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New thermosets obtained by copolymerization of DGEBA with 1,5,7,11-tetraoxaspiro[5,5]undecane catalyzed by lanthanide triflates

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Abstract

DGEBA epoxy resin was cured with different proportions of 1,5,7,11-tetraoxaspiro[5,5]undecane (TOSU) with ytterbium and lanthanum triflates as catalysts. The curing was studied by differential scanning calorimetry (DSC) and Fourier transform infrared in the attenuated-total-reflexion mode (FTIR/ATR).

FITR/ATR was used to monitor the competitive reactive processes and to quantify the evolution of the epoxide, orthocarbonate, linear carbonate and other groups formed in the curing process. The T_g of the cured materials decreased when the proportion of TOSU increased. The kinetics were studied by DSC experiments and analyzed with iso-conversional procedures. The systems catalyzed by ytterbium triflate had a higher curing rate and reached a higher degree of cross-linking. The addition of TOSU reduced the degree of overall shrinkage and even led to one material expanding. The flexibility and the degradability of these materials were improved by introducing higher proportions of TOSU.

Keywords: Epoxy resins; Shrinkage; Carbonates

1. Introduction

Epoxy resins can be cross-linked with Lewis acids as curing agents generally leading to highly cross-linked thermosets that are brittle. Various approaches have been used to improve such mechanical properties of epoxy thermosets as impact resistance, elasticity and toughness. One of these approaches is modification with reactive liquid rubber [1] or silicone rubbers [2]. Another drawback of epoxy resins is the shrinkage that takes place during curing, which introduces stress, produces microvoids and microcracks, and reduces adhesion to the substrate [3]. The premature failure of polymer-based composites is usually caused by poor adhesion between the filler and the matrix or from voids and cracks caused by polymerization shrinkage. One way to produce low-shrinkage/low-stress materials is to incorporate spiro-ortho carbonates, spiro-ortho esters and other strained bicyclic monomers [4,5].

Spiroortho carbonates (SOCs) are a type of monomers that expand during polymerization [6,7]. In 1973, Sakai et al. [8] first studied the cationic ring-opening polymerization of SOCs with different sized rings. The polymerization behavior of SOC clearly depends on the number of members in the ring. Thus, five-membered SOCs lead to polyether and poly(ether-carbonate) with partial loss of the corresponding five-membered cyclic carbonate. Moreover, the seven-membered SOCs generally lead to polycarbonate with complete elimination of tetrahydrofuran. One exception to this is benzene ring fused SOCs, which lead to the corresponding poly(ether-carbonate) by polymerization without eliminating a tetrahydrofuran derivative and show a 6.6% expansion in volume [9,10]. For these reasons the expansion in volume on the cationic ring-opening polymerization is limited to six-membered SOCs as they polymerize effectively to give poly(ethercarbonate) [8–10]. Some reports describe the possibility of copolymerizing epoxy compounds and six-membered SOCs by mixing and reacting them with BF_3 complexes in an attempt to control the volume shrinkage [11,12].

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In previous papers [13,14] we have studied the chemical incorporation of γ-butyrolactone (γ-BL) into epoxy networks by copolymerization. This lactone does not homopolymerize but reacts with oxirane groups to form spiro-orthoesters (SOEs) that are also expandable monomers when they polymerize. In these studies we proved that the shrinkage after gelation, where the stress is originated, was reduced.

The present paper deals with the use of a six-membered cycloaliphatic spiroortho carbonate (1,5,7,11-tetraoxaspiro[5,5]undecane, TOSU) for chemically modifying epoxy networks promoted by Lewis acid initiators such as lanthanide triflates. Recently, copolymerization between oxiranes and TOSU (using boron trifluoride monoethylamine and elevated temperature) was shown to have zero shrinkage [15].

Lanthanum and ytterbium triflates have been proved to be excellent Lewis acid initiators, stable in water and environmentally friendly [16], capable of cross-linking epoxy resins alone [17] or as mixtures with lactones [13,14]. For these reasons, these initiators have been selected here.

2. Experimental part

2.1. Materials

Diglycidylether of bisphenol A (DGEBA) EPIKOTE RESIN 828 from Shell Chemicals was used as received. The epoxy equivalent (187 g/equiv) was determined by the Dahmen and Dijstra method [18]. 1,5,7,11-tetraoxaspiro [5,5]undecane (TOSU) was prepared according to the reported method [19]. Mp = 131–135 °C, yield = 65%. ^{1}H MNR ($CDCl_3$/TMS, δ (ppm)): 4.0 (t, CH_2, 8H), 1.7 (m, CH_2, 4H). ^{13}C-NRM ($CDCl_3$/TMS, δ (ppm)): 114.2 (C), 62.5 (CH_2), 23.9 (CH_2). IR (KBr cm^{-1}): 1482, 1460, 1378, 1205, 1139, 1047, 846.

Lanthanum (III) and ytterbium (III) trifluoromethanesulfonates (Aldrich) were used without purification. The solvents were purified by standard methods.

2.2. Preparation of the curing mixtures

The samples were prepared by mixing the selected lanthanide triflate in the corresponding amount of TOSU and adding the required proportion of DGEBA with stirring. All the mixtures contained 1 pph of lanthanide triflate (1 part per 100 parts of mixture, w/w). The prepared mixtures were kept at −18 °C before they were used.

2.3. 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. The calorimeter was calibrated using an indium standard (heat flow calibration) and an indium–lead–zinc standard (temperature calibration). The samples weighed approximately 5 mg. In the dynamic curing process the degree of conversion by DSC (α_{DSC}) was calculated as follows:

$$\alpha_{DSC} = \frac{\Delta H_T}{\Delta H_{dyn}} \quad (1)$$

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_g's) 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.

Thermogravimetric analyses (TGAs) were carried out with a Mettler TGA/SDTA 851e thermobalance. Cured samples with an approximate mass of 5 mg were degraded between 30 and 600 °C at a heating rate of 10 °C/min in N_2 (200 cm^3/min measured in normal conditions).

The densities were determined before curing by the standard procedure of filling a pycnometer with liquid monomers without catalyst, in order to prevent polymerization, in a thermostated bath at 30 °C. The densities of the cured samples were determined by the weighed solid sample being placed in the pycnometer and water being added. The weight difference of the pycnometer filled only with water and the pycnometer containing the sample of the cured polymer enabled the volume of the sample and, therefore, the density of the cured material to be determined.

Thermomechanical analysis was carried out in a nitrogen atmosphere with a Mettler–Toledo TMA40 analyzer. The shrinkage ($\Delta L = L_t - L_0$) undergone by the resin during curing was measured by applying a force of 0.01 N. The mixtures, impregnated in a silanized fiberglass support, were placed between two Al_2O_3 discs. Isothermal curing was carried out several times at temperatures between 110 and 150 °C. The degree of shrinkage in TMA was calculated as follows [20]:

$$\alpha_{TMA} = \frac{L_t - L_0}{L_\infty - L_0} \quad (2)$$

where L_0, L_t and L_∞ are the values of the thickness of the sample at the onset, at time t and on the completion of the reactive process, when the material is fully cured, respectively.

The isothermal curing process at 140 °C was monitored with a Bomem Michelson MB 100 FTIR spectrophotometer with a resolution of 4 cm^{-1} in the absorbance mode. An attenuated-total-reflection (ATR) accessory with thermal control and a diamond crystal (golden gate heated single-reflection diamond ATR, Specac–Teknokroma) was used to determine FTIR spectra. After isothermal curing by means of FTIR, a dynamic scan by DSC was always carried out.

The thermal–dynamic–mechanical analysis was carried out with a TA Instruments DMTA 2980 analyzer. The samples were cured isothermally in a mould at 150 °C for 5 h and were then subjected to a post-curing for 2 h at 170 °C. Three point bending of 10 mm was performed on prismatic rectangular samples ($10\times5\times1.3\ \mathrm{mm}^3$, approximately). The apparatus operated dynamically, at 5 °C/min, from 35 to 200 °C. The frequency of application of the force was 1 Hz.

2.4. Kinetic analysis

Integral non-isothermal kinetic analysis was used to determine the kinetic triplet (A pre-exponential factor, E activation energy and $g(\alpha)$ integral function of degree of conversion).

Non-isothermal kinetic analysis may start with the kinetic equation:

$$\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T} = A\exp\left(\frac{-E}{RT}\right)f(\alpha) \tag{3}$$

where β is the heating rate, α is the conversion, R is the universal gas constant, T is the temperature and $f(\alpha)$ is the differential conversion function.

By using the Coats–Redfern [21] approximation to resolve the so-called temperature integral and considering that $2RT/E \ll 1$ may be written:

$$\ln\frac{\beta}{T^2} = \ln\left[\frac{AR}{g(\alpha)E}\right] - \frac{E}{RT} \tag{4}$$

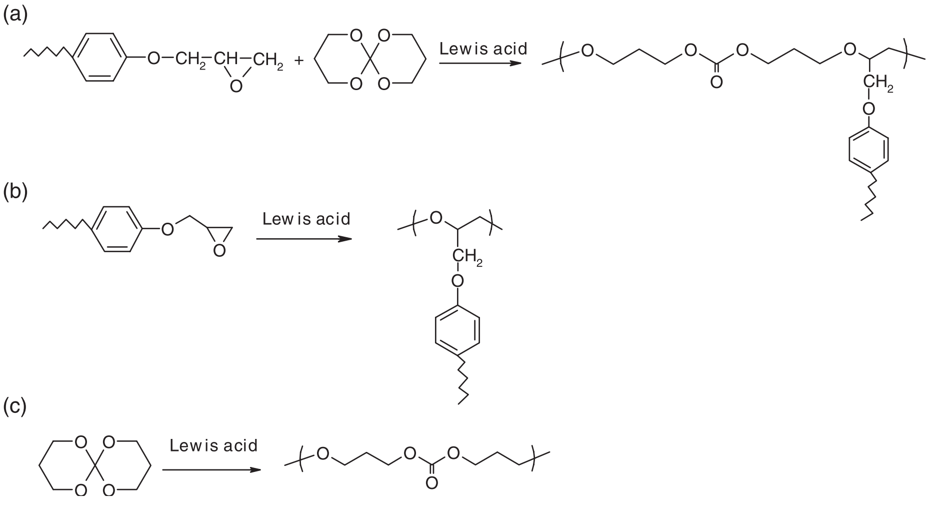
For each conversion degree, linear representation of $\ln[\beta/T^2]$ versus T^{-1} enables E and $\ln[AR/g(\alpha)E]$ to be determined from the slope and the ordinate in the origin, respectively. Eq. (4) can be applied at the peak (maximum reaction rate) if the degree of conversion in the peak does not vary with the heating rate. This iso-conversional procedure is similar to Kissinger's method [22]. If the reaction model, $g(\alpha)$, is known, for each conversion it is possible to calculate the corresponding pre-exponential factor for every activation energy. In this paper, in order to assign a reaction model to the systems studied, we used Criado's reduced master curves procedure [23], which is described elsewhere [24]. Various kinetic models have been studied: diffusion (D_1, D_2, D_3 and D_4), Avrami–Erofeev (A_2, A_3 and A_4), power law, phase-boundary-controlled reaction (R_2 and R_3), autocatalytic ($n+m=2$ and 3) and n order ($n=1$–3) [24]. We found that all the systems studied follow a kinetic model of the surface-controlled reaction type, R_3, with $g(\alpha)=[1-(1-\alpha)^{1/3}]$. The rate constant, k was calculated with E and A determined at $\alpha=0.5$, using the Arrhenius equation.

3. Results and discussion

Taking into account the facts we mentioned in Section 1, we studied the cationic curing process of mixtures of DGEBA epoxy resins with TOSU in different proportions using lanthanum and ytterbium triflates as catalysts.

Scheme 1 shows the individual reactions expected in the global curing process for diglycidylic resins with TOSU. The first reaction, (a) shows the copolymerization of both monomers, which leads to aliphatic polyether and poly(ether-carbonate) chains; the second, (b) is the homopolymerization of DGEBA, which leads to aliphatic poly(ether) chains; and the third (c) is the homopolymerization of TOSU, which leads to linear aliphatic poly(ether-carbonate) chains.

Table 1 shows some calorimetric results of the curing process of DGEBA/TOSU mixtures catalyzed by lanthanum and ytterbium triflates. As can be seen, when the proportion of TOSU is increased, the T_g value of the cured material decreases, as is described in the literature on related systems [11]. Moreover, the maximum of the exotherm decreases as the proportion of TOSU increases, indicating that the



Scheme 1.

Table 1
Calorimetric data and kinetic parameters of the systems studied catalyzed by 1 pph of lanthanide triflate

Entry	Formulations[a]	Lanthanide	mol catalyst/ eq. epoxide	T_g (°C)	T_{max} (°C)	Δh[b] (kJ/ee)	E_a[c] (kJ/mol)	ln A[d] (s^{-1})	$k\times10^{3}$[e] (s^{-1})
1	DGEBA	Yb	0.0030	130	183	103	81.8	15.71	0.30
2	DGEBA/TOSU 3:1	Yb	0.0034	93	171	101	72.9	13.97	0.71
3	DGEBA/TOSU 2:1	Yb	0.0037	73	168	105	53.5	8.76	1.10
4	DGEBA/TOSU 1:1	Yb	0.0043	38	146	117	57.1	10.22	1.64
5	DGEBA	La	0.0032	127	192	104	80.3	14.73	0.18
6	DGEBA/TOSU 3:1	La	0.0036	99	194	96	57.0	8.35	0.26
7	DGEBA/TOSU 2:1	La	0.0039	80	187	99	51.5	7.17	0.39
8	DGEBA/TOSU 1:1	La	0.0042	45	177	110	56.0	8.70	0.49

[a] The compositions of the formulations are given in molar ratios.
[b] Enthalpies are expressed by equivalent of epoxy groups.
[c] Values of activation energies were evaluated by isoconversional integral method applied at conversion of 0.5.
[d] The values of pre-exponential factor for model R3 and $g(\alpha)=1-(1-\alpha)^{-1/3}$.
[e] The values of rate constant at 140 °C calculated using the Arrhenius equation $\ln k=\ln A-(E/RT)$.

addition of TOSU facilitates the curing process, probably due to the mobility introduced into the network structure because of the linear aliphatic character of the moiety introduced. The enthalpy released per epoxy equivalent for mixtures containing TOSU increases as the proportion of this co-monomer increases. Thus, at the highest proportion of TOSU, the heat evolved is higher than for the homopolymerization of DGEBA. It should be taken into account that the experimental measurement of enthalpy includes the polymerization of epoxy and TOSU and a series of equilibrium reactions that are affected both by enthalpy and entropy. As we are measuring only the enthalpy by DSC we have no information about the entropic term. Therefore, for equilibrium reactions the enthalpic term should not be necessarily negative.

When we used ytterbium triflate a reduction of the enthalpy released on adding a little proportion of TOSU was also observed and then the enthalpy increases when we added a higher proportion of TOSU, which implies a similar trend than the observed for the lanthanum salt. However, because the individual reactions have different contributions to the global process there are some differences in the enthalpic contribution for both catalysts. In all cases we confirmed that the epoxy reacted completely and the process reached the maximum curing.

The kinetic effect of lanthanum and ytterbium triflates on the curing was dynamically studied by DSC. Fig. 1 shows the plot of conversions against temperature for DGEBA and mixtures with different proportions of TOSU in the curing catalyzed by 1 pph of lanthanum triflate. As we can see, the addition of TOSU increases the conversion at a selected temperature. Results were similar when we used ytterbium triflate. So the addition of TOSU accelerates the curing process. Table 1 shows the kinetic parameters obtained from the calorimetric curves for the different formulations studied. The apparent activation energies associated to the simultaneous reactive processes were calculated by an isoconversional integral method at a conversion of 0.5 and the pre-exponential factors for the R3 kinetic model. From both parameters, we calculated the rate constants by the Arrhenius equation. As we can see in Table 1, the addition of TOSU increases the rate constant, especially for the ytterbium salt. As has been proved in previous work [14,25], the higher the Lewis acidity is, the higher the reaction rate.

In order to monitor the evolution of the various reactive processes in the overall curing, when the initiator was

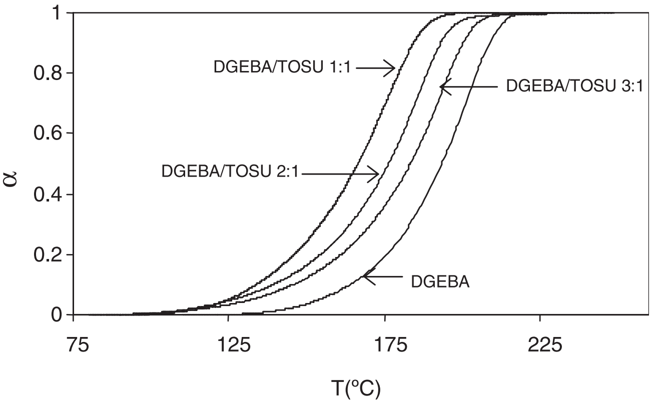


Fig. 1. Conversion degree versus temperature of curing for DGEBA/TOSU 2:1 (mol/mol) formulation with 1 pph of lanthanum triflate obtained through dynamic DSC experiments.

changed we used the FTIR/ATR technique, which also made it possible to determine the proportion of unreacted species in the final material. Fig. 2 shows the IR spectra of a mixture of DGEBA/TOSU 2:1 mol/mol with 1 pph of lanthanum triflate before and after curing at 140 °C. As we can see, the spectrum of the uncured sample shows a sharp absorption at 915 cm^{-1}, due to the deformation of the epoxy ring, and a weak absorption band at 1746 cm^{-1}, which can be assigned to the carbonyl group of a linear carbonate. This peak appears just after the mixture is prepared, and its formation could be rationalized by an initial homo or copolymerization of TOSU. After curing, the absorption at 915 cm^{-1} disappears, which indicates that the epoxide groups have completely reacted. The band at 1746 cm^{-1} increases as the result of incorporating linear carbonate groups into the network. Surprisingly, a weak new band at 1800 cm^{-1} appears, which coincides with the typical absorption of a five-membered cyclic carbonate. Hino et al. [26] described the formation of a cyclic six-membered carbonate from SOC with a Lewis acid catalyst in an equilibrium process (Scheme 2, Eq. (a)). Ariga et al. [27] reported an equilibrium reaction between epoxide groups and cyclic six-membered carbonates to give the corresponding unsymmetric SOC (Scheme 2, Eq. (b)). This SOC by transketalization evolved to give two symmetric SOCs of different cyclic sizes (Scheme 2, Eq. (c)). The formation of symmetrical five-membered SOCs can lead to a new reactive process (Scheme 3), which explains the appearance of the carbonyl absorption at 1800 cm^{-1} assigned to a five-membered cyclic carbonate.

Fig. 3 shows how the absorption of epoxy groups at 915 cm^{-1} evolves, taking as a reference the absorption of the aromatic ring at 1506 cm^{-1}, which remains unchanged during curing. As we can see, the initial absorption is different for each formulation of lanthanum and ytterbium triflate, which indicates that the reaction of epoxide groups initiates before the FTIR experiment begins. The initial reaction seems to be faster for the ytterbium catalyst. In all cases, the epoxy groups completely disappear, indicating that the material is fully cured.

Likewise, Fig. 4 shows the increase in the 1745 cm^{-1} band, due to the formation of linear carbonate groups over time. In the same way, the carbonate started to form before the first FTIR spectrum was recorded. In all cases a plateau was reached in a short period of time. For the 1:1 formulation, with a higher content of TOSU, the behavior of both catalysts was very different. The plateau was higher and the carbonate groups formed more quickly when we used the ytterbium salt. Thus, lanthanum triflate leads approximately to a half of formation of linear carbonate groups in reference to the results obtained with ytterbium catalyst. In the 2:1 formulation the carbonate is initially incorporated more quickly into the network with the ytterbium catalyst but there is little difference in the final amount of linear carbonate with both catalysts. It should be said that the formation of the band at 1745 cm^{-1} may be due to the copolymerization of TOSU with epoxides, which introduces the carbonate groups into the network, or to the homopolymerization of TOSU, which can form linear structures that may or may not be chemically linked to the network. This homopolymerization could lead to an important plastification effect.

The weakness of the absorption at 1800 cm^{-1} assigned to the five-membered cyclic carbonates does not allow us to evaluate its evolution accurately for the systems studied, but qualitatively it seems that this group formed more quickly when we used ytterbium triflate as a catalyst. However, in all the mixtures studied, the final absorption at 1800 cm^{-1} shows that the proportion of five-membered cyclic carbonate is similar and it does not seem to depend on the catalyst used.

From the results as a whole, we came to the conclusion

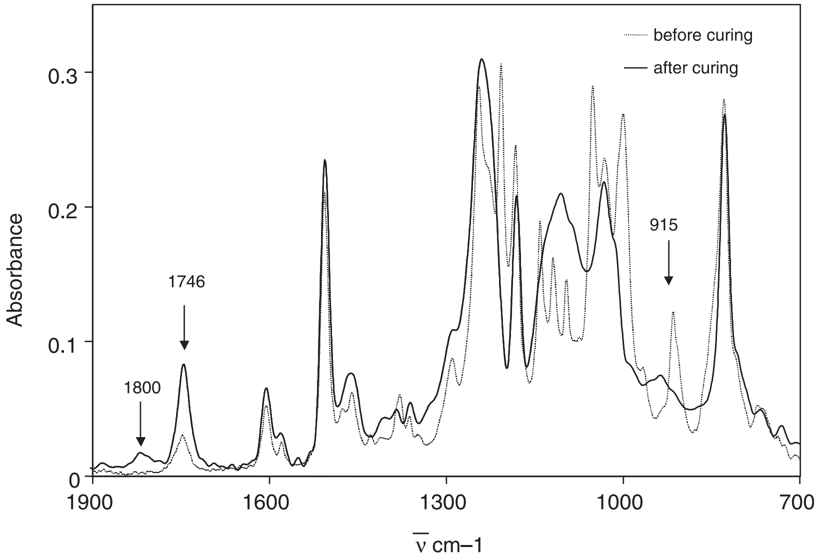
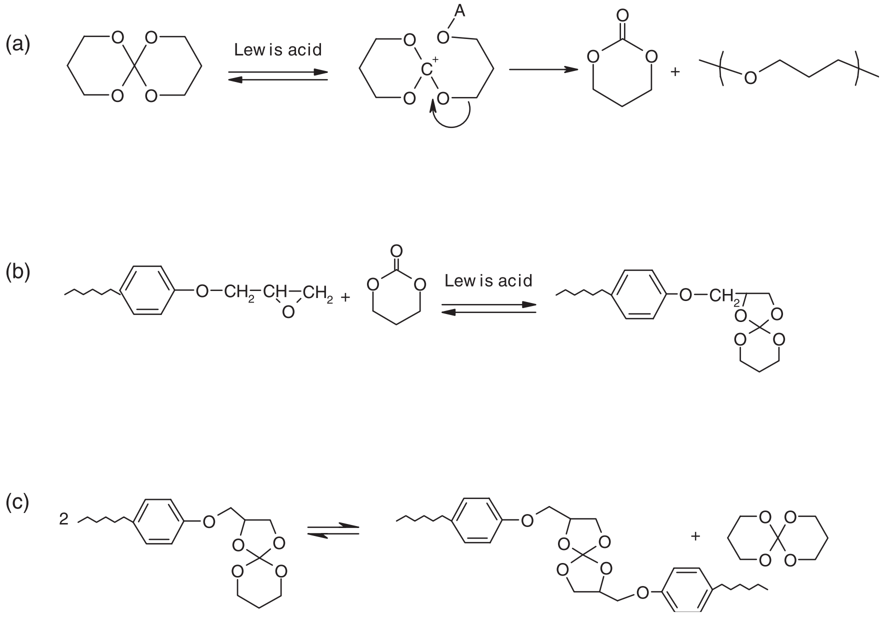


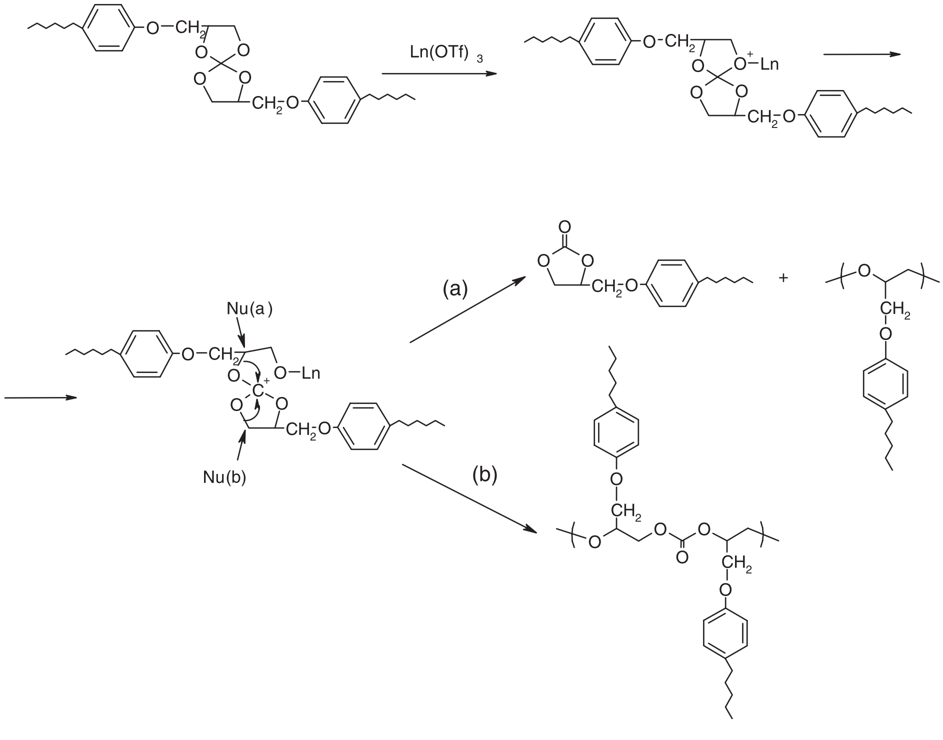
Fig. 2. FTIR spectra of a DGEBA/TOSU 2:1 (mol/mol) formulation with 1 pph of lanthanum triflate before and after curing at 140 °C.



Scheme 2.

that mixtures with the highest proportion of TOSU (1:1) lead to networks with unreacted TOSU entrapped in the material when lanthanum triflate was used as the initiator. Because less linear carbonate is introduced for this catalyst, the network is more rigid and the T_g, therefore, increases.

One of the goals of this work was to reduce the shrinkage of the material during curing. Therefore, we studied the volumetric changes during the process and the densities of the materials before and after curing were determined in order to calculate the overall expansion or shrinkage. The results can be seen in Table 2. As expected, when the proportion of TOSU increases, the shrinkage decreases and in the mixture with the highest proportion of TOSU the shrinkage is practically zero. When ytterbium triflate is used as the catalyst, even a slight expansion can be observed (assay 4). As we saw by FTIR, the ytterbium catalyst incorporates a higher proportion of TOSU, which explains the overall expansion observed. Thus, we can confirm, as



Scheme 3.

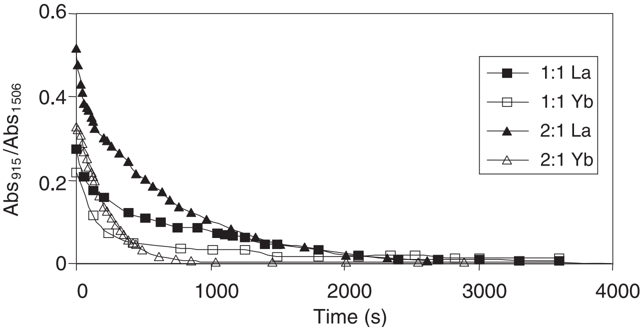


Fig. 3. Evolution of Abs_{915}/Abs_{1506} against time for DGEBA/TOSU 1:1 and 2:1 formulations with 1 pph of ytterbium and lanthanum triflates during curing at 140 °C by FTIR/ATR.

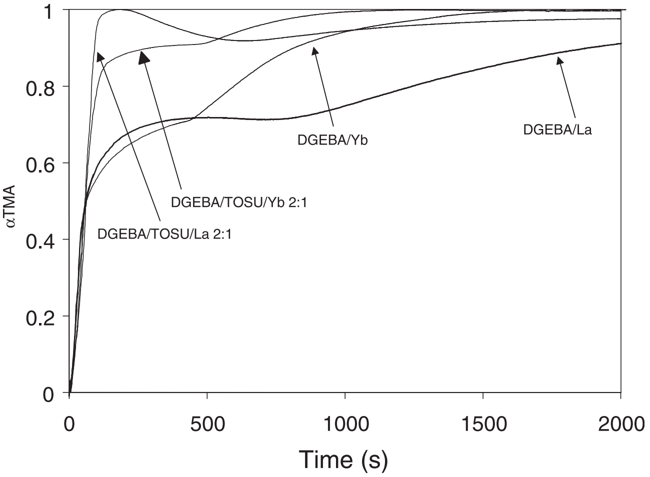


Fig. 5. Degree of shrinkage versus conversion for the DGEBA/TOSU 2:1 formulation with 1 pph of ytterbium or lanthanum triflates during curing at 140 °C.

several authors did before [11,15], that the copolymerization of epoxy resins with spiroortho carbonates is a good strategy for reducing the shrinkage of the material on curing. As important as the overall shrinkage is the material's evolution during curing. Fig. 5 shows the normalized degree of contraction against curing time obtained by TMA for the DGEBA and DGEBA/TOSU 2:1 (mol/mol) mixture catalyzed by ytterbium and lanthanum triflates. These systems show two stages of contraction and an intermediate region without contraction, associated with gelation, such as we observed in the copolymerization of DGEBA with γ-BL [13,25]. We can see that the initial shrinkage is greater for samples containing TOSU, whereas the contraction after gelation is much lower because of after gelation the homopolymerization of epoxide takes place in a little extent (Fig. 3). It must be pointed out that the DGEBA/TOSU formulation initiated by lanthanum triflate even shows an expansion after gelation.

Another objective of this research is to increase the degradability of thermosets by introducing functional groups, in our case carbonate moieties, that break on heating. First of all, we tested the thermal stability of the cured materials by thermogravimetry. Table 3 shows the onset and the maximum rate degradation temperatures and the char yield. As we can see, the higher the proportion of TOSU in the initial mixture, the lower the onset temperature is, which reflects the greater degradability of the materials with a higher proportion of carbonate groups in the polymer backbone. The introduction of aliphatic units leads to a lower char yield. However, the different chemical structure of the networks is not directly reflected in the temperature at which the maximum degradation occurs.

The mechanical properties of these materials were studied by DMTA. Figs. 6 and 7 show the evolution of E' storage moduli and tan δ with the temperature for the thermosets obtained by catalysis with ytterbium triflate. The characteristic parameters that can be drawn from these experiments are shown in Table 4.

In Fig. 6 we can see how the storage moduli of the samples undergo relaxation at lower temperatures when the proportion of TOSU increases, because of the flexibility introduced by the linear aliphatic carbonate moieties. TOSU acts as a bifunctional monomer, so higher proportions should increase the distance between cross-links and, therefore, diminish the value for the relaxed modulus as observed in the figure. In general, we can see that the value of the relaxed modulus decreases with the proportion of TOSU for both ytterbium- and lanthanum triflate-initiated systems.

If we assume that the cured material is uniformly

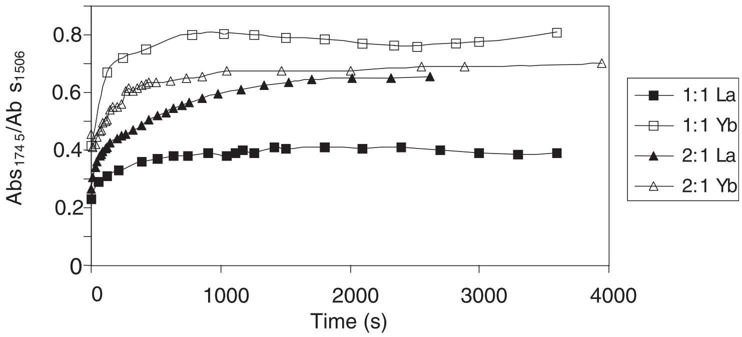


Fig. 4. Evolution of Abs_{1745}/Abs_{1506} against time for DGEBA/TOSU 1:1 and 2:1 formulations with 1 pph of ytterbium and lanthanum triflates during curing at 140 °C by FTIR/ATR.

Table 2
Densities and shrinkage of the systems studied catalyzed by 1 pph of lanthanide triflate

Entry	Formulations[a]	Lanthanide	mol catalyst/eq. epoxide	ρ_{monomer} (g/cm^3)	ρ_{polymer} (g/cm^3)	Shrinkage (%)
1	DGEBA	Yb	0.0030	1.159	1.197	3.3
2	DGEBA/TOSU 3:1	Yb	0.0034	1.174	1.190	1.4
3	DGEBA/TOSU 2:1	Yb	0.0037	1.181	1.190	0.8
4	DGEBA/TOSU 1:1	Yb	0.0043	1.201	1.195	−0.5
5	DGEBA	La	0.0032	1.159	1.194	3.0
6	DGEBA/TOSU 3:1	La	0.0036	1.174	1.202	2.4
7	DGEBA/TOSU 2:1	La	0.0039	1.181	1.201	1.7
8	DGEBA/TOSU 1:1	La	0.0042	1.201	1.202	0.1

[a] The compositions of the formulations are given in molar ratios.

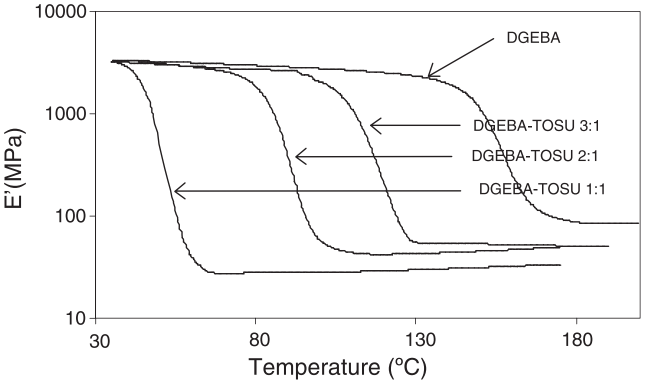


Fig. 6. Storage modulus (log E') against temperature for the various DGEBA/TOSU formulations catalyzed by 1 pph of ytterbium triflate.

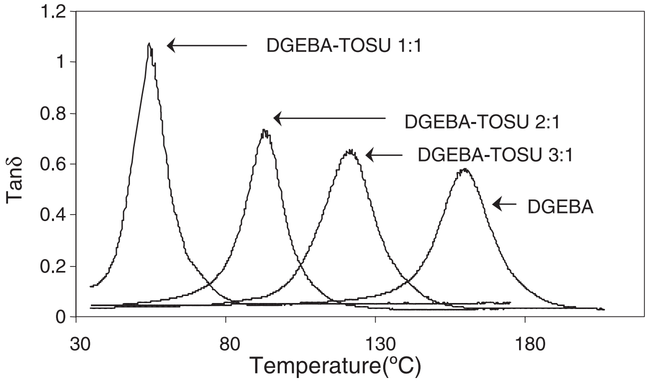


Fig. 7. Tan δ against temperature for the various DGEBA/TOSU formulations catalyzed by 1 pph of ytterbium triflate.

cross-linked, we can apply the following equation, which corresponds to the rubber elasticity theory [28] that allows to calculate the average molecular weight between cross-links ($\bar{M}_c$).

$$\bar{M}_c = \frac{3\phi\delta RT}{E'_r} \quad (5)$$

where R is the gas constant, T is the absolute temperature in K and takes the value of $T_g + 50$, E'_r is the relaxed modulus at this temperature, δ is the density of the cured sample, and ϕ is an experimental factor that takes a value of 1 for most polymers. As the content of TOSU in the sample increases, the M_c value increase as well. This is generally what happens. The M_c values suggest that ytterbium triflate leads to a higher degree of cross-linking than lanthanum salt, but the values of tan δ and T_g (Table 1) are higher for the systems catalyzed by lanthanum triflate. This may be explained if we assume that linear structures, not chemically incorporated into the network, were formed by the homopolymerization of TOSU, which should have a plastifying effect. These structures are more probably formed with ytterbium, because it produces a higher conversion of TOSU (Fig. 4) than lanthanum.

The values of tan δ confirmed the expected general trend: that is, the values decrease as the content of TOSU increases, because of the flexibility introduced into the network (see Fig. 7 for ytterbium cured samples). This figure also shows the dispersity of the samples in terms of

Table 3
Thermogravimetric parameters of the systems studied catalyzed by 1 pph of lanthanide triflate

Entry	Formulations[a]	Lanthanide	mol catalyst/eq. epoxide	T_{onset} (°C)	$T_{\max}$ (°C)	Char yield (%)
1	DGEBA	Yb	0.0030	275	383	19
2	DGEBA/TOSU 3:1	Yb	0.0034	250	370	17
3	DGEBA/TOSU 2:1	Yb	0.0037	231	368	18
4	DGEBA/TOSU 1:1	Yb	0.0043	218	310	15
5	DGEBA	La	0.0032	265	344	22
6	DGEBA/TOSU 3:1	La	0.0036	235	341	15
7	DGEBA/TOSU 2:1	La	0.0039	225	340	14
8	DGEBA/TOSU 1:1	La	0.0042	195	347	12

[a] The compositions of the formulations are given in molar ratios.

Table 4
Thermomechanical parameters of the systems studied catalyzed by 1 pph of lanthanide triflate

Entry	Formulations[a]	Lanthanide	mol catalyst/eq. epoxide	Tan $\delta_{\max}$ (°C)	E'_{rel} (MPa)	$\bar{M}_c$ (g/mol)
1	DGEBA	Yb	0.0030	160	86.6	166
2	DGEBA/TOSU 3:1	Yb	0.0034	123	51.5	258
3	DGEBA/TOSU 2:1	Yb	0.0037	93	44.4	278
4	DGEBA/TOSU 1:1	Yb	0.0043	55	28.4	395
5	DGEBA	La	0.0032	158	66.7	215
6	DGEBA/TOSU 3:1	La	0.0036	122	44.4	300
7	DGEBA/TOSU 2:1	La	0.0039	101	37.1	342
8	DGEBA/TOSU 1:1	La	0.0042	64	21.0	552

[a] The compositions of the formulations are given in molar ratios.

the amplitude of the peak. It seems that the dispersity is not increased by copolymerization because the materials obtained appear homogeneous. The height of the peak of tan δ is also an indicator of the significance of the relaxation of the material when it undergoes the glass transition. So, we can conclude that the higher the proportion of TOSU in the initial mixture, the higher the relaxation peak is and the lower the temperature of the glass transition. The higher flexibility of these materials together with the lower contraction during the curing could be of significance for developing coatings for high requirement applications.

4. Conclusions

The copolymerization of DGEBA with TOSU catalyzed by lanthanide triflates leads to carbonate moieties being incorporated into the chemical structure and to the formation of five-membered cyclic carbonate end groups through the formation of six-membered cyclic carbonates and transketalization equilibrium processes.

When ytterbium triflate is used as the initiator more TOSU is incorporated into the material than when lanthanum salt is used, especially at the highest proportion of TOSU.

The greater the amount of TOSU added to the reaction mixture, the lower the T_g of the material and the higher the reaction rate are.

Because of its higher Lewis acidity, ytterbium triflate produces the highest acceleration of the curing.

The materials studied shrink in two different steps, which are separated by the gelation. The higher the proportion of TOSU in the reaction mixture, the lower the overall shrinkage is and even some expansion was observed.

When the proportion of TOSU is increased in the curing mixture, the onset decomposition temperature decreases, which indicates greater degradability.

The increase in the proportion of TOSU in the formulation increases the flexibility of the material, which decreases the tan δ values and increases the height of the relaxation peaks in DMTA experiments.

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