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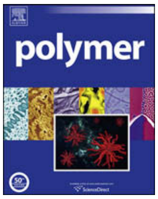

Cationic copolymerization of DGEBA with two bicyclic bis(γ-lactone) derivatives using rare earth metal triflates as initiators

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ABSTRACT

The thermal cationic curing of mixtures in different proportions of diglycidylether of bisphenol A (DGEBA) with two differently substituted condensed bis(γ-lactone)s (BisMe and BisPhe) initiated by scandium, ytterbium and lanthanum triflates or a conventional $BF_3\cdot MEA$ initiator was investigated. Non-isothermal differential scanning calorimetry (DSC) experiments at a controlled heating rate were used to evaluate the evolution of the reactive systems. $BF_3\cdot MEA$ and rare earth metal triflates initiated curing systems follow a different evolution. Among rare earth metal triflates tested, the scandium was the most active initiator. The phenomenological changes that take place during curing were studied and represented in time–temperature–transformation (TTT) diagrams. The improvement in the reworkable character of the materials prepared was confirmed by thermogravimetry. The thermomechanical characteristics were also evaluated.

1. Introduction

The purpose of our research is not only the improvement of the characteristics of the cured epoxy resins to wide their application field, but to make easier and economically efficient their curing process. In previous publications we reported the copolymerization of commercially available epoxy resins with lactones [1], spirobislactones [2] or carbonates [3] modifying the network structure with the aim to improve some characteristics of the thermosets such as: a) their "reworkable" character by introduction of labile ester or carbonate groups that increase the thermal and chemical degradability [4,5]; b) the reduction of the shrinkage during curing by adding or generating "in situ" expandable monomers to minimize the internal stresses generated in the process [6,7]; and c) the toughness enhancement by increasing the flexibility of the network and increasing the distance between crosslinks [8].

Because of condensed bis(γ-lactone)s can copolymerize with epoxides introducing two ester groups per unit of lactone in the network and increasing in six atoms the distance between crosslinks, they has been selected as good candidates to improve the above mentioned characteristics of the epoxy thermosets. Due to the fact that these copolymerizations take place by a ring-opening mechanism it is necessary to select the most adequate initiator and its proportion.

It has been reported that spiranic or condensed bis(γ-lactone)s copolymerize with epoxides in an alternating way by anionic mechanism via a tandem double ring-opening of bis(γ-lactone)s and ring-opening of the epoxides [9–11]. However, when we cured rich-epoxy DGEBA/condensed bis(γ-lactone) formulations unexpected reactions occurred. These reactions led to the practically total disappearance of the expected poly(ester-ketone) units in the network and to the formation of five-membered lactone rings. Thus, to obtain poly(ester-ketone) networks, which are the most degradable by the presence of ester groups in the network, stoichiometric DGEBA/condensed bis(γ-lactone) mixtures are always required [12].

One of the general advantages of the copolymerization strategy is the possibility to select the comonomer composition to tune the final properties of the thermosets obtained. Because anionic systems fail in the possibility to choose the proper formulation, we moved to cationic mechanisms to see if they are able to copolymerize the different formulations leading to poly(ester-ketone) structures and the conditions that should be applied to reach the complete curing in the selected times. Cationic copolymerization of these bis(γ-lactone)s with DGEBA has not been reported in the literature up to now.

As cationic initiators we chose rare earth metal triflates (Sc, La and Yb) because they were successfully used in the curing of DGEBA with several lactones [1] and bislactones [2], leading to thermosets with ester moieties in the final materials. These initiators are active in very little proportions, even in humid environments, and have a low toxicity. These characteristics make them advisable in front of

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the conventional boron trifluoride complexes and those that contain transition metals [13,14]. The presence of rare earth triflates in the network structure facilitates the degradation of the thermosetting materials, decreasing the initial temperature of cleavage of the polymeric network, which enhances the reworkability of this type of materials when they are applied as coatings which need to be removed from the substrate [15,16].

As we saw in previous studies [1,2,6], the cationic copolymerization of epoxides and lactones takes place by the formation of an intermediate spiroorthoester (SOE), which can homopolymerize or copolymerize with epoxide leading to poly(ether-ester) networks. If epoxide is in excess, polyetherification also occurs. Usually, the homopolymerization of SOE units takes place at the end of the curing and this fact is responsible of the reduction of shrinkage after gelation observed by us [2,17]. The contribution of these four processes will depend on the composition of the mixture, on the initiator selected and its proportion, which influence the kinetics of each process. During curing, different physical processes can also occur (gelation and vitrification), which affect not only the curing process but also the final characteristics of the thermosets.

The present work is devoted to the study of the curing kinetics by means of the isoconversional methodology and to the determination of gelation and vitrification of these systems. The results obtained will be collected and represented in TTT diagrams for a non-stoichiometric mixture of DGEBA with BisMe or BisPhe condensed bis(γ-lactone)s. The thermal degradability and the thermomechanical characteristics of the materials prepared have been studied.

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 and benzoic anhydrides and 4-(*N*,*N*-dimethylaminopyridine) (DMAP) (ALDRICH) were used as received.

Lanthanum (III), ytterbium (III) and scandium (III) trifluoromethanesulfonates and boron trifluoride monoethylamine ($BF_3 \cdot MEA$) (Aldrich) were used without purification.

The solvents were purified by standard methods.

2.2. Monomer synthesis

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) were synthesized from tricarballylic acid and acetic anhydride or benzoic anhydride, respectively, in the presence of DMAP as previously described [12].

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. Calorimetric study

Calorimetric studies were carried out on a Mettler DSC-821e thermal analyzer in covered Al pans under N_2 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. In the dynamic curing process the degree of conversion by DSC (α_{DSC}) was calculated as follows:

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

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 T_g was measured as the half-way point of the jump in the heat capacity when the material changed from the glassy to the rubbery state at 10 °C/min.

In order to establish the relations T_g–α we performed a series of non-isothermal scans from 20 °C to several temperatures, below 225 °C, at a heating rate of 10 °C/min. Then, the samples were immediately quenched and a second scan from −100 °C to 225 °C at a heating rate of 10 °C/min was registered to determine the T_g value and the residual heat. The degree of conversion was calculated on the basis of residual heat taking into account the total reaction heat.

The kinetic analysis was carried out using an integral isoconversional method as we will explain next. The basic assumption of this method is that the reaction rate at a given conversion is only a function of the temperature [18,19]. Isoconversional methods make it possible to easily determine the dependence of *E* on the degree of conversion in complex processes.

The kinetics of the reaction is usually described by the following rate equation:

$$\frac{d\alpha}{dt} = Af(\alpha)\exp\left(-\frac{E}{RT}\right) \tag{2}$$

where *t* is time, *A* is the pre-exponential factor, *E* is the activation energy, *T* is the absolute temperature, *R* is the gas constant, and $f(\alpha)$ is the differential conversion function.

By integrating the rate equation, Eq. (2), under non-isothermal conditions and using the Coats–Redfern [20] approximation to solve the so-called temperature integral and considering that $2RT/E$ is much lower than 1, the Kissinger–Akahira–Sunose (KAS) equation may be written [21]:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left[\frac{AR}{g(\alpha)E}\right] - \frac{E}{RT} \tag{3}$$

where β is the heating rate and $g(\alpha)$ is the integral conversion function.

For each conversion degree, the linear plot of $\ln(\beta/T^2)$ versus $1/T$ enables *E* and $\ln[AR/g(\alpha)E]$ to be determined from the slope and the intercept.

If the reaction model, $g(\alpha)$, is known, for each conversion the corresponding pre-exponential factor can be calculated for every activation energy. In this study, we used the reduced master curves procedure of Criado [22], described elsewhere, to assign a reaction model to the systems studied [23]. Different kinetic models have been studied: diffusion (D_1–D_4), Avrami–Erofeev (A_2–A_4), power law, phase-boundary-controlled reaction (R_2 and R_3), autocatalytic ($n + m = 2$ and 3) and order *n* ($n = 1$–3). We found that all systems studied follow a kinetic model of the surface-controlled reaction type, R_2, with $g(\alpha) = [1 - (1 - \alpha)^{1/2}]$. The rate constant, *k*, was calculated with *E* and *A* determined at conversion of 0.5, using the Arrhenius equation.

2.5. Thermogravimetric analysis

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).

2.6. Thermomechanical analysis

Thermal-dynamic-mechanical analyses (DMTAs) were carried out with a TA Instruments DMTA 2980 analyzer. The samples were cured isothermally in a mould at 140 °C for 3 h and were then subjected to a post-curing for 2 h at 160 °C. Three point bending of 10 mm was performed on cylindrical samples (10 × 4 mm, approximately). The apparatus operated dynamically at 3 °C/min from 35 to 200 °C at a frequency of 1 Hz.

2.7. Gel point determination

The conversions at the gelation were determined by the residual enthalpy in the DSC of the gelled sample at different temperatures. The gel point was confirmed by solubility tests and the conversions at the gel point proved to be 0.58 for the mixture with bisMe and 0.56 for bisPhe.

3. Results and discussion

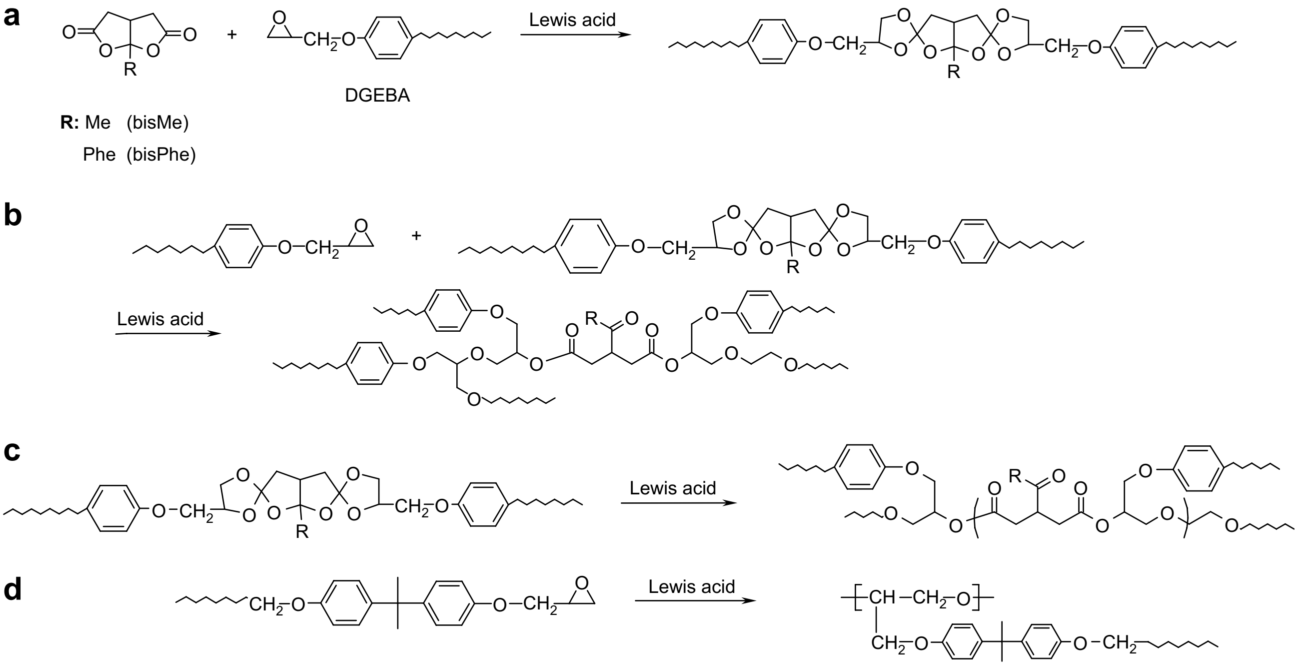
The multistep reactive mechanism implied in the cationic curing of DGEBA/condensed bis(γ-lactone)s (BisMe and BisPhe) is detailed in Scheme 1. Reaction a is the formation of the corresponding intermediate SOE catalyzed by the Lewis acid. The presence of two lactone groups in the monomer can lead to the formation of a bis-SOE structure. This compound can copolymerize with epoxide (reaction b) or homopolymerize (reaction c) leading to a poly(ester-ether-ketone) structure. Epoxide groups can also homopolymerize (reaction d). It should be commented that, by reaction with epoxides, γ-lactones lead to poly(ether-ester) units but condensed bis(γ-lactone)s could experiment a tandem reaction that leads to the formation of ketone groups in the repetitive unit. In this reaction two ester groups could be formed, which are interesting from the point of view of the enhancement of the thermal and chemical degradability.

The formation of the expected chemical structure of poly(ether-ester-ketone), irrespective of the comonomer feed, was confirmed by FTIR. The concurrence among the different reactive processes, on changing the ratio between comonomers and the initiator selected, lead to some variations in the chemical structure of the network and therefore in the characteristics of the final material, which will be discussed in a forthcoming paper.

Fig. 1 shows the thermograms corresponding to the dynamic curing for the formulation DGEBA/bisMe 2:1 with 1 phr of the rare earth triflates tested or 3 phr of $BF_3{\cdot}MEA$, which were the proportions required to reach the complete curing. As we can see, all the curves are unimodal but finish at different temperatures, being the lowest those of scandium and ytterbium triflates. From the conversion curves, we can clearly see that the highest active initiator is the scandium salt. The boron trifluoride complex needs a higher temperature to initiate the curing because of the formation of the true reactive species [24], but once initiated, it goes quicker than the curing with lanthanum triflate and at the end it slows down and higher temperatures are needed to reach the complete curing. This evolution is in accordance to the complex reaction mechanism when boron complexes are used as initiators [24]. The order of reactivity of rare earth metal triflates follows the Lewis acidity trend, from lanthanum to scandium, as observed previously [1,3].

The effect of the triflate salt and the structure of the lactone on the kinetics were also analyzed. Fig. 2 shows the conversion–temperature plots, which were obtained by the integration of the calorimetric signals for the formulations studied. It can be seen that the curves of both lactones have a similar shape, but bisMe reacts slightly faster than bisPhe when we used scandium or ytterbium salt as initiators.

The accelerative effect of the proportion of initiator was studied with ytterbium triflate and is plotted in Fig. 3. The curves of 0.5 and 1 phr of initiator show similar shapes. The curve corresponding to 3 phr has an initial broad exotherm that begins at about 60 °C before the main exothermic process, which finish before 160 °C. The broad initial exotherm can be attributed to the coexistence of a competitive mechanism. In a previous paper [25], we could assign the exotherm at lower temperatures to the activated monomer mechanism (AM), which takes place in addition to the activated chain end mechanism (ACE) in the copolymerization of epoxides



Scheme 1. Expected reactions in the cationic curing of DGEBA/condensed bis(γ-lactone) mixtures.

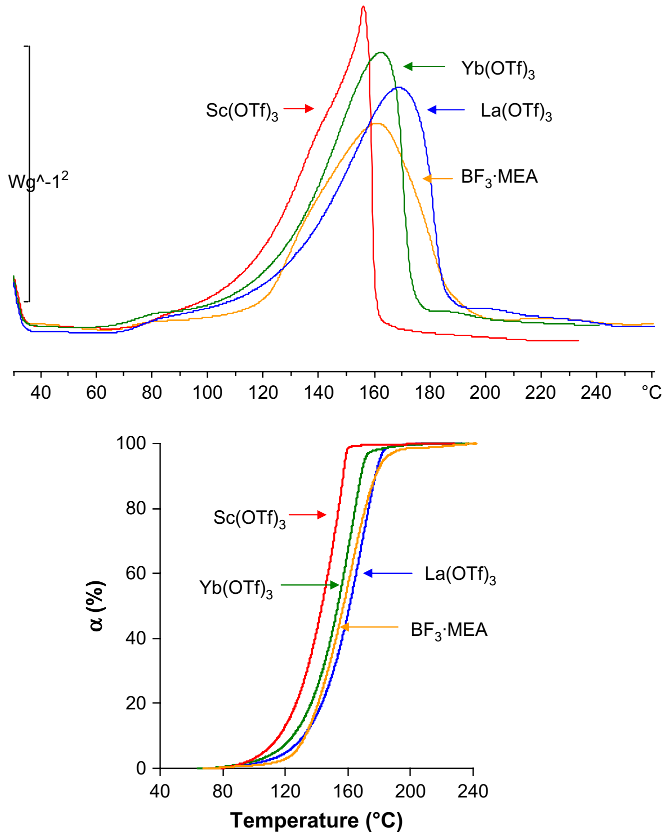


Fig. 1. DSC scanning and conversion curves versus temperature of DGEBA/bisMe 2:1 (mol/mol) mixture initiated by 1 phr of the rare earth triflates tested or 3 phr of $BF_3 \cdot MEA$ at a heating rate of 10 °C/min.

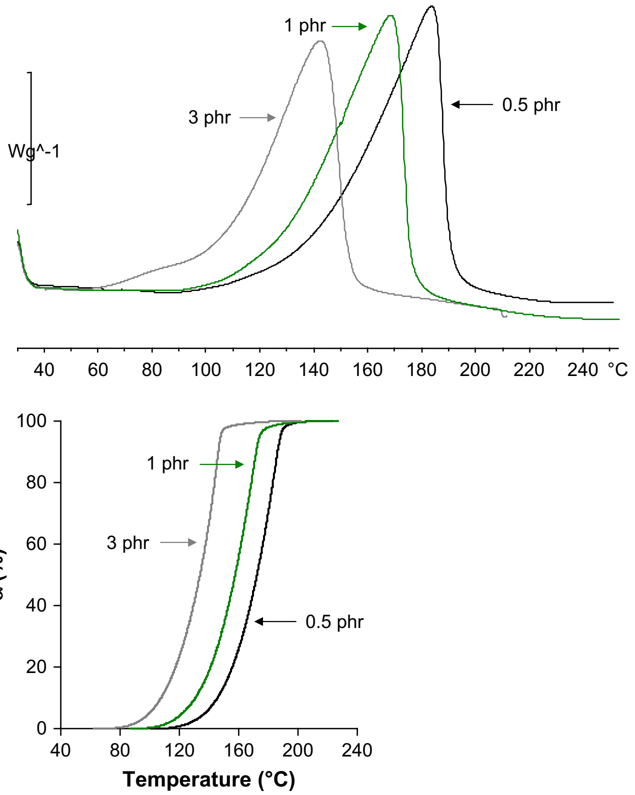


Fig. 3. DSC scanning and conversion curves versus temperature of DGEBA/bisMe 2:1 (mol/mol) mixture initiated by 0.5, 1 and 3 phr of $Yb(OTf)_3$ at a heating rate of 10 °C/min.

with lactones. AM mechanism becomes favoured in the presence of a higher proportion of initiator. As can be seen in the α-T curves, much higher conversions are reached at a selected temperature when the proportion of the initiator increases, i.e. for 160 °C, the curing with 3 phr is practically complete, whereas with 0.5 phr is less than 30%.

The effect of adding different proportions of lactone to DGEBA is represented in Fig. 4 for ytterbium triflate initiated systems containing bisMe. The shape of the exotherms is similar but on increasing the proportion of lactone there are little differences at the beginning and at the end of the exotherm. At the beginning there is a broad endotherm, which can only be seen in the 1:1 formulation, due to the melting of the lactone that is not totally dissolved in the DGEBA matrix. At the end of the curves of the formulations 2:1 and 1:1 we can see a broad exotherm, more important for the latter, which can be attributed to the homopolymerization of SOE that takes place only at high temperatures [17]. The conversions increase, at a given temperature, on increasing the lactone proportion in the mixture. The accelerative effect can be attributed to the formation of more reactive species as we saw in similar systems [2,17].

In Tables 1 and 2 the calorimetric data of all the systems studied are collected. The T_gs of the materials decrease on increasing the proportion of bislactone in the formulation, because of the flexibility introduced in the network. The lower functionality of the lactone in comparison to the DGEBA enlarges the distance between crosslinks, which also reduces the crosslinking density. Whereas the materials obtained from pure DGEBA with all the initiators tested have a T_g over 120 °C, only $La(OTf)_3$ allows to exceed 100 °C for a DGEBA/bisMe 2:1 mol/mol formulation. On changing methyl by phenyl in the lactone structure, T_gs slightly increase and are about 100 °C for the DGEBA/bisPhe 2:1 mol/mol formulations. For any selected formulation the T_g value depend on the rare earth metal triflate selected, being the highest for the materials obtained with La and the lowest those obtained with Sc.

In previous works [26] we saw how the Lewis acidity of the metal triflate influences the proportion in which ACE and AM propagation mechanisms occur. The latter and the transfer chain reactions associated to it are favoured on increasing the acidity of the initiator ($Sc > Yb \gg La$). This can explain that the formulations

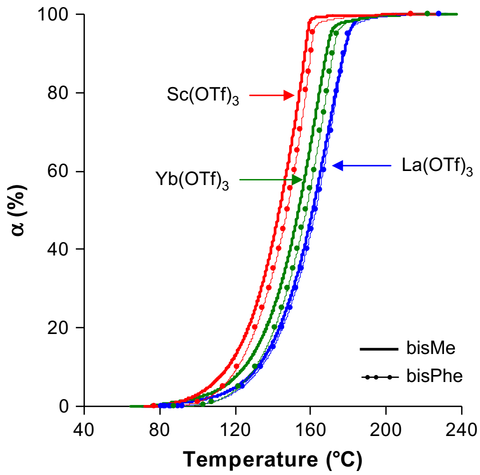


Fig. 2. Conversion curves obtained by DSC from DGEBA/bisMe and bisPhe 2:1 (mol/mol) formulations with 1 phr of the rare earth triflates tested.

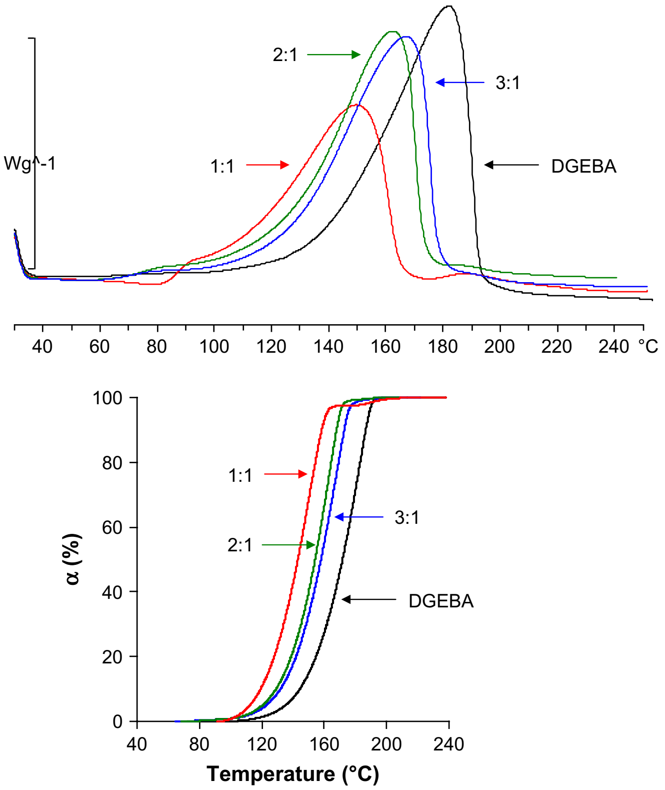


Fig. 4. DSC scanning and conversion curves versus temperature of pure DGEBA and different DGEBA/bisMe formulations initiated by 1 phr of $Yb(OTf)_3$ at a heating rate of 10 °C/min.

initiated by Sc present the lowest T_gs, whereas those initiated by La have the highest T_gs.

Similarly, the proportion of initiator can also influence the final T_g of the materials because AM mechanism is favoured by high proportions of initiator. Because of we added 1 phr of each initiator, the lower molecular weight of scandium triflate makes its molar proportion greater, and this fact can also affect the T_gs of the materials.

The enthalpies released per gram of mixture or by epoxy equivalent decrease on increasing the proportion of bislactone because of the polymerization enthalpy of γ-lactones is far less than that of epoxy groups [27]. On changing the initiator, any significant difference can be observed in the enthalpy released, which can be explained in the basis of the same degree of epoxy reaction with all the initiators tested. However, if we take into account the differences in the T_gs, the networks should have some structural variations. This might be due to the above mentioned factors and to the different ability of each initiator to homopolymerize the SOE groups, as we saw in the study of other DGEBA/lactone systems [6]. The proportion of initiator practically does not influence the enthalpy released and only slightly influences the T_gs of the materials with bisMe (Table 1). It seems that 0.5 phr of the ytterbium salt is enough to complete the curing, but 1 phr is better from the point of view of the kinetics (see Fig. 3). Higher proportions could initiate the curing during storage at room temperature and decrease the T_g.

By the isoconversional method we obtained the evolution of the activation energies during the curing process. From the calorimetric curves and applying Eq. (3), we obtained the activation energy for each degree of conversion in all the formulations studied. Fig. 5 shows the plot of the apparent activation energy against the degree of conversion for the DGEBA/bisPhe 2:1 mol/mol formulation initiated by 1 phr of the rare earth triflates or 3 phr of $BF_3 \cdot MEA$. It can be seen that the activation energies are practically constant during the curing process and the boron trifluoride initiator leads to the highest activation energy. The high magnitude of the activation energy for $BF_3 \cdot MEA$ systems should be related with the formation of the true initiator species HBF_4 [24,28].

The values of the activation energies calculated at 50% of conversion, collected in Tables 1 and 2, do not show any regular trend and they do not agree with the different curing rates, due to the compensation effect between activation energy and pre-exponential factor [25,29]. In this case we needed to determine the kinetic model and then estimate the pre-exponential factor and the kinetic constant by means of the Arrhenius equation. To establish the kinetic model for the systems studied we used the reduced master curves procedure [22] for all the models given in the experimental part. Among them, R_2 model was considered as the best. Using this model we calculated the pre-exponential factors using the kinetic parameters obtained by applying Eq. (3) and the constant rate at 160 °C. As we can see in Tables 1 and 2, the constant rate increases with the proportion of bislactone added to the curing mixture and with the proportion of initiator. Moreover, the rate constants are higher when scandium triflate is the initiator and

Table 1
Calorimetric data and calculated parameters of the DGEBA/bisMe formulations studied.

Formulation (mol/mol)	Proportion of initiator (phr)	Initiator	Mols initiator /eq. epoxy	T_g (°C)	ΔH (J/g)	ΔH^a (kJ/ee)	$T_{max}{}^b$ (°C)	E_a (kJ/mol)	$\ln A^c$ (s^{-1})	$k_{160\,°C} \times 10^{3c}$ (s^{-1})	T (5%)^d (°C)	$T_{max}{}^e$ (°C)
DGEBA	1	$La(OTf)_3$	0.003106	127	531	97.6	192	78.4	13.8	0.79	314	360
DGEBA/bisMe 3:1	1	$La(OTf)_3$	0.003550	113	442	92.0	175	74.8	14.5	1.93	297	358
DGEBA/bisMe 2:1	1	$La(OTf)_3$	0.003773	108	401	88.7	169	71.8	13.9	2.47	289	345
DGEBA	1	$Yb(OTf)_3$	0.002935	137	526	96.7	180	85.5	17.4	1.50	299	345
DGEBA/bisMe 3:1	1	$Yb(OTf)_3$	0.003355	108	438	91.1	167	74.8	15.0	3.01	290	340
DGEBA/bisMe 2:1	0.5	$Yb(OTf)_3$	0.000178	99	388	85.9	178	80.4	16.1	1.95	288	356
DGEBA/bisMe 2:1	1	$Yb(OTf)_3$	0.003565	97	397	87.7	163	77.4	16.0	4.03	282	335
DGEBA/bisMe 2:1	3	$Yb(OTf)_3$	0.010696	94	395	87.3	141	78.8	17.7	14.79	267	316
DGEBA/bisMe 1:1	1	$Yb(OTf)_3$	0.004194	72	327	85.1	150	87.1	19.4	8.42	255	330
DGEBA	1	$Sc(OTf)_3$	0.003699	120	521	95.6	183	75.1	15.0	1.04	296	338
DGEBA/bisMe 3:1	1	$Sc(OTf)_3$	0.004228	103	439	91.3	164	72.4	14.6	4.10	277	328
DGEBA/bisMe 2:1	1	$Sc(OTf)_3$	0.004493	94	400	88.4	156	79.9	17.2	6.97	268	326
DGEBA/bisMe 2:1	3	BF_3.MEA	0.058259	102	391	86.5	161	87.6	18.7	3.62	286	429

[a] Enthalpies given by epoxy equivalent.
[b] Temperature of the maximum of the exotherm.
[c] Calculated using R_2 as a model.
[d] Temperature of a 5% of weight loss.
[e] Temperature of the maximum degradation rate.

Table 2
Calorimetric data and calculated parameters of the DGEBA/bisPhe formulations studied.

Formulation (mol/mol)	Proportion of initiator (phr)	Initiator	Mols initiator /eq. epoxy	T_g (°C)	ΔH (J/g)	ΔH^a (kJ/ee)	$T_{max}{}^b$ (°C)	E_a (kJ/mol)	ln A^c (s^{-1})	$k_{160\,°C} \times 10^{3c}$ (s^{-1})	T (5%)^d (°C)	$T_{max}{}^e$ (°C)
DGEBA	1	$La(OTf)_3$	0.003106	127	531	97.6	192	78.4	13.8	0.79	314	360
DGEBA/bisPhe 3:1	1	$La(OTf)_3$	0.003727	116	426	93.0	178	80.9	16.2	1.93	300	359
DGEBA/bisPhe 2:1	1	$La(OTf)_3$	0.004037	110	369	87.3	173	79.9	16.1	2.31	293	356
DGEBA	1	$Yb(OTf)_3$	0.002935	137	526	96.7	180	85.5	17.4	1.50	299	345
DGEBA/bisPhe 3:1	1	$Yb(OTf)_3$	0.003522	113	424	92.6	170	77.1	15.5	2.85	290	341
DGEBA/bisPhe 2:1	0.5	$Yb(OTf)_3$	0.001908	106	364	86.1	184	79.4	15.5	1.45	289	358
DGEBA/bisPhe 2:1	1	$Yb(OTf)_3$	0.003815	102	372	88.0	168	75.6	15.2	3.07	284	345
DGEBA/bisPhe 2:1	3	$Yb(OTf)_3$	0.011446	98	371	87.7	150	73.9	16.1	11.35	265	322
DGEBA/bisPhe 1:1	1	$Yb(OTf)_3$	0.002286	81	282	82.1	158	91.7	20.3	5.61	265	329
DGEBA	1	$Sc(OTf)_3$	0.003699	120	521	95.6	183	75.1	15.0	1.04	296	338
DGEBA/bisPhe 3:1	1	$Sc(OTf)_3$	0.004439	105	429	93.7	176	78.7	16.1	2.99	276	333
DGEBA/bisPhe 2:1	1	$Sc(OTf)_3$	0.004808	94	376	89.0	159	74.9	15.6	5.14	269	330
DGEBA/bisPhe 2:1	3	$BF_3.MEA$	0.010391	109	387	91.6	153	–	–	–	288	428

[a] Enthalpies given by epoxy equivalent.
[b] Temperature of the maximum of the exotherm.
[c] Calculated using R2 as a model.
[d] Temperature of a 5% of weight loss.
[e] Temperature of the maximum degradation rate.

lower for the lanthanum salt. BisMe mixtures have slightly higher constant rates than the analogous mixtures containing bisPhe. All these kinetic results agree with the kinetic effect shown in Figs. 1–3.

We constructed the time–temperature–transformation (TTT) diagram to understand and conceptualize the changes occurring during curing. Such a diagram displays the states of the material and characterizes the evolution of the curing and the phenomenological changes in the material during isothermal cure versus time. The various changes occurring in the material during isothermal cure are characterized by contours of the times to reach the events as gelation, corresponding to the conversion at the gel point and vitrification, corresponding to the glass transition temperature. The basic parameter governing the state of the material is the chemical conversion. Thus, to know how the rate changes with the curing temperature is basic for predicting the chemical conversion achieved after a cure schedule.

Three critical temperatures should be considered: T_g^0, the glass transition temperature of the uncured mixture, ${}_{gel}T_g$, the temperature at which molecular gelation and vitrification coincide, and T_g^∞, the glass transition temperature of the fully cured material. Fig. 6 shows the TTT cure diagram of a DGEBA/bisMe 2:1 (mol/mol) mixture with 1 phr of $Yb(OTf)_3$. The bold lines represent the time necessary to reach the gelation (red line) and vitrification (black line) at a selected curing temperature. This diagram was constructed using the experimental data determined previously (the isoconversional lines, the T_g–α relationship, the conversion at gelation, the T_g^0 and the T_g^∞) following the methodology previously reported by us [30] and the use of the Di Bendetto equations [31,32]. We found a value of 30 °C for the lowest temperature at which the material gels before vitrification (${}_{gel}T_g$), a value for T_g^0 of −17 °C, below which the material does not crosslink at all, and a value for T_g^∞ of 105 °C, which is the lowest temperature at which the complete curing can be achieved. The TTT diagram has a shape similar to other obtained in the copolymerization of epoxy resins with lactones [30].

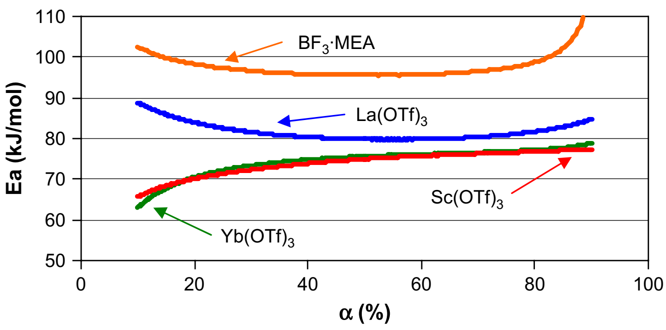


Fig. 5. Dependence of the activation energy on the degree of conversion for the curing of DGEBA/bisPhe 2:1 mol/mol formulation initiated by 1 phr of the rare earth triflates or 3 phr of $BF_3 \cdot MEA$.

Fig. 7 shows the TTT diagram for the curing process of a mixture DGEBA/bisPhe 2:1 (mol/mol) with 1 phr of $Yb(OTf)_3$. There are not many differences in shape on changing the lactone but they have different parameters governing the state of the material. For bisPhe the ${}_{gel}T_g$ is 20 °C, T_g^0 of −16 °C and T_g^∞ of 102 °C.

If we compare both TTT diagrams with the diagram of the cure of neat DGEBA with ytterbium triflate ($T_g^\infty = 137$ °C) [30], we can say that the addition of bis(γ-lactone)s makes possible to reduce the curing temperature and, consequently, the thermal stresses generated on cooling from the curing temperature. In addition, the curing at lower temperature also implies an important energy saving.

The introduction of ester groups in the epoxy network has the purpose to facilitate the reworkability of the coated materials when their service life is over. The thermal degradation of the materials

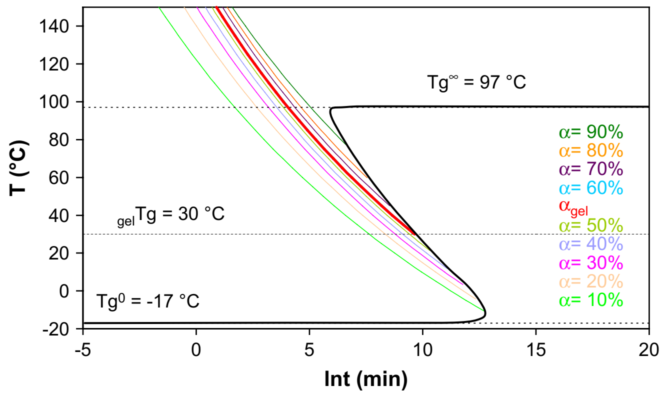


Fig. 6. Time–temperature–transformation diagram for the curing of the mixture DGEBA/bisMe 2:1 (mol/mol) mixture with 1 phr of $Yb(OTf)_3$. Vitrification curve (—), gelification curve (▬).

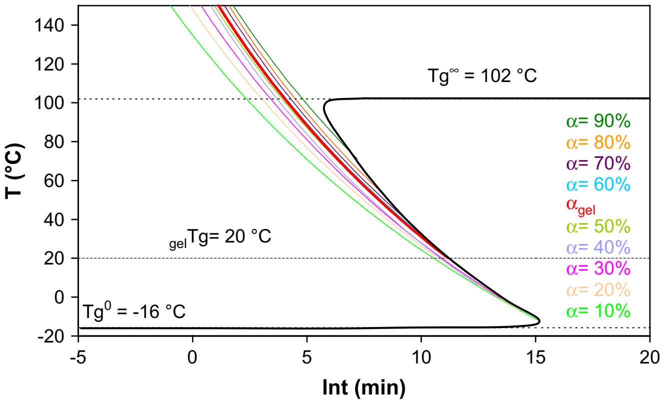


Fig. 7. Time–temperature–transformation diagram for the curing of the mixture DGEBA/bisPhe 2:1 (mol/mol) mixture with 1 phr of $Yb(OTf)_3$. Vitrification curve (—), gelification curve (▬).

prepared was studied by thermogravimetry. The values obtained are collected in Tables 1 and 2. From the point of view of the reworkability, the most important parameter is the initial temperature of degradation, which we take as $T_{5\%}$, because at this temperature the main process is the breakage of labile ester bonds. When a 5% of weight loss occurs, the mechanical properties go down and the coating can be eliminated by solvents or brushing.

The values of the tables make evident that on increasing the proportion of lactone in the formulation the temperature of initial degradation decreases; however no differences are observed on changing the lactone.

In previous studies we observed that rare earth metal triflates play an important role in the degradation mechanism, facilitating it because of their Lewis acid characteristics. The effect on the degradation increases with the Lewis acidity of the cation [16]. In the tables we can see that the materials obtained with scandium triflate have the lowest $T_{5\%}$ and those with lanthanum the highest. $T_{5\%}$ also decreases on increasing the proportion of initiator, which supports the role of rare earth triflates in the degradation process. The different T_g values can also influence the thermal stability. In general, materials with low T_g (i.e. formulations with scandium triflate or with 3 phr of initiator) present lower stability. Analogous materials obtained anionically using *N*,*N*-dimethylaminopyridine (DMAP) [12] as initiator showed higher $T_{5\%}$, and only stoichiometric DGEBA/lactone 1:2 mol/mol formulations led to more degradable materials than those obtained cationically in the present study. The materials obtained with DMAP showed two step degradation curves with the main process, the rupture of ether bonds, at a temperature higher than 400 °C. Thermosets obtained in the present work present an only degradative process, due to the partial overlapping of the ester and ether ruptures. This overlapping can be explained because of rare earth triflates catalyze the ether rupture and lead to a lower T_{max} for the cationically obtained materials.

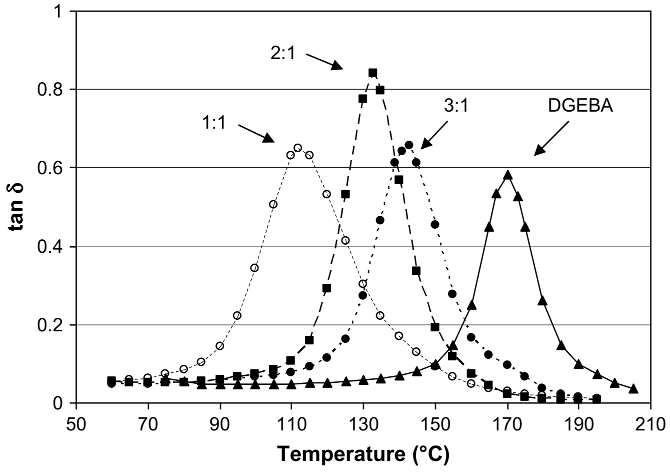


Fig. 8. Dependence of tan δ versus temperature for pure DGEBA and the materials obtained from different DGEBA/bisMe formulations initiated by 1 phr of $Yb(OTf)_3$ obtained by DMTA.

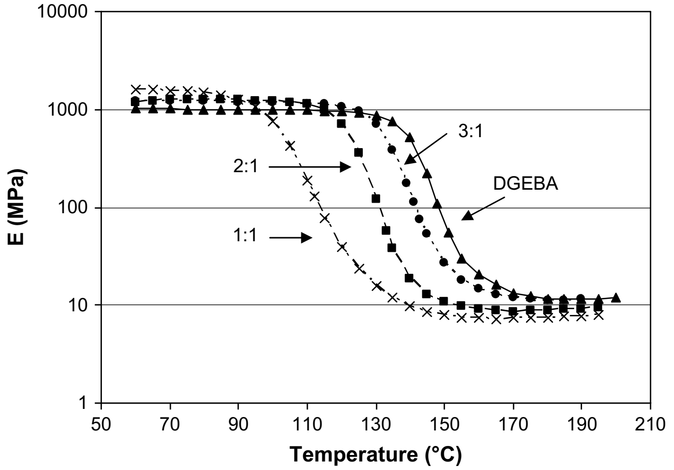


Fig. 9. Dependence of storage modulus versus temperature for pure DGEBA and the materials obtained from different DGEBA/bisPhe formulations initiated by 1 phr of $Yb(OTf)_3$ obtained by DMTA.

The materials prepared were also characterized by thermomechanical analysis. The effect of the proportion of lactone in the value of loss tangent can be observed in Fig. 8 for bisMe. The material obtained from pure DGEBA has been included to compare. As can be seen, the addition of lactone clearly reduces the temperature of the maximum of tan δ. The curves are unimodal, which indicates that the materials are homogeneous, but the curve becomes broader in the 1:1 (mol/mol) DGEBA/lactone formulation. As expected, the values of relaxed modulus decreased as the lactone content in the formulation increased, due to the flexibility introduced in the network structure, as is represented in Fig. 9 for DGEBA/bisPhe formulations.

4. Conclusions

The kinetic studies performed by calorimetry showed that, among rare earth metal triflates, the more active initiator was the scandium and the less the lanthanum triflate. This behaviour can be correlated to their Lewis acidity. Moreover, on increasing the lactone proportion in the mixture the curing process accelerated. The acceleration was slightly higher with bisMe as lactone.

The T_gs of the materials prepared decreased on increasing the proportion of bislactone in the formulation, because of the flexibility introduced in the network. The materials obtained from bisPhe showed a slightly higher T_g than those obtained from bisMe.

The use of calorimetric experiments and the determination of the gel point allowed us to construct the TTT diagrams for the curing of DGEBA/bisMe and bisPhe 2:1 (mol/mol) mixtures initiated by $Yb(OTf)_3$ and the curing interval temperatures could be determined.

By thermogravimetry, the materials showed that the temperature of the 5% of weight loss went down on increasing the proportion of bislactone in the formulation. The materials prepared with $Sc(OTf)_3$ were the most degradable. The change in the lactone structure did not produce any substantial difference.

By DMTA experiments we observed that the materials presented unimodal tan δ curves, irrespective to the initiator used, which account for the homogeneity of these materials. The tan δ curves shifted to lower temperatures and the relaxed moduli decreased on increasing the proportion of lactone in the formulation.

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