

Curing of Mixtures of Epoxy Resins and 4-Methyl-1,3-dioxolan-2-one with Several Initiators

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ABSTRACT: Diglycidyl ether of bisphenol A or 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexane carboxylate were mixed with different proportions of 4-methyl-1,3-dioxolan-2-one and cured using lanthanide triflates as initiators. In order to compare the materials obtained, conventional initiators such as boron trifluoride complexes and *N,N*-dimethylamino-pyridine were also tested. The curing process was followed by differential scanning calorimetry (DSC) and Fourier transform IR in attenuated total reflectance mode. This technique

proved that the carbonate accelerates the curing process because it helps to form the active initiating species, although it was not chemically incorporated into the network and remained entrapped in the material. The DSC kinetic study was also reported. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2086–2093, 2006

Key words: epoxy resins; crosslinking; cationic polymerization; thermosets; carbonates

INTRODUCTION

The catalytic curing of epoxy resins leads to thermosets that are highly crosslinked and consequently generally brittle. A variety of approaches have been used to improve the impact resistance, elasticity, toughness, and other properties of these materials. They usually involve copolymerization with epoxy monomers that have flexible units or the addition of oligomeric additives. Another drawback of epoxy resins is shrinkage during curing, which introduces stress, produces microvoids and microcracks, and reduces the adhesion to the substrate.¹

Because catalytic systems lead to the homopolymerization of epoxy groups by the “ring-opening” mechanism, another possible approach for improving the mechanical and adhesive properties is copolymerization with other cyclic monomers that can introduce flexible chains into the network. In this way, the impact resis-

tance and toughness of the material can be improved. Moreover, if expandable monomers are used in the copolymerization, there will be less shrinkage.

In previous articles^{2,3} we studied the chemical incorporation of γ -butyrolactone (γ -BL) into the epoxy network. This lactone does not homopolymerize but reacts with oxirane groups to form spiroorthoesters that are expandable monomers when they polymerize. In these studies we proved that the shrinkage after gelation, which causes the stress, was reduced. Moreover, the curing process was also observed to be faster.

Cyclic carbonates have also been recognized as expandable monomers^{1,4,5} because the polymers that are formed can have lower densities than the monomers from which they are derived. Moreover, cyclic carbonates react with oxiranes in the presence of a Lewis acid to give spiroortho carbonates (SOCs). These monomers may be polymerized by cationic initiators to yield poly(ether carbonate)s.^{6,7}

Rokicki and Nguyen studied the reaction of five-membered cyclic carbonates with epoxy compounds using boron trifluoride ($\text{BF}_3 \cdot \text{OEt}_2$) as the initiator.⁸ They show that this reaction leads to SOC, poly(ether carbonate), or polyether, depending on the oxirane ring substituents. They also reported that the copolymerization of phenylglycidylether (PGE) with cyclic carbonates favors their conversion into SOC and poly(ether carbonate)s, and they used BF_3 amine complexes to study the copolymerization of diglycidyl ether of bisphenol A (DGEBA) epoxy resins with oligomers that had carbonate groups at the ends.⁹

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Their conclusions were that the incorporation of carbonate moieties into the material increases the strength of the resins and the gel time and the pot-life of the epoxide cyclic carbonate compositions can be controlled by the amount of carbonate and initiator. Moreover, the presence of aliphatic carbonates increases the extent of the conversion of epoxy groups.

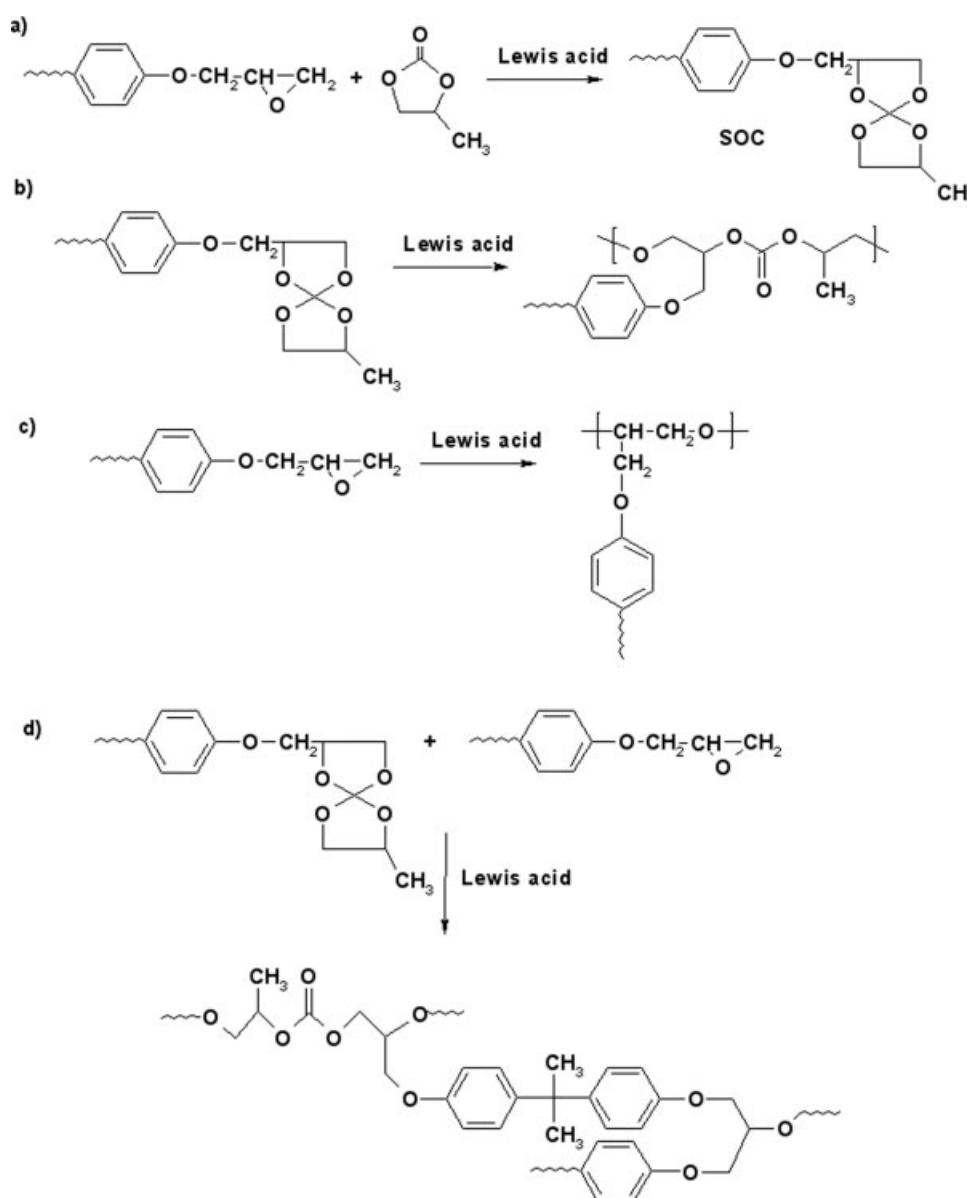
The present study describes how a cyclic aliphatic carbonate can be used to modify epoxy networks promoted by cationic initiators such as lanthanide triflates, which have proved to be excellent Lewis acid initiators that are not only stable in water but also environmentally friendly catalysts.¹⁰ The strong electron-withdrawing capacity of the trifluoromethanesulfonate anion enhances the Lewis acid character of the initiator and its stability can help to reduce the termination

process. In order to compare them with other conventional initiators, we tested the complex of BF_3 -monoethylamine ($\text{BF}_3 \cdot \text{MEA}$) and an anionic initiator, *N,N*-dimethylaminopyridine (DMAP). Because five-membered cyclic carbonates do not homopolymerize in mild conditions, we selected 4-methyl-1,3-dioxolan-2-one (propylene carbonate, PC) as a comonomer to modify epoxy resins.

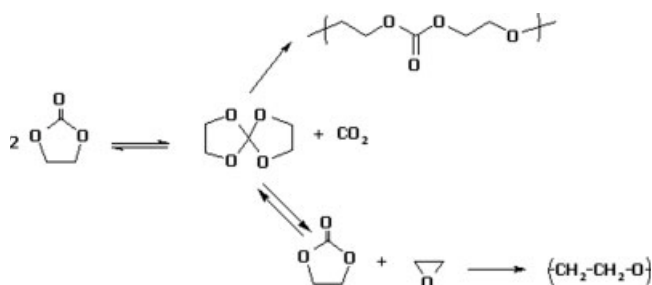
EXPERIMENTAL

Materials

DGEBA (Epikote 828 resin, epoxy equivalent = 187 g/equiv, Shell Chemicals), 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexane carboxylate (ECH, Araldite CY



Scheme 1 The individual reactions expected in the global curing process for diglycidyl resins with cyclic carbonates in the presence of Lewis acids.



Scheme 2 The polymerization of PC with diethyl zinc as catalyst through the formation of a different five-membered SOC and the loss of CO_2 .

179, gift from Vantico), PGE (Aldrich), and PC (gift from Bayer) were used as received.

Lanthanum(III), samarium(III), erbium(III), ytterbium(III) trifluoromethanesulfonates, $\text{BF}_3 \cdot \text{MEA}$, and DMAP (Aldrich) were used as received.

Preparation of curing mixtures

The samples were prepared by mixing the selected catalyst in the corresponding amount of PC and adding the required proportion of epoxy resin with stirring. All the mixtures contained the corresponding catalyst in proportions of 1 or 3 phr (w/w). The prepared mixtures were kept at -18°C before use.

Characterization and measurements

Calorimetric studies were carried out on a Mettler DSC-821e thermal analyzer in covered Al pans under N_2 at $10^\circ\text{C}/\text{min}$. 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

differential scanning calorimetry (DSC, α_{DSC}) was calculated as follows:

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

where ΔH_T is the heat released up to a temperature T , which is obtained by integrating 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) were calculated by means of a second scan after complete curing as the temperature of the halfway point of the jump in the heat capacity when the material changed from the glassy to the rubbery state.

Thermogravimetric analyses (TGA) 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 $10^\circ\text{C}/\text{min}$ in N_2 ($200 \text{ cm}^3/\text{min}$ measured in normal conditions).

The isothermal curing process at 100, 130, and 150°C was monitored with a Jasco Fourier transform IR (FTIR) spectrophotometer at a resolution of 4 cm^{-1} in absorbance mode. An attenuated total reflectance (ATR) accessory with thermal control and a diamond crystal (Golden Gate heated single-reflection diamond ATR, Specac–Teknokroma) was used to determine the FTIR spectra. The conversions of the reactive groups were determined by the Lambert–Beer law from the normalized changes in absorbance, as we explained previously.²

After isothermal curing by means of FTIR, a dynamic scan by DSC was always carried out to ensure that the cure was complete.

Kinetic analysis

An integral isoconversional nonisothermal kinetic analysis, combined with the Coats–Redfern procedure and the compensation effect, was used to determine

TABLE I
Calorimetric Data of Formulations

Entry	Formulations (mol/mol)	Catalyst	Proportion of catalyst (phr)	Catalyst (mol)/epoxide (eq)	T_g ($^\circ\text{C}$)	Δh (J/g)	Δh (kJ/ee)	T_{max} ($^\circ\text{C}$)
1	DGEBA	La (OTf) ₃	1	0.0030	130	551	104.1	192
2	DGEBA/PC 4 : 1	La (OTf) ₃	1	0.0034	81	417	85.1	187
3	DGEBA/PC 3 : 1	La (OTf) ₃	1	0.0035	74	409	85.0	174
4	DGEBA/PC 2 : 1	La (OTf) ₃	1	0.0036	59	400	86.7	172
5	DGEBA/PC 1 : 1	La (OTf) ₃	1	0.0041	25	371	91.8	164
6	DGEBA/PC 2 : 1	La (OTf) ₃	2	0.0072	58	371	82.0	153
7	DGEBA/PC 2 : 1	Sm (OTf) ₃	1	0.0036	58	400	86.7	172
8	DGEBA/PC 2 : 1	Er (OTf) ₃	1	0.0035	61	401	87.1	165
9	DGEBA/PC 2 : 1	Yb (OTf) ₃	1	0.0034	63	395	85.8	160
10	DGEBA/PC 2 : 1	$\text{BF}_3 \cdot \text{MEA}$	1	0.0188	77	285	62.1	152
11	DGEBA/PC 2 : 1	$\text{BF}_3 \cdot \text{MEA}$	3	0.0565	86	400	88.6	151
12	DGEBA/PC 2 : 1	DMAP	1	0.0174	44	186	40.4	149
13	DGEBA/PC 2 : 1	DMAP	3	0.0522	82	341	75.5	135

the kinetic triplet, in which A is the preexponential factor, E_a is the activation energy, and $g(\alpha)$ is the integral function of the degree of conversion (α).^{11–13}

RESULTS AND DISCUSSION

Rokicki and Nguyen^{8,9} reported the reaction of oxiranes with cyclic carbonates. Using monofunctional epoxides and carbonates, they showed that polymerization takes place in CH_2Cl_2 solution to give poly(ether carbonates). They also studied the cross-linking process of mixtures of DGEBA with bifunctional cyclic carbonate oligomers. In both studies they used BF_3 complexes as the initiator and suggested that, depending on the substituents in the oxirane ring, SOCs can be formed. They concluded that the conversion of epoxide groups was higher when cyclic carbonates were present in the composition, although 5% (w/w) initiator was needed for the epoxy band at 910 cm^{-1} in the FTIR spectrum to disappear completely.

In this context we studied the cationic curing process of mixtures of DGEBA with PC in different proportions and with different lanthanide triflates as the initiator. In order to compare their effectiveness, we also tested conventional cationic ($\text{BF}_3 \cdot \text{MEA}$) and anionic (DMAP) initiators.

Scheme 1 shows the individual reactions expected in the global curing process for diglycidyl resins with cyclic carbonates in the presence of Lewis acids.^{6–8} The first reaction shows the formation of SOC from epoxide and PC. This reaction takes place with shrinkage because the van der Waals distance between both reactants converts into covalent bonds in the final product. The second reaction is the polymerization of the SOC formed previously, which takes place with volume expansion. The third reaction is the homopolymerization of DGEBA, which leads to polyether chains; and

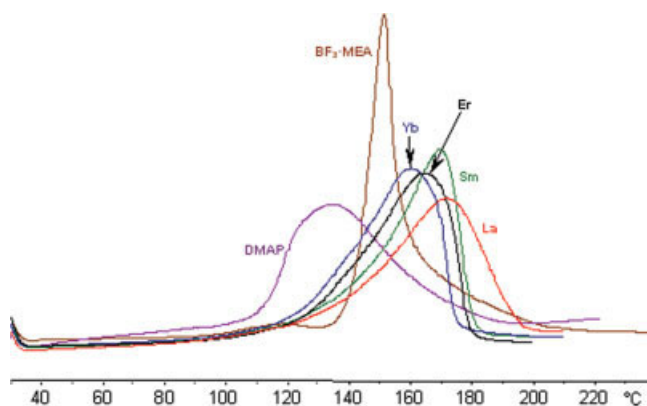


Figure 1 DSC scanning curves of 2 : 1 DGEBA/PC (mol/mol) mixtures catalyzed by 1 phr of lanthanide triflates or 3 phr of DMAP or $\text{BF}_3 \cdot \text{MEA}$ at a heating rate of $10^\circ\text{C}/\text{min}$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

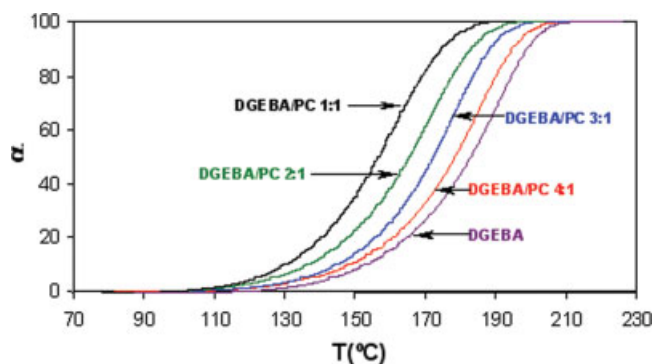


Figure 2 The degree of conversion versus the temperature of curing for DGEBA and DGEBA/PC mixtures with different molar ratios catalyzed by 1 phr of lanthanum triflate obtained through dynamic DSC experiments. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

the fourth is the copolymerization of SOC and DGEBA, which leads to a network containing carbonate and ether structures in proportions that depend on the composition of the initial mixture. For thermodynamic reasons, PC cannot homopolymerize.¹⁴ However, Soga et al.¹⁵ described the polymerization of PC with diethylzinc as the catalyst through the formation of a different five-membered SOC and the loss of CO_2 (Scheme 2). This SOC polymerizes to give poly(ether carbonate) or decomposes to produce PC and epoxide, which in turn can homopolymerize. All these possibilities encouraged us to study the curing process by FTIR.

It should be said that, in this type of copolymerization, the DGEBA resin acts as a tetrafunctional monomer and the PC and SOCs formed act as bifunctional monomers. Therefore, a higher proportion of DGEBA leads to a more densely crosslinked network, whereas a higher proportion of PC should lead to a longer linear chain between crosslinks.

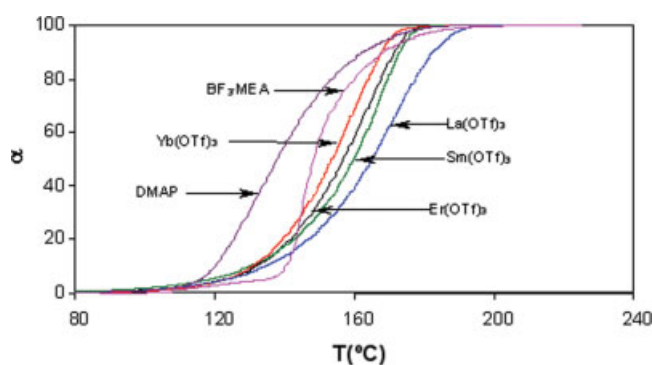


Figure 3 The degree of conversion versus the temperature of curing for 2 : 1 DGEBA/PC (mol/mol) mixtures catalyzed by 1 phr of lanthanide triflates or 3 phr of DMAP or $\text{BF}_3 \cdot \text{MEA}$ obtained through dynamic DSC experiments. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

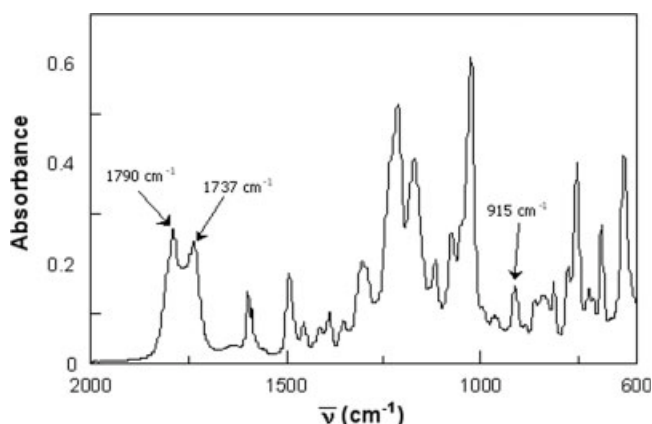


Figure 4 FTIR spectra of a mixture of PGE/PC/lanthanum triflate with a molar ratio of 5 : 5 : 1.

Table I provides the calorimetric results of the curing process of DGEBA/PC mixtures catalyzed by several initiators. Note that when the proportion of carbonate is increased, the T_g value of the cured material decreases considerably (entries 1–5) when lanthanum triflate is the initiator, and the change of the cation in the triflate salt does not affect this parameter notably (entries 4, 7–9). Nevertheless, the use of $\text{BF}_3 \cdot \text{MEA}$ or DMAP in a proportion of 3 phr leads to materials with a slightly higher T_g (entries 11, 13). The enthalpy released per gram is lower (entries 1–5) when the proportion of PC in the curing mixture is increased. However, the heat released per epoxy equivalent remains practically constant in samples containing PC and does not depend on the formulation, if the initiator is a lanthanide triflate, which means that the degree of curing achieved should be practically the same. However, this value is lower than the one for pure DGEBA (entry 1), which is similar to the value reported for the homopolymerization of epoxides.¹⁶

As we can see, higher proportions of both $\text{BF}_3 \cdot \text{MEA}$ and DMAP (entries 10–13) should be used if enthalpy

values are to be similar to the values obtained with the triflates. However, an increase in the proportion of lanthanide triflate (entry 6) does not increase the T_g or the enthalpy evolved. The maximum of the curing exotherm decreases slightly as the proportion of PC increases (entries 1–5). There is also a slight variation when the lanthanide salt changes (entries 4, 7–9) and ytterbium triflate, the most acidic cation, leads to the lowest maximum temperature. Thus, varying the lanthanide salt has only a kinetic effect on the reaction process. In addition, increasing the proportion of initiator shifts the maximum of the exotherm to lower temperatures, when lanthanum triflate (entries 4, 6) or DMAP was used (entries 12, 13).

The kinetic effect caused by the presence of PC in the formulations and the efficiency of the initiators in the curing were dynamically studied by DSC. Figure 1 shows the calorimetric curves for the 2 : 1 DGEBA/PC formulation catalyzed by 1 phr of lanthanide triflates or 3 phr of $\text{BF}_3 \cdot \text{MEA}$ and DMAP. As we can see, most initiators lead to similar Gaussian exotherms whereas the shape of the curve obtained with $\text{BF}_3 \cdot \text{MEA}$ is sharp and has a small exotherm at about 120°C, which could be attributed to the formation of the initiating species.¹⁷

Figure 2 shows the effect of adding PC to the reactive mixture on the degree of conversion for different formulations initiated by lanthanum triflate. An increase in the PC concentration leads to a higher α value at a preset temperature, which could be attributed to the activation of the monomers.³ Figure 3 shows the effect of the different initiators on the conversion for the 2 : 1 DGEBA/PC formulation. The evolution for the different lanthanide triflates is similar but the higher the Lewis acidity of the cation is, the higher the conversion at a selected temperature. A quantity of 3 phr of DMAP begins the crosslinking at lower temperatures than lanthanide salts and the reactivity is higher at low temperatures. Compound $\text{BF}_3 \cdot \text{MEA}$ behaves

TABLE II
Apparent Activation Energy Values, Preexponential Factor Values, and Rate Constants from DSC of Systems

Entry	Formulations (mol/mol)	Catalyst	Proportion of catalyst (phr)	Catalyst (mol)/epoxide (eq)	E_a (kJ/mol)	$\ln A$ (s^{-1})	$k_{160^\circ\text{C}} \times 10^3$ (s^{-1})
1	DGEBA	La (OTf) ₃	1	0.0030	80.3	14.73	0.52
2	DGEBA/PC 4 : 1	La (OTf) ₃	1	0.0034	74.3	13.21	1.10
3	DGEBA/PC 3 : 1	La (OTf) ₃	1	0.0035	70.9	12.69	1.22
4	DGEBA/PC 2 : 1	La (OTf) ₃	1	0.0036	72.7	13.59	1.36
5	DGEBA/PC 1 : 1	La (OTf) ₃	1	0.0041	70.4	13.21	1.75
6	DGEBA/PC 2 : 1	La (OTf) ₃	2	0.0072	61.4	10.88	2.08
7	DGEBA/PC 2 : 1	Sm (OTf) ₃	1	0.0036	72.9	13.91	1.78
8	DGEBA/PC 2 : 1	Er (OTf) ₃	1	0.0035	62.1	11.0	1.91
9	DGEBA/PC 2 : 1	Yb (OTf) ₃	1	0.0034	67.6	12.54	1.96

The values of the activation energies (E_a) were evaluated by the isoconversional integral method applied at a conversion of 0.5. The values of the preexponential factor ($\ln A$) were calculated by the R_3 kinetic model with $g(\alpha) = 1 - (1 - \alpha)^{-1/3}$. The values of the rate constant at 160°C ($k_{160^\circ\text{C}} \times 10^3$) were calculated using the Arrhenius equation $\ln k = \ln A - (E/RT)$, where E is the activation energy, T is the absolute temperature and R is the gas constant.

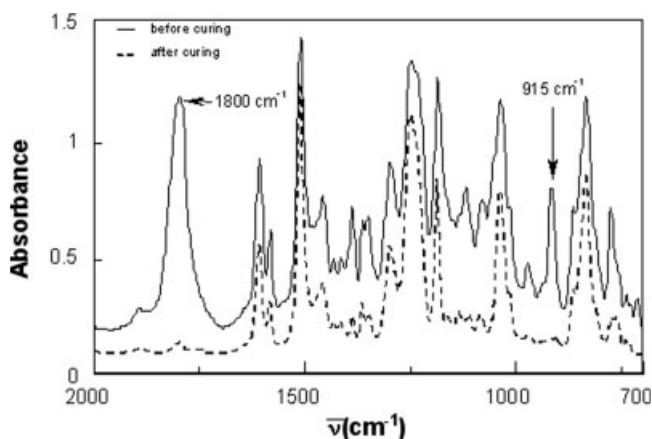


Figure 5 FTIR spectra of a 2 : 1 DGEBA/PC (mol/mol) mixture with 1 phr of lanthanum triflate before and after curing at 120°C.

differently, because the reaction begins at higher temperatures and the crosslinking is faster, which seems to indicate that this initiator has a higher latency. At higher conversion, the reaction is slower than when lanthanide triflates are used.

We used FTIR to show how PC affects the formation of the initiating active species, using PGE as a model compound. Figure 4 provides the spectrum of a PGE/PC/lanthanum triflate sample with a molar ratio of 5 : 5 : 1. The carbonyl absorption at 1800 cm^{-1} , typical of PC, shifts to 1790 cm^{-1} and a new carbonylic band appears at 1737 cm^{-1} , which indicates that the carbonate group coordinates with the lanthanum triflate. Moreover, the epoxy band at 915 cm^{-1} remains, which indicates that this group does not coordinate to the initiator. Thus, it seems that lanthanum triflate is more able to coordinate to the carbonate than to the epoxide group, so the initiating active species could be formed in this way.

To find the kinetic parameters associated with the set of calorimetric curves obtained for the formulations under study, we applied an isoconversional integral method at a conversion of 0.5. We calculated the apparent activation energy (E_a) value associated with the simultaneous reactive processes and the preexponential factor for each formulation of the kinetic model selected, which was R_3 on the basis of the reduced master curves procedure of Criado,¹⁸ which is described elsewhere.¹² The results are summarized in Table II. Although the addition of PC to DGEBA decreased the activation energy, there was no clear tendency when the proportion was varied, similar to when γ -BL was added.³ Likewise, a general trend is not observed in the preexponential factor. However, because of the compensation effect, the reaction rate constant increases when the proportion of PC in the sample is increased (entries 1–5). Moreover, the reaction rate constant increases when the proportion of initiator

increases (entry 6). Table II also shows the kinetic parameters associated with the curing of a 2 : 1 DGEBA/PC sample with different lanthanide triflates (entries 4, 7–9). Note that there is no relation between the activation energies or preexponential factors and the Lewis acidity of the initiator. However, there is a relation with the calculated rate constant. Thus, the ytterbium initiator, the most acidic compound, leads to the highest reaction rate. The curing of the systems initiated by $\text{BF}_3 \cdot \text{MEA}$ or DMAP did not follow the R_3 model and they are not kinetically similar to the systems with lanthanide triflates, so they were not included in the table. Thus, the addition of PC to DGEBA produces an acceleration in the curing process.

To investigate the reactive processes, which take place in the copolymerization of DGEBA and PC, we recorded FTIR/ATR spectra before and after curing (see Fig. 5). The most significant absorptions in the spectrum of the uncured sample are a strong band at 1800 cm^{-1} and a medium band at 915 cm^{-1} , which are attributable to the stretching of the carbonyl group of the cyclic carbonate and to the deformation of the epoxy ring, respectively. In the spectrum of the cured sample, both the epoxide absorption and the cyclic carbonate band disappear, suggesting that the curing was complete. However, the band expected at 1745 cm^{-1} that is due to the linear carbonate does not appear at all. In fact, the FTIR/ATR spectra recorded during the curing process showed a slow but progressive decrease in the carbonyl absorption, which could be because PC evaporates or SOC forms in two different ways: epoxide reacts with PC (Scheme 1) or two molecules of PC react with the parallel evolution of CO_2 (Scheme 2). Because there are no bubbles in the polymeric bulk, we can conclude that SOC is not formed by the reaction in Scheme 2. If SOCs were

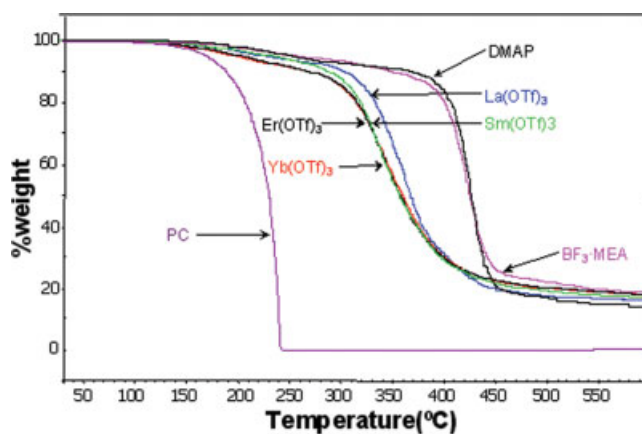


Figure 6 TGA curves of pure PC and the materials obtained from 2 : 1 DGEBA/PC (mol/mol) mixtures catalyzed by 1 phr of lanthanide triflates or 3 phr of DMAP or $\text{BF}_3 \cdot \text{MEA}$ at a heating rate of 10°C/min in an N_2 atmosphere. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

TABLE III
Calorimetric Data and Kinetic Parameters of Formulations Catalyzed by La(OTf)₃

Entry	Formulations (mol/mol)	Proportion of catalyst (phr)	Catalyst (mol)/epoxide (eq)	T_g (°C)	Δh (J/g)	Δh (kJ/ee)	T_{max} (°C)	E_a (kJ/mol)	$\ln A$ (s ⁻¹)	$k_{100^\circ\text{C}} \times 10^3$ (s ⁻¹)
1	ECH	1	0.0021	170	579	73.9	146	75.2	17.37	1.02
2	ECH/PC 3 : 1	1	0.0024	145	514	74.2	120	78.8	20.28	5.83
3	ECH/PC 3 : 1	0.5	0.0012	149	490	70.4	134	78.1	10.07	2.60
4	ECH/PC 2 : 1	1	0.0026	129	470	71.9	112	82.4	21.89	9.21
5	ECH/PC 1 : 1	1	0.0030	108	424	75.7	98	84.7	23.07	14.12
6	ECH/PC 1 : 1	0.5	0.0015	122	454	80.7	105	75.8	19.65	8.21

The values of the activation energies (E_a) were evaluated by the isoconversional integral method applied at a conversion of 0.5. The values of the preexponential factor ($\ln A$) were calculated by the n th-order kinetic model with $n = 1.5g(\alpha) = 2[-1 + (1 - \alpha)^{-1/2}]$. The values of the rate constant at 100°C ($k_{100^\circ\text{C}} \times 10^3$) were calculated using the Arrhenius equation $\ln k = \ln A - (E/RT)$, where E is the activation energy, T is the absolute temperature, and R is the gas constant.

formed, they should polymerize to linear poly(ether carbonate)s and a new carbonyl absorption at 1745 cm⁻¹ should be observed. These results seem to indicate that PC does not incorporate into the chemical structure and is lost on heating, although some of it remains entrapped and acts as a plasticizer, thus reducing the T_g and facilitating the curing process. FTIR/ATR experiments with DMAP or BF₃ · MEA gave similar results: the complete curing of epoxy resins and the partial loss of PC.

Figure 6 shows the TG curves for the materials obtained from the 2 : 1 DGEBA/PC (mol/mol) mixture with all of the studied initiators. The curve of the pure PC is also included to show the temperature at which it disappears in the TGA. As can be seen, all the materials lose weight at the beginning, coinciding with the evaporation of PC, which confirms the presence of entrapped PC. The materials cured with lanthanide triflates degrade in a similar way, although lanthanum leads to a slightly higher degradation temperature. However, both DMAP and BF₃ · MEA initiated materials have much higher thermal stability, which seems to indicate a higher crosslinking density.

The fact that the reactivity of cycloaliphatic resins was higher when lanthanide triflates were used as initiators¹⁹ prompted us to study the copolymerization of ECH with PC. We studied different proportions of both comonomers using two different proportions of lanthanum triflate as the initiator. The calorimetric results are given in Table III. Note that all the crosslinked mixtures have a relatively high T_g , which decreases when the proportion of PC increases (entries 1, 2, 4, 5). This parameter increases slightly when the proportion of initiator decreases (entries 3, 6).

Figure 7 shows the degree of conversion versus the temperature for the same systems. Clearly, all the mixtures containing PC reacted faster than pure ECH, even with a lower proportion of initiator. The higher the proportion of PC in the mixture was, the higher the acceleration was. The kinetic parameters can be seen in Table III. In this case, the crosslinking of ECH and its mixtures follows an n th-order kinetic model different

from the R₃ used for DGEBA resins. The higher reactivity of these systems led us to calculate the rate constants at 100°C. The table shows that, when the proportion of both PC and the initiator increased, the reaction rate also increased.

When mixtures of different proportions of ECH and PC were cured in the FTIR/ATR apparatus at 100°C, we observed that, like the DGEBA resins, PC does not incorporate chemically into the network. The FTIR spectrum of the pure cycloaliphatic epoxy resin shows some characteristic bands at 1726 cm⁻¹ (carbonyl absorption of the ester group) and at 745 cm⁻¹ (deformation of the oxirane ring). During the curing the epoxy band disappears completely and new bands appear in the region of linear ether absorptions (1075 cm⁻¹). However, the only variation in the carbonylic region is the progressive decrease in the PC absorption at 1800 cm⁻¹, which indicates a loss of PC by evaporation. The presence of PC entrapped in the network was confirmed by TGA experiments.

Thus, it seems that the role that PC plays in the curing of DGEBA and cycloaliphatic epoxy resins is that it accelerates the reactive process. The fact that PC is not chemically incorporated into these materials may be because SOC only forms with great difficulty and, if it does, it is unable to polymerize. The low boiling point of PC may prompt the SOC formation equilibrium to revert

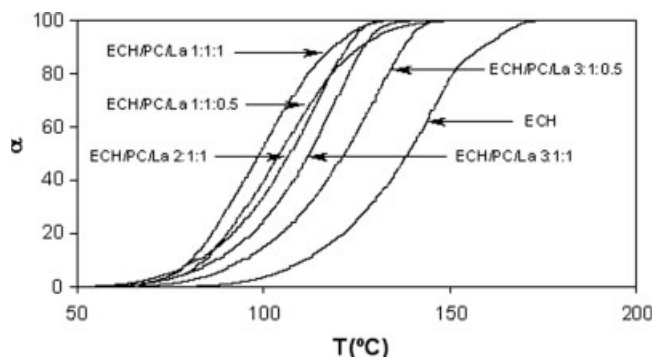


Figure 7 The degree of conversion versus the temperature of curing for ECH and ECH/PC mixtures with different molar ratios and catalyzed by 0.5 or 1 phr of lanthanum triflate obtained through dynamic DSC experiments.

to the initial compounds, which decreases the amount of SOC available to polymerize. Thus, future work should focus on changing the structure of the carbonate.

CONCLUSIONS

PC did not incorporate covalently into the network in its copolymerization with epoxy resins with any of the anionic or cationic initiators tested in this study and PC acted only as a plasticizer.

The addition of PC to the epoxy resins accelerated the curing process by the formation of an active species in which the carbonate participates.

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