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Study on the effect of rare earth metal triflates as initiators in the cationic curing of DGEBA/γ-valerolactone mixtures and characterization of the thermosets obtained

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ABSTRACT

The thermal cationic curing of mixtures in different proportions of diglycidylether of bisphenol A (DGEBA) with γ-valerolactone (γ-VL) initiated by scandium, ytterbium and lanthanum triflates or a conventional BF_3·MEA initiator was investigated. The non-isothermal differential scanning calorimetry (DSC) experiments at a controlled heating rate were used to evaluate the evolution of the reactive systems. BF_3·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 a time-temperature-transformation (TTT) diagram. Some characteristics of the materials were also evaluated.

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1. Introduction

The processability of an epoxy resin critically depends on the rate and extent of polymerization under process conditions. Therefore, kinetic characterisation of the reactive system is not only important for a better understanding of structure-properties relationships but it is also fundamental in optimizing process conditions and product quality.

The choice of a particular curing initiator depends on the processing requirements, e.g. viscosity, pot-life, curing temperature, mixing ratio, etc. and the end-use requirements, e.g. thermal and chemical resistance or toughness of the cured material. Initiators also have a large influence on the molecular weight between crosslinks, long term stability and reactivity in different chemical and physical environments and even in the total cost of the resulting material. Differential scanning calorimetry (DSC) is one of the most used experimental techniques to evaluate the kinetics of a reactive system. The results of the kinetic study can be used for various purposes, i.e. to analyze how an initiator or different proportions of a co-reactant can affect a reactive system or how the temperature can affect the evolution of the reaction [1].

The cure reaction of thermosetting polymers has been investigated extensively [2,3]. Among them, epoxy resins studies are relevant because of their industrial applications [4–6]. However, they have been mainly performed on epoxy-amine traditional systems and few studies are based on cationic systems [7,8]. The catalytic curing of epoxy resins has been applied as an alternative to amine or anhydride agents. Generally, cationic initiators involve complexes such as BF_3·amine or BF_3·ether [9]. Although boron trifluoride complexes have been used for several decades, they are not only hygroscopic, but also at high

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temperature and high humidity the electrical properties of the thermosets obtained tend to deteriorate. Moreover, BF_3 complexes are difficult to solve in DGEBA resins.

Rare earth triflates are commercially available Lewis acids that maintain their catalytic activity even in water and are regarded as environmentally friendly catalysts [10–12]. Generally, scandium triflate shows a higher catalytic effect than lanthanide triflates, due to its higher Lewis acidity attributed to its small ionic radium [13]. We demonstrated that lanthanide triflates can effectively act as cationic initiators in the curing of epoxy resins [14].

The ionic character of the rare earth metal triflates makes difficult to dissolve these initiators in DGEBA resins. To form a homogeneous mixture, Chabanne et al. [15] added a little proportion of a γ-lactone to a DGEBA/BF_3·amine complex. They observed that this lactone was incorporated into the network structure in spite of γ-lactones cannot homopolymerize in cationic systems. Their incorporation was explained by the formation of an intermediate spiroorthoester when reacting with DGEBA. This intermediate compound further homo- or copolymerize to produce poly(ether–ester) three-dimensional networks. The introduction of γ-lactone in the reactive system increases its reactivity and, when a larger proportion of lactone is added to the mixture, some characteristics of the materials can be improved. In previous studies we could demonstrate that thermal degradability, desirable to obtain reworkable thermosets, was highly increased [16]. Moreover, the incorporation of aliphatic structures between crosslinks improved the flexibility and in some cases the shrinkage after gelation was reduced. This fact diminishes the internal stress generated during curing [17].

The present study deals with the curing of mixtures of diglycidylether of bisphenol A (DGEBA) with γ-valerolactone (γ-VL) in several proportions using scandium, ytterbium and lanthanum triflates or BF_3·MEA as initiators and with the characterization of the materials obtained. The copolymerization of DGEBA with γ-valerolactone in the presence of rare earth triflates led, in addition to the four expected reactions (formation of SOE, homopolymerization of SOE and copolymerization with epoxide, and epoxide homopolymerization) to the reversion of SOE, producing different proportions of free lactone which remained entrapped in the thermoset (Scheme 1).

The cationic copolymerization between DGEBA and lactones are scarcely studied from the point of view of the kinetics [15,18–20]. As has been previously demonstrated, the copolymerization mechanism is rather complex and in the case of γ-valerolactone a depolymerization process that leads to the appearance of free lactone in the material has also been detected [21]. Moreover, cationic ring-opening polymerizations of cyclic monomers can occur by the activated chain end (ACE) or by the activated monomer (AM) mechanisms and also back-biting processes can take place [22]. All these processes overlap during curing and therefore only a global study of curing can be made. At the same time, physical processes (gelation and vitrification) also take place and can affect not only the curing process but also the physical properties of the material [4]. The progress of the isothermal curing process and the state of the material has been summarized in a TTT diagram.

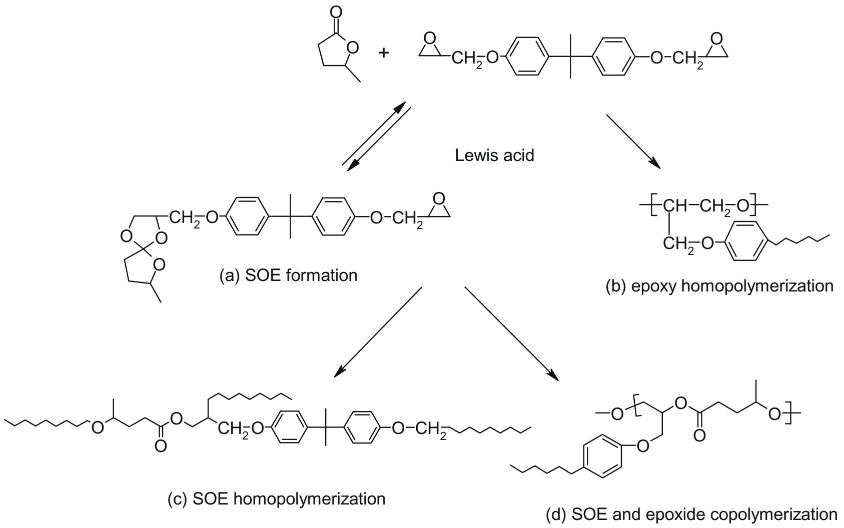
2. Experimental

2.1. Materials

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

γ-Valerolactone (γ-VL) (Aldrich) was used as received.

Lanthanum (III), ytterbium (III) and scandium (III) trifluoromethanesulfonates and borontrifluoride monoethylamine (BF_3·MEA) (Aldrich) were used without purification.



Scheme 1.

Table 1
Calorimetric and thermomechanical data from the systems studied.

Entry	Formulation[a]	Initiator	Prop. init. (phr)	Mols init./ eq. epoxy	T_g[b] (°C)	ΔH[c] (J/g)	ΔH[d] (kJ/ee)	E_a (kJ/mol)	E'_r (MPa)	Tan δ_{max} (°C)
1	DGEBA	$La(OTf)_3$	1	0.003106	127	531	97.6	78.41	9.36	144
2	DGEBA/γ-VL 3:1	$La(OTf)_3$	1	0.003391	105	453	91.0	82.54	7.49	117
3	DGEBA/γ-VL 2:1	$La(OTf)_3$	1	0.003534	95	412	89.4	87.49	6.65	107
4	DGEBA	$Yb(OTf)_3$	1	0.002935	137	526	96.7	85.53	12.20	149
5	DGEBA/γ-VL 3:1	$Yb(OTf)_3$	1	0.003205	100	453	91.1	82.47	11.46	117
6	DGEBA/γ-VL 2:1	$Yb(OTf)_3$	0.5	0.001669	96	442	89	84.13	6.87	104
7	DGEBA/γ-VL 2:1	$Yb(OTf)_3$	1	0.003339	93	430	90.1	85.23	7.40	102
8	DGEBA/γ-VL 2:1	$Yb(OTf)_3$	3	0.010017	82	442	89	71.69	10.96	97
9	DGEBA/γ-VL 1:1	$Yb(OTf)_3$	1	0.003743	65	378	88.8	89.75	4.89	80
10	DGEBA	$Sc(OTf)_3$	1	0.003699	120	521	95.6	75.11	14.65	155
11	DGEBA/γ-VL 3:1	$Sc(OTf)_3$	1	0.004039	93	455	91.4	75.32	10.32	103
12	DGEBA/γ-VL 2:1	$Sc(OTf)_3$	1	0.004208	79	425	89.0	74.09	9.68	96
13	DGEBA/γ-VL 2:1	$BF_3{\cdot}MEA$	3	0.058765	124	360	79.6	116.98	11.18	117

[a] The composition of the formulations are given in molar ratios.
[b] T_gs obtained by DSC in a second scan after dynamic curing.
[c] Enthalpies per gram of mixture.
[d] Enthalpies are expressed by the equivalent of epoxy groups.

2.2. Preparation of the curing mixtures

The samples were prepared by mixing the selected initiator in the corresponding amount of γ-VL and adding the required proportion of DGEBA with manual stirring. The amount of initiator is collected in Table 1 and it is expressed in phr (1 part for 100 parts of lactone/resin mixture, w/w). The prepared mixtures were kept at −18 °C before use.

2.3. Characterization and measurements

2.3.1. 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.

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 and Redfern [23] 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 [24]:

$$\ln\left(\frac{\beta_i}{T^2_{\alpha,i}}\right) = \ln\left[\frac{A_\alpha R}{g(\alpha)E_\alpha}\right] - \frac{E_\alpha}{RT_{\alpha,i}} \tag{3}$$

where β is the heating rate, $g(\alpha)$ is the integral conversion function, the subscript α refers to the value related to a considered conversion, and i to a given heating rate.

For each conversion degree, the linear plot of $\ln(\beta_i/T^2_{\alpha,i})$ versus $1/T_{\alpha,i}$ enables E_α and $\ln[A_\alpha R/g(\alpha)E_\alpha]$ to be determined from the slope and the intercept. These non-isothermal kinetic parameters are directly related for every value of α with the isothermal integral kinetic parameter $\ln[g(\alpha)/A_\alpha]$. So we can simulate isothermal by using non-isothermal data curing without knowing $g(\alpha)$.

The kinetic analysis was carried out using an integral isoconversional method Eq.(3). The basic assumption of this method is that the reaction rate at a given conversion is only a function of the temperature [25,26]. Isoconversional methods make it possible to determine easily the dependence of $E\alpha$ on the degree of conversion in complex processes. Isoconversional STARe software from Mettler-Toledo was used in order to calculate conversion degrees and kinetics of the processes.

2.4. Gelation point determination

The gelation point was determined by solubility tests. Before gelation the material is completely soluble in dichloromethane and once past the gel point the solubility falls steeply. The conversion at the gelation was determined by the residual enthalpy in the DSC of the gelled sample.

2.5. 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

150 °C for 1 h and were then subjected to a post-curing for 5 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.

The linear thermal expansion coefficients in the glassy and rubbery states were measured by thermal mechanical analysis using a Mettler-Toledo TMA40 heating at 10 °C/min as:

$$\alpha = \frac{1}{L_0}\frac{dL}{dT} = \frac{1}{L_0}\frac{dL/dt}{dT/dt} \tag{4}$$

where, L_0 is the initial length. The gel conversion was determined by the residual enthalpy in the DSC of the sample gelled in TMA, as we explain in a previous paper [27].

2.6. Mechanical tests

Microhardness was measured with a Wilson Wolpert (Micro-Knoop 401MAV) device following the ASTM D1494-98(2002) standard procedure. The Knoop microhardness (HKN) was calculated from the following equation:

$$\mathrm{HKN} = \frac{L}{A_p} = \frac{L}{l^2 C_p} \tag{5}$$

where, L is the load applied to the indenter (0.025 kg), A_p is the projected area of indentation in mm^2, l is the measured length of long diagonal of indentation in mm, C_p is the indenter constant (7.028×10^{-2}) relating l^2 to A_p.

Young modulus was measured with the Universal Testing Machine Hounsfield 10-KS. Tensile tests were performed on cylindrical samples of 4 mm of diameter. The gauge length was 50 mm and the test cross-head speed was 5 mm/min.

3. Results and discussion

In a previous work [21] we studied the curing of mixtures of DGEBA/γ-VL 2:1 (mol/mol) initiated by scandium, ytterbium and lanthanum triflates and BF_3·MEA as Lewis acids by FTIR/ATR. When we used 1 phr of scandium triflate or 3 phr of ytterbium triflate as initiator, a depolymerization process was also observed. This process was related to the highest Lewis acidity of these catalysts. The homopolymerization of epoxide on changing the metal triflate was favoured in the order Sc > Yb > La, which is in accordance to the Pearson's hardness [28].The homopolymerization was also favoured when a higher proportion of $Yb(OTf)_3$ was used.

In the present work we studied the evolution of the curing process on changing the initiator and its proportion and the co-monomers ratio in the mixture. Previously, [29,30] we observed that the higher the Lewis acidity of the lanthanide triflates (from lanthanum to ytterbium) the higher the curing rate was. The BF_3 complex need to be used in a higher proportion to reach the total curing and the materials obtained showed a higher T_g, which seems to indicate that the curing process present some differences.

In many exothermic polymerizations is difficult an accurate determination of the heat of reaction through isothermal experiments and the subsequent deduction of the kinetics from these values. When reactions are performed at high temperatures, some of the heat can be lost during the stabilization of the apparatus, whereas at low temperatures, the heat is released slowly and can fall below the sensitivity of the calorimeter. Another problem arises when a physical phenomenon (e.g. vitrification) takes place. One alternative in both cases is to simulate isothermal curing from non-isothermal data [31]. Thus, in this work we used the non-isothermal differential scanning calorimetry experiments at a controlled heating rate as the most suitable procedure for obtaining kinetic information of the reactive systems.

Fig. 1 shows the calorimetric curves of the curing process for the formulation DGEBA/γ-VL 2:1 (mol/mol) with the four initiators tested. As we can see, the curves of the scandium and ytterbium triflates initiated curing show a main maximum and a shoulder, greater for scandium. The contribution of this shoulder to the total enthalpy re-

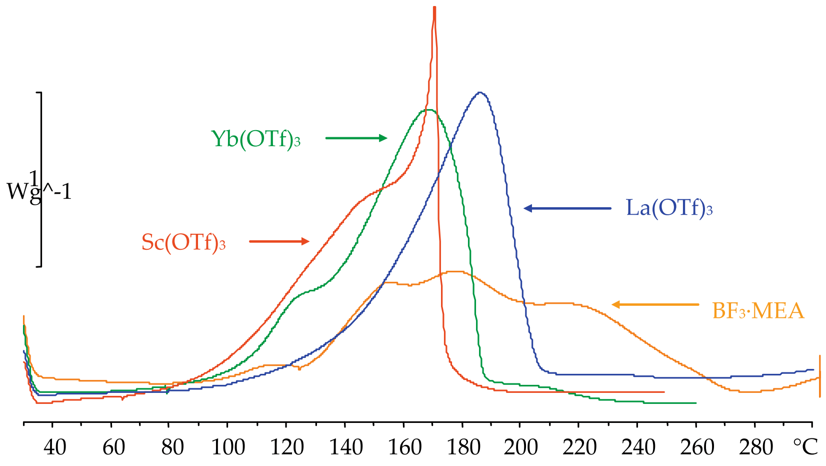
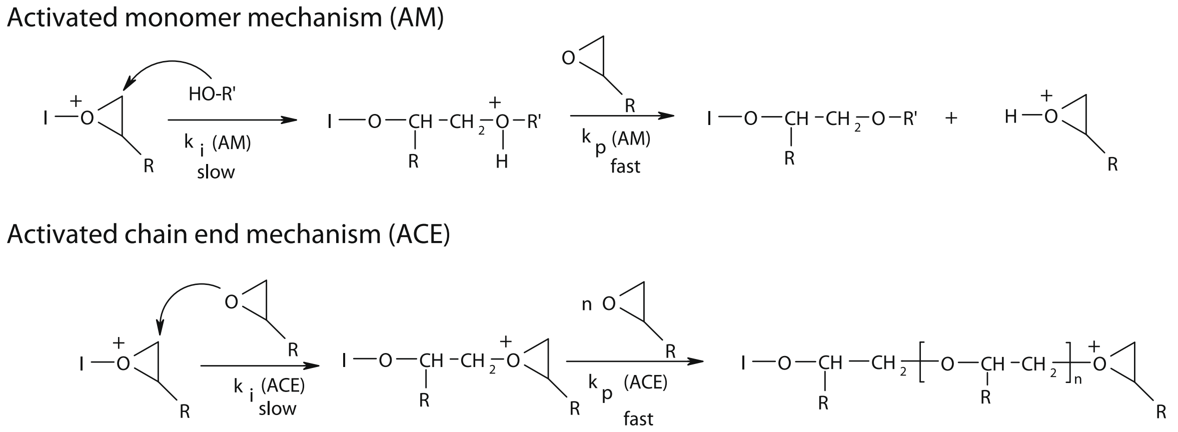


Fig. 1. DSC scanning curves versus temperature of curing obtained through dynamic DSC experiments of DGEBA/lactone 2:1 (mol/mol) mixture initiated by 1 phr of Sc, Yb and La triflates and BF3·MEA at a heating rate of 10 °C/min.

leased can be related to the extension of the homopolymerization of epoxide, as we previously saw by FTIR spectroscopy [21].

In a previous work [20] on the curing of DGEBA/γ-butyrolactone (γ-BL) mixtures with ytterbium triflate we saw the appearance of two partially overlapped exotherms that change in shape depending on the competition between two propagation mechanisms related to the epoxy homopolymerization: monomer activated mechanism (AM) and activated chain end mechanism (ACE) and the exotherm at lower temperature could be assigned to the AM contribution (see Scheme 2). In that paper we could prove that the higher the acidity of the polymerization medium the higher the contribution of the AM mechanism. Thus, the pattern of the curves in Fig. 1 seems to indicate a greater contribution of AM mechanism when we move from the lanthanum to scandium. AM mechanism requires the activation of epoxy monomer by the initiator and therefore the oxophilicity (related to Lewis acidity) of Sc, Yb and La, which are 2.37, 2.09 and 1.36, respectively [32], can justify the behavior observed. Fig. 1 also shows the curve corresponding to the BF_3·MEA initiated curing. For this initiator, the exotherm is very broad with final curing temperatures as high as 280 °C and the curing could overlap with the beginning of the degradation. The complex pattern can be attributed to the formation of the reactive species and to a complex reaction mechanism [33]. In Fig. 2 the influence of the proportion of ytterbium triflate on the shape of the calorimetric curves is shown. As the proportion increases the curves shift to lower temperatures and the shoulder rises, due to the higher contribution of the AM mechanism, as we described for similar DGEBA/γ-BL systems [20].

Thermal data obtained from non-isothermal DSC for the curing of the samples studied are collected in Table 1. As can be seen, the T_g of the materials decrease on increasing the proportion of lactone in the mixture as expected from the flexibility introduced by its aliphatic structure. On



Scheme 2.

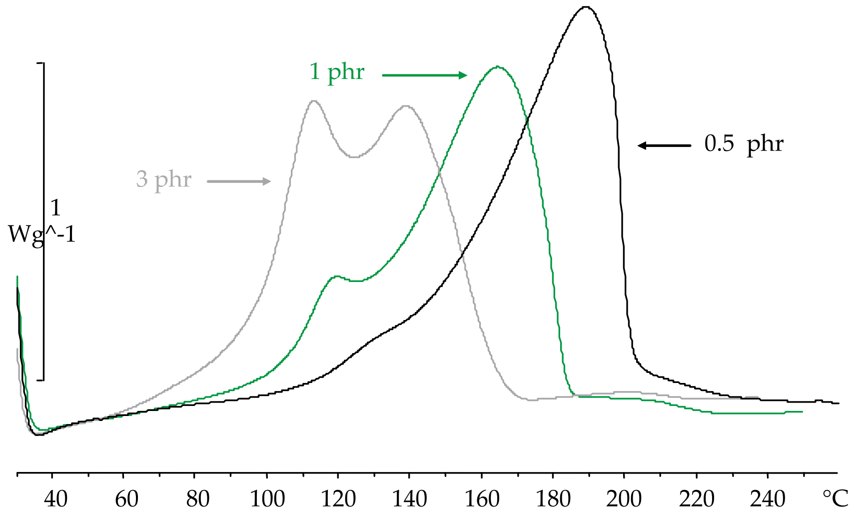


Fig. 2. DSC scanning curves versus temperature of curing obtained through dynamic DSC experiments of DGEBA/lactone 2:1 (mol/mol) mixture initiated by 0.5, 1 and 3 phr of $Yb(OTf)_3$ at a heating rate of 10 °C/min.

increasing the proportion of initiator a diminution of the T_g is observed confirming the coexistence of the AM mechanism that leads to chain transfer reactions, which produces a higher proportion of hydroxylic dangling chains and therefore to a higher segmental mobility. However, dangling chains have a smaller plasticizing effect in networks than in linear polymers, because the free volume effect of the chain ends is counterbalanced by some physical crosslinking role of the branching point [34]. Among the initiators tested, BF_3 complex leads to materials with the highest T_g value.

The total enthalpy per gram strongly decreases as the proportion of γ-VL increases. If we look at the enthalpy released per epoxy equivalent we can see a significant diminution on adding lactone, but on increasing its proportion only a low further diminution of the enthalpy can be observed. We should take into account that the heat released is mainly due to the opening of the strained epoxy ring. If we consider the heat evolved during curing for the DGEBA/γ-VL mixtures cured with the different metal triflates, we observed no great differences, indicating that the proportion of epoxide reacted is similar. The initiation with the boron trifluoride complex leads to a lower enthalpy release and a greater proportion (3 phr) of this initiator was necessary to reach the complete curing. The fact that this material has the highest T_g seems to be contradictory with the lower enthalpy released. The broadness of the exotherm and the high temperature reached should be the responsible of this unexpected result, which could be related to the occurrence of an endothermic process, as the evaporation of the lactone, which was proved by weighing the DSC pans after curing. This was also observed by FTIR experiments, which practically did not show any linear ester band in the materials obtained with BF_3 complex [21].

Although the change of the metal triflate or its proportion did not affect the total enthalpy released, the temperature of the maximum of the exotherm was influenced due to their different catalytic activity. The addition of lactone reduces this temperature, which indicates an accelerative effect of the lactone, as we proved for other DGEBA/lactone systems [29]. Fig. 3 shows the variation of the conversion degree against temperature of the DGEBA/γ-VL 2:1 (mol/mol) formulation with all the initiators tested, where we can see that scandium triflate leads to the highest conversion for a prefixed temperature. The conversion evolution of the curing with $BF_3 \cdot MEA$ is quite different, especially after a 30% of conversion, when the evolution become much slower. Moreover, higher temperatures are needed to reach the complete curing with this initiator.

The accelerative effect of the proportion of ytterbium triflate can be observed in Fig. 4. The curves of 0.5 and 1 phr of initiator show similar shapes, whereas the corresponding to 3 phr seems to reflect the coexistence of a competitive mechanism. As can be seen, much higher conversions are reached at lower temperatures when the proportion of the initiator increases, e.g. for 150 °C, the curing with 3 phr is practically complete, whereas with 0.5 phr is less than 20%.

In Fig. 5 we can see the effect of adding different proportions of lactone to DGEBA. The conversions increase with the proportion of γ-VL, although very little differences are observed at the highest proportion of lactone. The accelerative effect can be attributed to the formation of more reactive species as we saw in a similar system [29] but also to the lower viscosity of the mixture, which facilitates the reaction.

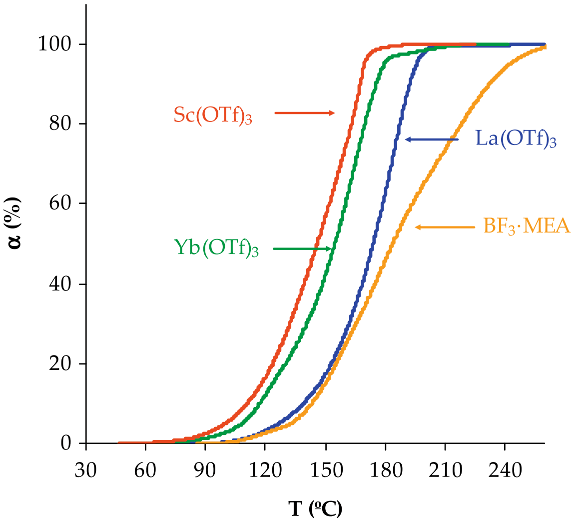


Fig. 3. Conversion curves versus temperature of curing obtained through dynamic DSC experiments of DGEBA/lactone 2:1 (mol/mol) mixture initiated by Sc, Yb and La triflates and $BF_3 \cdot MEA$ at a heating rate of 10 °C/min.

By the isoconversional method we calculated the evolution of the activation energy along the curing process. From the calorimetric curves at different heating rates and applying the Eq. (3), we obtained the activation energy for each degree of conversion in all the formulations studied. Fig. 6 shows the plot of the apparent activation energy against the degree of conversion for the DGEBA/γ-VL 2:1

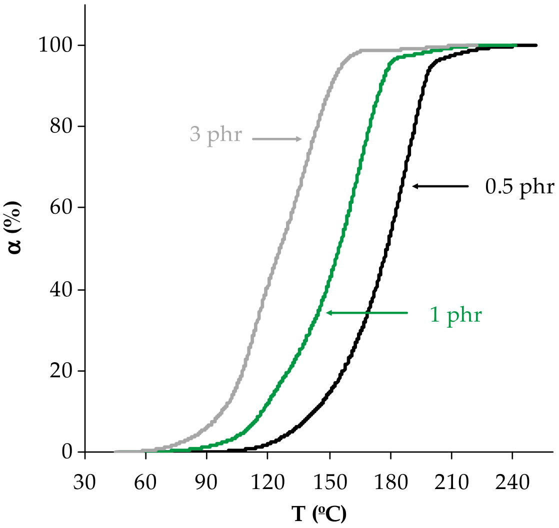


Fig. 4. Conversion curves versus temperature of curing obtained through dynamic DSC experiments of DGEBA/lactone 2:1 (mol/mol) mixture initiated by 0.5, 1 and 3 phr of $Yb(OTf)_3$ at a heating rate of 10 °C/min.

(mol/mol) formulation with the four initiators. The main difference is observed in boron trifluoride, which leads to the highest activation energy in all the range, due to the formation of the true active initiating specie, HBF_4. Among metal triflates, the differences are not as high. In the initial steps of the curing, activation energies follow the trend Sc < Yb < La < BF_3, related to the Pearson's theory hardness [28] and agree with the conversion evolutions represented in Fig. 3. $La(OTf)_3$ shows a practically constant activation energy, which can be associated to an ACE propagation mechanism during all the curing process. On increasing the Lewis acidity of the metal triflate, the AM mechanism contributes in a higher extent. With scandium and ytterbium, especially with the former, the curing begins through the AM mechanism, which has lower activation energy, and then progressively the ACE mechanism, with higher activation energy, becomes more important. Thus, the activation energy during curing steadily increase until it reaches a similar value to the lanthanum, for both scandium and ytterbium triflates.

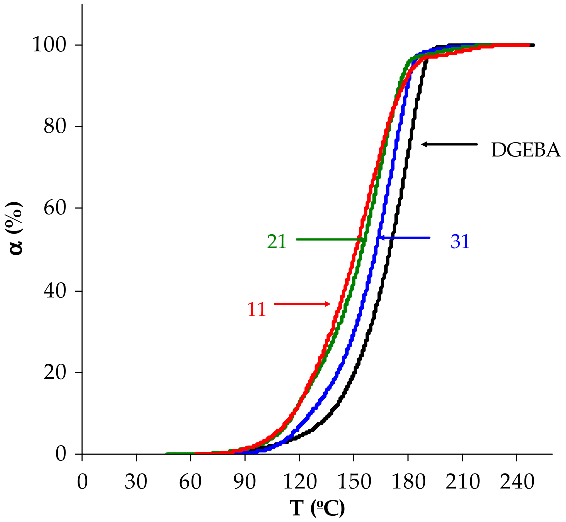


Fig. 5. Conversion curves versus temperature of curing obtained through dynamic DSC experiments from pure DGEBA and mixtures DGEBA/lactone in different proportions initiated by 1 phr of $Yb(OTf)_3$ at a heating rate of 10 °C/min.

The values of the activation energies calculated at 50% of conversion, collected in Table 1, do not show any regular trend, but scandium leads to the lowest value and boron trifluoride complex to the highest.

A useful framework for understanding and conceptualizing the changes that occur during curing of a thermosetting system is the isothermal time-temperature-transformation (TTT) diagram. Such a diagram displays the states of the material and characterizes the 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. Relevant contours could include molecular gelation, corresponding to the unique conversion at the molecular gel-point and vitrification, corresponding to the glass transition temperature. The basic parameter governing the state of the material is the chemical conversion. Therefore, the knowledge of how the rate changes with cure temperature is important and useful 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 reactants, ${}_{gel}T_g$, the temperature at which molecular gelation and vitrification coincide, and T_g^∞, the glass transition temperature of the fully cured material. Fig. 7 shows the TTT cure diagram of a DGEBA/γ-VL 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) in a selected curing temperature. This diagram was constructed using the experimental data determined previously (the isoconversional lines, the T_g-α relationship,

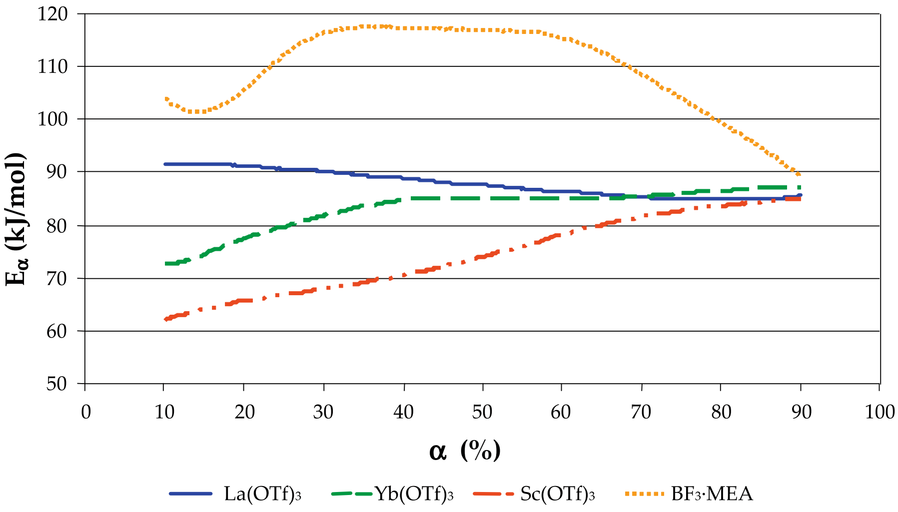


Fig. 6. Dependence of the activation energy on the degree of conversion for DGEBA/lactone 2:1 (mol/mol) mixture initiated by 1 phr Sc, Yb and La triflates and BF_3·MEA.

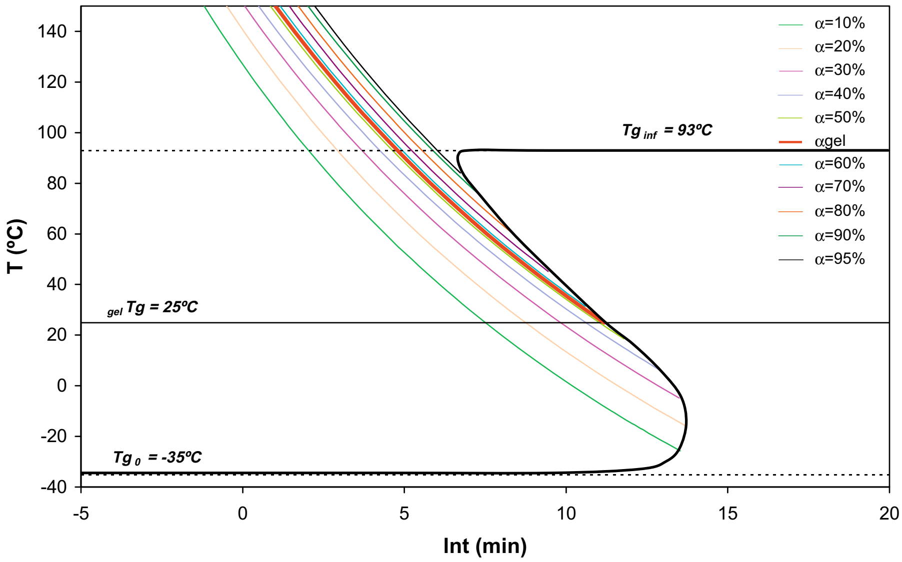


Fig. 7. TTT diagram for the curing of the mixture DGEBA/γ-VL 2:1 (mol/mol) initiated by 1 phr of Yb(OTf)3. Vitrification curve (▬), gelification curve (▬). Isoconversional lines, T_g^0, T_g^∞ and $_{\mathrm{gel}}T_g$ are also indicated.

the conversion at gelation, the T_g^0 and the T_g^∞) following the methodology previously reported [35].

The TTT diagram has a shape similar to other obtained by curing epoxy resins [36,37] and shows a value of 25 °C for the lowest temperature at which the material gels before vitrification ($_{\mathrm{gel}}T_g$), a value for T_g^0 of −35 °C, below which the material does not crosslink at all, and a value for T_g^∞ of 93 °C, which is the lowest temperature at which complete curing can be achieved. If we compare this TTT diagram with the diagram of the pure DGEBA cured with ytterbium triflate (T_g^∞ = 137 °C) [35] we can see that the addition of γ-VL makes it possible to reduce the curing temperature and consequently the thermal stresses. Moreover, performing the curing at low temperature implies an important energy saving.

Fig. 8 shows the mechanical relaxation spectra at 1 Hz and tan δ for the materials obtained from DGEBA/γ-VL 2:1 mol/mol formulations with all the initiators tested. The values of the modulus in the rubbery state and the tan δ are collected in Table 1. The practically unimodal shape of the curves of tan δ reflects the homogeneity of these materials. The relaxed modulus notably depends on

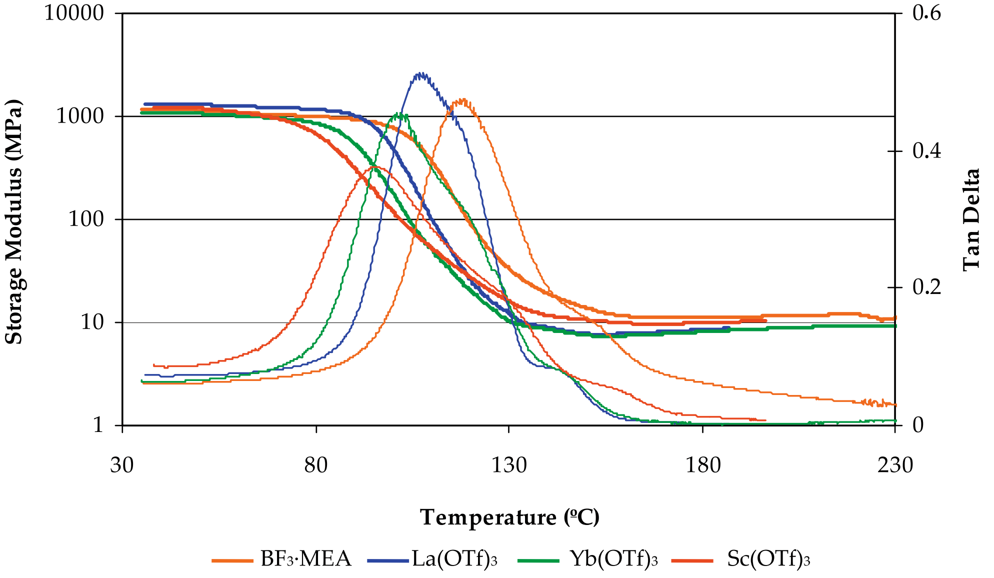


Fig. 8. Storage modulus and loss tangent (Tan δ) versus temperature obtained by DMTA for the materials prepared from DGEBA/γ-VL 2:1 (mol/mol) formulation initiated by all the initiators tested.

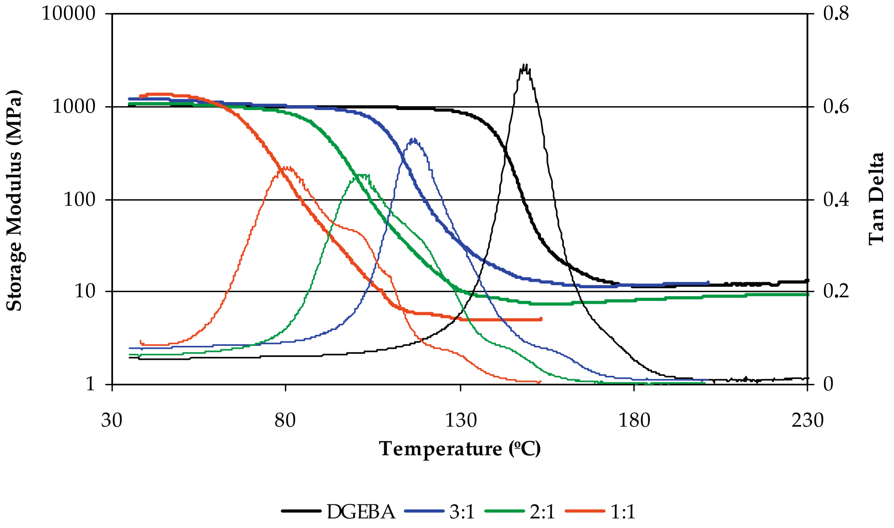


Fig. 9. Storage modulus and loss tangent (Tan δ) versus temperature obtained by DMTA for the materials prepared from pure DGEBA and DGEBA/γ-VL formulations initiated by 1 phr of Yb(OTf)$_3$.

the initiator used and increases in the order La(OTf)$_3$ < Yb(OTf)$_3$ < Sc(OTf)$_3$ < BF$_3$·MEA. Moreover, there is a difference in the broadness of the relaxation of these materials, being the broadest that of Sc(OTf)$_3$. The value of tan δ does not follow the above trend for materials obtained with rare earth triflates. However, the highest also corresponds to the material obtained with BF$_3$·MEA. These differences are based in two characteristics of the materials: the crosslinking density achieved, which is the highest for the boron complex, and the chemical structure of the network that in turn depends on the initiator used. We showed in a previous paper [21] that the scandium salt induced a depolymerization process, which led to the presence of a great proportion of free lactone in the material that can act as a plasticizer, reducing the tan δ value. A similar behaviour was observed when the proportion of Yb(OTf)$_3$ was varied (entries 6–8 in Table 1). On increasing the proportion of initiator tan δ decreases whereas the relaxed modulus increases. A high proportion of initiator leads to a more densely crosslinked material because the depolymerization process allows a higher epoxide homopolymerization, but this process also leads to the formation of free lactone that remains entrapped in the network.

When the proportion of lactone increases both tan δ and relaxed modulus decreases. Fig. 9 shows the thermomechanical curves for ytterbium initiated materials. When the proportion of lactone increases the materials seems to be less homogeneous. However, the materials are more homogeneous than those obtained from DGEBA/γ-caprolactone mixtures studied previously by us [17], which showed bimodal tan δ curves.

The expansion of materials is characterized by the volumetric or lineal expansion coefficient, being the last one the most important in coatings applications. Polymers expand more than metals and ceramics and their linear thermal expansion coefficient is in the range of 20–100 ppm/°C [38]. The high value of the thermal expansion coefficient (CTE) of polymers is caused by the low energy barrier for the chain conformation changes. Crosslinking decreases the thermal expansion coefficient whereas the introduction of aliphatic chains between crosslinks increases it. For these reasons, it could be of interest to evaluate how the thermal expansion coefficisent varies when different proportions of lactone are copolymerized with epoxy resins. Table 2 collects the CTE values determined in the glassy and rubbery state for the samples obtained from mixtures of DGEBA with different proportions of γ-VL initiated by 1 phr of Yb(OTf)$_3$. To compare the values, CTEs of pure DGEBA are also included. The T_gs collected in this table were determined by TMA, calculated as the cross of the tangents, and therefore they are slightly different from those determined by DSC and DMTA. As it was expected, on increasing the proportion of lactone in the mixtures, CTE values increase, but all these values lie in the usual range described for epoxy resins.

Microhardness measurements are very useful in rating coatings on rigid substrates for their resistance to mechanical abuse, such as that produced by blows, gouging and scratching. These measurements do not necessarily characterize the resistance to mechanical abuse of coatings that are required to remaining intact when deformed. This technique is used in the industry to characterize the mechanical properties related to resistance and hardness of materials and it measures their capability to resist static loads or applied at low rates. Fig. 10 collects the values

Table 2

T_g values and thermal expansion coefficients in the glassy and rubbery status from materials obtained for different DGEBA/γ-VL formulations initiated by 1 phr of Yb(OTf)$_3$ determined by TMA.

Formulation (mol/mol)	T_g (°C)	$\alpha_{glass} \times 10^6$ (K^{-1})	$\alpha_{rubber} \times 10^6$ (K^{-1})
DGEBA	137	54	182
DGEBA/γ-VL 3:1	107	60	193
DGEBA/γ-VL 2:1	90	67	202
DGEBA/γ-VL 1:1	73	74	246

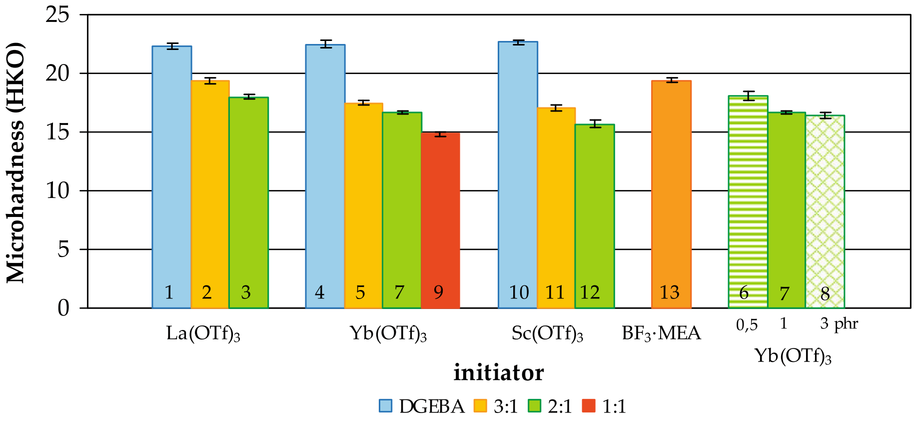


Fig. 10. Knoop microhardness values in front of the composition for all the materials prepared. Numbers in the bars corresponds to the entries in Table 1. The colours indicate the composition of the initial mixtures.

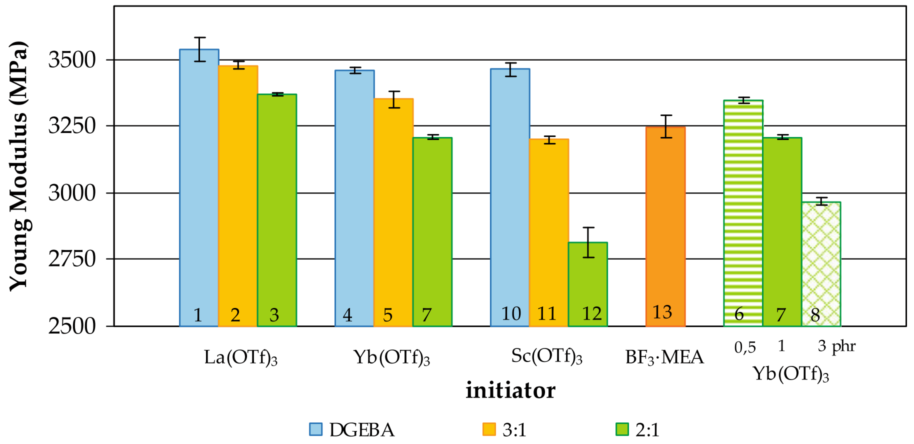


Fig. 11. Young modulus in front of the composition for all the materials prepared. Numbers in the bars corresponds to the entries in Table 1. The colours indicate the composition of the initial mixture.

obtained for all the materials prepared with the calculated precision, taken into account that we made six determinations for each material with a confidence level of 95%. As we can see, the addition of lactone slightly reduces the microhardness in reference to pure cured DGEBA with all the cationic initiators tested and this reduction is more evident when the proportion of lactone increases. In general, a higher flexibility of the network is reflected in a lower microhardness value. In case of pure epoxy resin the change in the metal triflates scarcely influences the microhardness. BF_3·MEA leads to the highest value when comparing all the materials obtained from DGEBA/γ-VL 2:1 mixtures. Among triflates, lanthanum led to the harder materials for all the composition studied. The highest the proportion of initiator the lowest the microhardness for the same composition is (samples 6, 7 and 8), which can be related to the extension of the depolymerization process.

Fig. 11 represents the values of Young modulus for all the materials prepared. For these measurements we also made six determinations for each material with a confidence level of 95%. In general, the addition of lactone decreases this value. The addition of lactone to scandium triflate produces a greater variation, which can be attributed to the depolymerization process, more significant for this initiator. On increasing the proportion of ytterbium triflate as initiator the modulus also decrease, due to two different facts: the higher chemical incorporation of lactone in the network on increasing the initiator proportion and the depolymerization process that becomes evident when the proportion used is 3 phr [21].

4. Conclusions

The addition of γ-VL to the DGEBA accelerates the cationic curing and reduces the T_g of the materials obtained. Rare earth triflates are more active than BF_3·MEA as initiators and their activity increases from lanthanum to scandium. Moreover, the higher the acidity of the polymerization medium the higher is the contribution of the AM mechanism. As the proportion of initiator increases the curves shift to lower temperatures and the contribution of AM mechanism becomes more important.

The relaxed modulus of the materials obtained depends on the initiator used and increases in the order $La(OTf)_3 < Yb(OTf)_3 < Sc(OTf)_3 < BF_3{\cdot}MEA$. The materials obtained showed a practically unimodal tan δ, reflecting their homogeneous character.

The thermal expansion coefficient increase on adding lactone to DGEBA, but all the values lie in the usual range described for conventional epoxy resins.

The addition of lactone slightly reduces the microhardness and the Young modulus in reference to pure cured DGEBA. On increasing the proportion of initiator used both parameters slightly decrease.

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