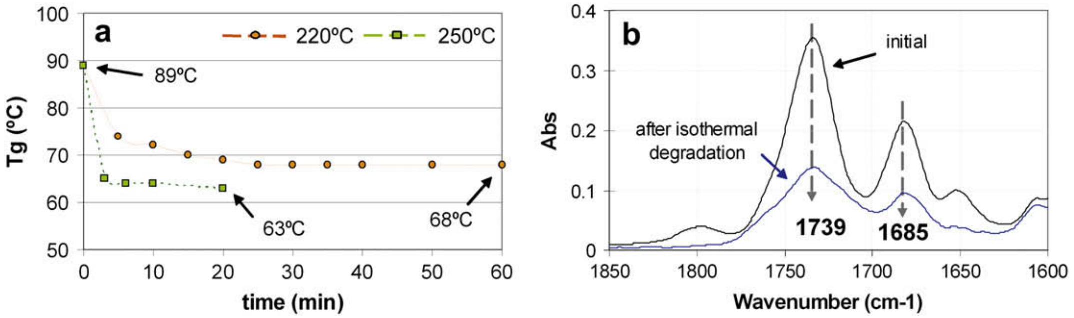


Fig. 9. (a) Variation of the T_g on heating at 220 and 250 °C of a material obtained from a DGEBA/bisPhe 1:2 (mol/mol) formulation initiated by 2 phr of DMAP. (b) Carbonylic region of the FTIR spectra of the material before and after isothermal degradation at 250 °C.

heating. To confirm this, the material obtained from a stoichiometric mixture DGEBA/bisPhe, was maintained at 220 or 250 °C for several times and then the T_g of the degraded material was determined and the FTIR spectrum was registered. Fig. 9a shows the evolution of T_g on heating for both temperatures. At both temperatures the T_g strongly decreases until a plateau is reached, more quickly when the temperature is higher. The final T_g achieved is slightly lower at 250 °C. A temperature in the range 230–250 °C has been described as optimal for safe rework operations in nitrogen atmosphere [25]. In Fig. 9b is represented the carbonyl region of the FTIR spectra before and after heating, where we can see the significant diminution of the ester and ketone groups. The loss of both groups not only implies the rupture of ester bonds, but the loss of ester–ketone fragments, which is responsible for the weight loss that occurs.

The thermosets obtained from stoichiometric mixtures were completely soluble in ethanolic KOH as a consequence of the presence of ester groups regularly distributed in the network structure, similarly to the observed for DGEBA/spiranic bis(γ-lactone)s formulations [16].

4. Conclusions

The anionic thermal curing of DGEBA with condensed bis(γ-lactone)s needs a lower proportion of tertiary amine as initiator than the curing of pure DGEBA. Among the initiators tested, DMAP is the most active and DBU is the least efficient. On increasing the proportion of bislactone in the reactive mixture, an acceleration effect is observed.

Stoichiometric proportions of DGEBA/bis(γ-lactone) lead to the expected alternate poly(ether–ester–ketone) structure and, in a dynamic scan, it produces a single exotherm in the DSC curves.

When DGEBA is in excess, the DSC curve shows two exotherms, being the first attributed to the copolymerization of epoxy and lactone, and the second to the homopolymerization of the epoxide and the unexpected processes. By FTIR we can see that these unexpected processes lead to the formation of five-membered lactones in the final material and to the practically total disappearance of the linear ester and ketone groups.

Thermogravimetric analysis allows confirming the reworkable character of the thermosets obtained. The higher proportion of bislactone in the formulation, the higher the thermal degradability is.

Thermosets obtained from stoichiometric formulations are completely soluble in ethanolic KOH.

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