Cationic Curing of Diglycidyl Ether of Bisphenol A and 2,2,5,5-Tetramethyl-4,6-dioxo-1,3-dioxane and Degradation of the Thermosets Obtained

Lidia González,[1] Xavier Ramis,[2] Josep Maria Salla,[2] Ana Mantecón,[1] Angels Serra[1]

[1]Departament de Química Analítica i Química Orgànica, Universitat Rovira i Virgili, C/Marcel·lí Domingo s/n, 43007 Tarragona, Spain
[2]Laboratori de Termodinàmica, Escola Tècnica Superior de Enginyeria Industrial de Barcelona (ETSEIB), Universitat Politècnica de Catalunya, Avenida Diagonal 647, 08028 Barcelona, Spain

ABSTRACT: Ytterbium and lanthanum triflates were used as cationic initiators to cure mixtures of diglycidyl ether of bisphenol A and 2,2,5,5-tetramethyl-4,6-dioxo-1,3-dioxane in several proportions. The evolution of the epoxy and lactone during curing and the linear ester groups in the final materials were evaluated with Fourier transform infrared in the attenuated total reflection mode. The shrinkage after curing and the thermal degradability of the materials with variations in the comonomer ratios and initiator used were evaluated and related to the chemical structure of the final network. The expandable character of 2,2,5,5-tetramethyl-4,6-dioxo-1,3-dioxane was confirmed. The obtained materials were more degradable than conventional epoxy resins because of the tertiary ester groups incorporated into the network by copolymerization. The kinetic parameters of the curing and degradation processes were calculated with differential scanning calorimetry and thermogravimetric analysis, respectively, with isoconversional procedures applied in both cases. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 1229–1237, 2008

Key words: cationic polymerization; crosslinking; FTIR; kinetics (polym.); networks; thermosets

INTRODUCTION

Epoxy resins are thermosetting materials that are used in electronic applications as encapsulants or coatings because of their good characteristics as insulators. However, they present some disadvantages, such as the shrinkage produced during curing, their permanency in the environment when their service life is over, and their fragility. All these drawbacks should be reduced to improve their applicability.

Ring opening is the polymerization mechanism that leads to the lowest shrinkage during curing because when a cyclic monomer opens, a covalent bond is converted into a van der Waals distance, which reduces the shrinkage produced in the formation of covalent bonds between monomer molecules.[1] This method has other advantages such as the possibility of copolymerizing heterocyclic monomers with different groups and functionalities. Moreover, the selection of the initiator and its proportion influences the kinetics and mechanism of the polymerization process. A disadvantage of catalytically cured epoxy resins is that they generally are fragile because of their high density of crosslinking. Copolymerization enables the improvement of their mechanical properties because it allows the introduction of flexible chains into the structure with adequate heterocyclic comonomers and also diminishes the crosslinking density.

Previous publications of our research group have dealt with the copolymerization of commercially available lactone monomers with commercial epoxy resins.[2–4] In these studies, we demonstrated that the shrinkage after gelation is notably reduced in this way, and in some cases, the global shrinkage of the material during curing is even lowered.

One strategy for reducing the permanency of thermosets in the environment when their service life is over is the introduction of labile linkages, such as ester groups, into the structure. Ester groups are thermally cleavable over 200°C and therefore facilitate the reworking of the thermosets in which they are chemically incorporated.[5–7] Among ester groups, the tertiary ones are the most easily broken, and so we considered in a previous study their introduction by the

WILEY InterScience®
DISCOVER SOMETHING GREAT

copolymerization of diglycidyl ether of bisphenol A (DGEBA) resins with a Meldrum acid (MA) derivative, 6,6-dimethyl-(4,8-dioxaspiro[2.5]octane-5, 7-dione) (MCP), with a spiranic skeleton.[8,9] MCP was selected because it allows the introduction of tertiary ester groups into the network, which facilitates the degradation process of the thermoset. The expandable behavior of MCP on curing was also demonstrated. Moreover, other studies[10] have demonstrated that the copolymerization of MA and DGEBA solid epoxy resins improves the adhesion and mechanical properties.

In our studies, lanthanide triflates have been selected as initiators because they have been proved to be excellent Lewis acids, are commercially available, are stable in water, and can be considered environmentally friendly catalysts.[11] These initiators have been proved to be capable of copolymerizing epoxy resins with lactones by a ring-opening mechanism through the formation of intermediate spirocyclic compounds, spiroorthoesters (SOEs).[2] The presence of lanthanide triflates in the cured material also facilitates the thermal degradation of the thermoset.[9]

EXPERIMENTAL

Materials

DGEBA (Epikote Resin 827, Shell Chemicals, Rotterdam, Netherlands; epoxy equivalent = 182.08 g/equiv), methyl iodide (Fluka, Steinheim, Germany) silver oxide (Fluka), and 2,2-dimethyl-4,6-dioxo-1,3-dioxane (i.e., MA; Aldrich, Steinheim, Germany) were used as received.

Lanthanum(III) and ytterbium(III) trifluoromethanesulfonates (Aldrich) were used without purification.

Organic solvents were purified by standard methods.

Synthesis of 2,2,5,5-tetramethyl-4,6-dioxo-1, 3-dioxane (MDM)

Into a suspension of 10 g (0.043 mol) of Ag_2O in a mixture of 50 mL of acetonitrile and 8 mL (0.129 mol) of methyl iodide was dropped a solution of 5.56 g (0.039 mol) of MA in 20 mL of acetonitrile during stirring at 10°C for 1 h. After stirring overnight, the silver oxide/silver iodide was filtered, and then the solvent was eliminated by distillation below 60°C in the vacuum of a water pump. The residual oil was treated with water, and after 10 min, the product solidified. The suspension was transferred to a mortar, and the solid was broken up to facilitate washing. After filtration by suction and washing with water, the product was dried *in vacuo* and sublimated.

Yield: 3.1 g (46%) of white crystals. mp: 60–62°C (lit.[12] 62°C). ^{1}H-NMR (CDCl$_3$, δ, ppm): 1.64 (s, 6H, $-CH_3-C-O-$); 1.74 (s, 6H, $CH_3-C=O$). ^{13}C-NMR (CDCl$_3$, δ, ppm): 25.77; 29.01; 44.74; 104.93; 171.22. IR (cm^{-1}): 1778, 1733, 1455, 1387, 1288, 1193, 1166, 1058, 1008, 966.

Preparation of the curing mixtures

The samples were prepared through the mixing of the selected initiator in the corresponding amount of MDM and the addition of the required proportion of DGEBA with manual stirring. The prepared mixtures were kept at −18°C before use. Lanthanide triflates were added in a molar ratio of 0.006 mol/mol of DGEBA and 0.003 mol/mol of MCP.

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 with 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 differential scanning calorimetry (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 temperature T, which is 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 state to the rubbery state.

The isothermal curing process at 150°C was monitored with an FTIR-680PLUS Fourier transform infrared (FTIR) spectrophotometer from Jasco (Tokyo, Japan) 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. The conversions of the reactive groups were determined from the normalized changes in absorbance by the Lambert–Beer law, as we explained previously.[2] After isothermal curing by means of FTIR, a dynamic scan by differential scanning calorimetry (DSC) was always carried out to prove that the curing was complete.

Thermogravimetric analyses (TGAs) were carried out with a Mettler TGA/SDTA 851e thermobalance. Cured samples with an approximate mass of 7 mg were degraded between 30 and 600°C at a heating

rate of 10°C/min in N_2 (200 cm³/min) measured under normal conditions.

Shrinkage was determined from the densities of the samples before and after curing. These densities were determined with a Micromeritics (USA) Accu-Pyc 1330 gas pycnometer thermostated at 30°C.

Kinetic analysis

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

Nonisothermal kinetic analysis can start with the kinetic equation:

$$\beta\frac{d\alpha}{dT} = A\exp\left(\frac{-E}{RT}\right)f(\alpha) \qquad (2)$$

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 approximation[13] to resolve the so-called temperature integral and considering that $2RT/E$ is much lower than 1, we can write the Kissinger–Akahira–Sunose equation as follows:[14–16]

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

For each conversion degree, the 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 ordinate in the origin. If the reaction model, $g(\alpha)$, is known, for each conversion the corresponding value of A can be calculated for every value of E. In this article, to assign a reaction model to the systems studied, we used Criado's reduced master curve procedure,[17] which is described elsewhere.[18] Different 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 ($n = 1$, 2, and 3).[17] We found that the curing of the studied systems follows a kinetic model of surface-controlled reaction type R_3 with $g(\alpha) = [1 - (1 - \alpha)^{1/3}]$, and the degradation processes follow an n-order model with $n = 3$ and $g(\alpha) = 2^{-1}[-1 + (1 - \alpha)^{-2}]$. The rate constant ($k$) values were calculated with E and A determined at $\alpha = 0.5$ with the Arrhenius equation.

RESULTS AND DISCUSSION

In a previous work,[8] we studied the curing of mixtures of DGEBA epoxy resin with a cyclopropylic spiranic MA derivative (MCP), using lanthanide triflates as initiators. We observed that the higher the proportion was of MCP in the curing mixture, the lower the global shrinkage was. Because of the characteristics of this spiranic compound with a highly strained cyclopropyl ring, a double ring opening of the skeleton could be suspected, which could justify the expandable behavior observed. Some spiranic compounds can be considered expandable monomers according to the definition proposed by Bailey and others.[19,20] In this work, we synthesized another MA derivative with a similar structure but with no spiranic skeleton, MDM, to determine whether the lower shrinkage observed in the copolymerization could be attributed to a double ring opening of MCP upon copolymerization or to the expandable character of the six-membered ring.

The copolymerization of DGEBA and MDM is a complex process in which four different reactions can occur to different extents that depend on the proportions of the comonomers in the mixture and on the lanthanide triflate used. These reactions are represented in Scheme 1. It has been experimentally proved that MDM does not homopolymerize under these conditions.

Study by FTIR/ATR

By FTIR, we followed the evolution of the different species that are implied in the global curing. Figure 1 shows the initial and final spectra of the 2 : 1 mol/mol DGEBA/MDM mixture with 0.015 mol of Yb(OTf)$_3$ at 150°C. In the initial spectrum, we can see two carbonylic bands at 1782 and 1745 cm⁻¹ attributable to the unsymmetrical and symmetrical stretching of ester groups and two bands at 962 and 912 cm⁻¹ due to the deformation of the six-membered lactone ring and the deformation of the oxirane group, respectively. All these absorptions disappear in the final spectrum, and a new band at 1734 cm⁻¹ appears because of the linear ester group that forms. The disappearance of the absorptions indicates the complete consumption of the initial species. Because MDM does not homopolymerize, the disappearance of the bands at 1782, 1745, and 962 cm⁻¹ must be attributed to the formation of the corresponding SOE, from which the poly(ether ester) units are formed upon polymerization. The partial overlapping of cyclic and linear carbonyl ester absorptions hindered a quantification of the evolution of the linear ester group on curing. However, the disappearance of MDM could be quantified from the 962-cm⁻¹ absorption. The incorporation of the epoxy group into the network was followed by the diminution of the 912-cm⁻¹ band. The evolution of MDM and epoxy with both initiators is presented in Figures 2 and 3, respectively. We can see a different evolution of the conversions of MDM with both initiators, whereas there are
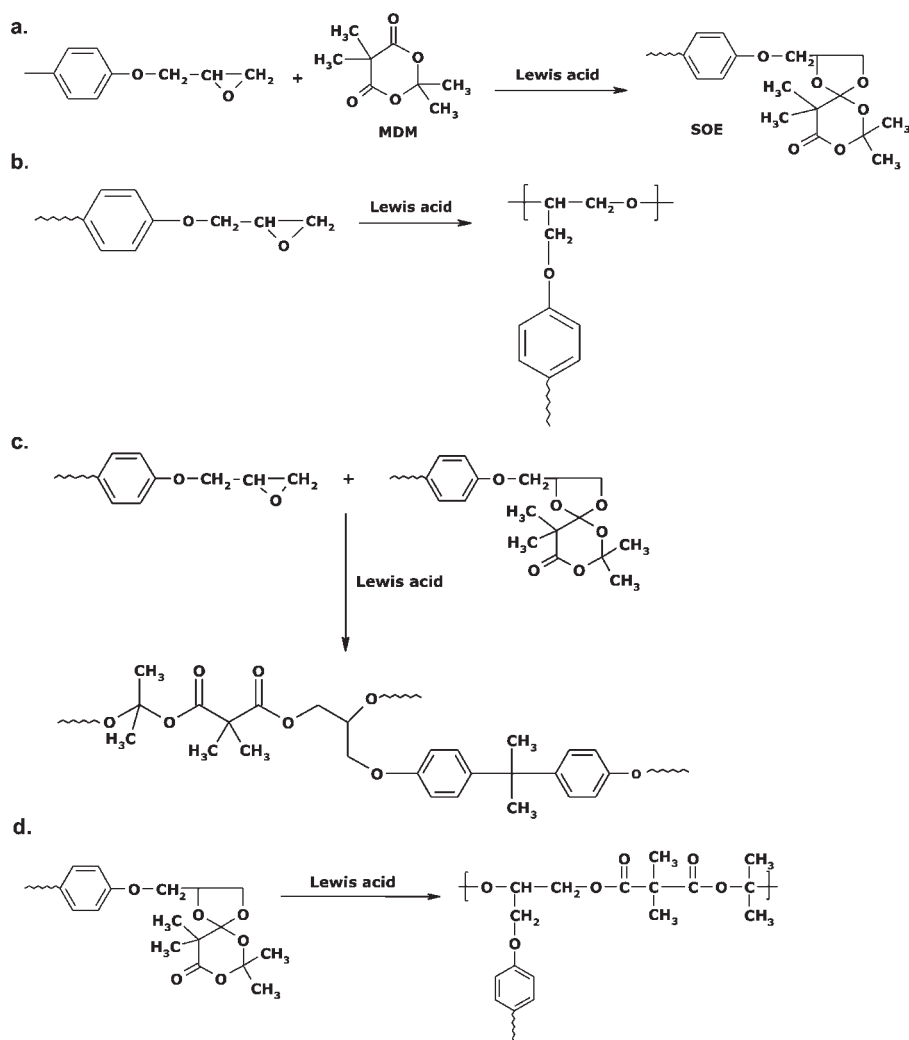
Scheme 1 Reactive processes during curing.

not big differences in the evolution of epoxide groups. To understand the reactive process, we should take into account that in the reactive mixture there are four epoxy groups per MDM group. Thus, lanthanum salt, in the initial steps, leads to a quicker evolution of MDM in comparison with epoxide, and this indicates that in addition to the formation of SOE, a superficial elimination, facilitated by the easy sublimation, also occurs. This fact is related to the low proportion of linear ester groups in the final material (Fig. 4). In contrast, with the ytterbium salt, the SOE formation and the homopolymerization of epoxide occur simultaneously from the beginning of curing, and a much lower elimination by sublimation of MDM occurs (Fig. 2). This is confirmed by the FTIR spectrum of the final material, in which the use of $Yb(OTf)_3$ produces a high proportion of linear ester. This different behavior can be related to the higher Lewis acid character of the ytterbium cation, which leads to a quicker curing, and so a lower elimination of MDM by sublimation occurs. From the normalized areas of the carbonyl linear ester absorption in both spectra (Fig. 4), we can estimate that the relation of linear ester groups in both materials is about 3.5.

Calorimetric studies

The curing of the mixtures was studied, and T_g of the materials was determined by means of calorimetry. Table I shows the results obtained. T_g's are similar for both initiators, but with the amount of MDM in the mixture increasing, T_g slightly decreases because of the flexibility introduced by the linear ester moiety. The experimental reaction enthalpy decreases when the proportion of MDM increases. This is due to the low opening enthalpy that has evolved from the nonstrained MDM ring. The heat released per epoxy equivalent is not as different but is slightly lower when lanthanum triflate is the initiator, and this can be justified by the endothermic sublimation process of MDM. The values from the curing of pure DGEBA with both initiators were added to the table for com-
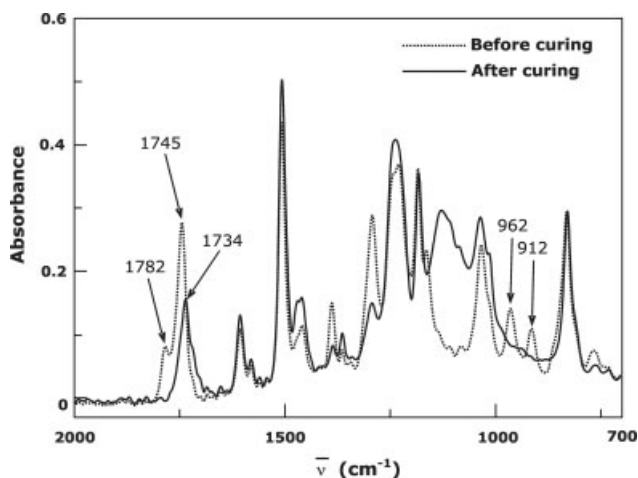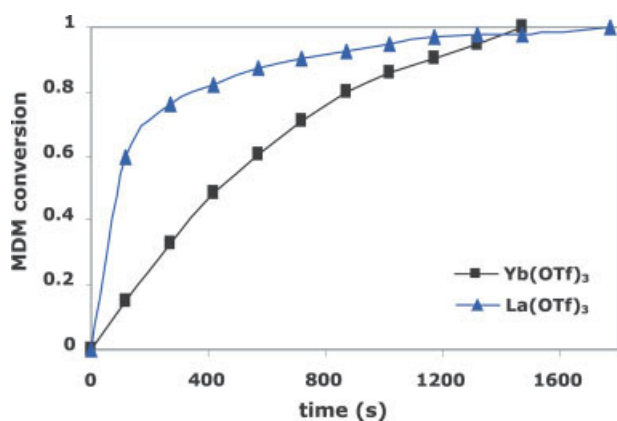
Figure 1 ATR–FTIR spectra of a 2 : 1 mol/mol mixture of DGEBA and MDM with 0.015 mol of Yb(OTf)$_3$ before and after curing at 150°C.

Figure 3 Epoxy conversion degree (912 cm^{-1}) versus the time for the 2 : 1 mol/mol DGEBA/MDM formulation with 0.015 mol of each initiator during curing at 150°C by ATR–FTIR. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
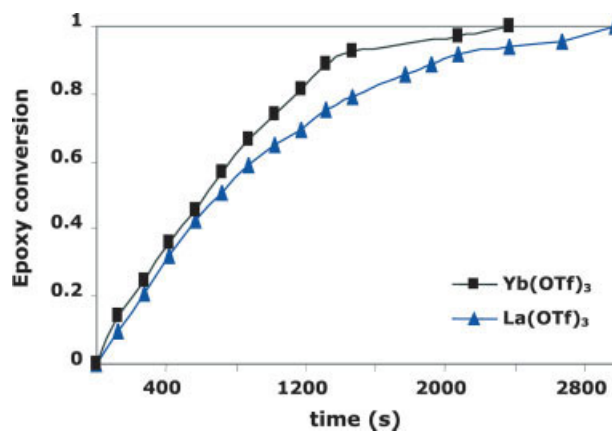
parison with the mixtures. The maximum of the curing exotherm shifts to lower temperatures as the proportion of MDM increases, but it is higher for the lanthanum initiator, indicating lower reactivity.

Table I shows the kinetic parameters associated with the dynamic curing by DSC for a conversion of 0.5. The values of the activation energies are similar for all the mixtures, but they are higher for the systems initiated by ytterbium triflate. This trend is not very significant and does not clearly show the acceleration effect of MDM due to the compensation effect between the activation energy and the pre-exponential factor.[16,21]

To show more clearly the effect of MDM on the curing kinetics, the rate constant at 150°C was calculated. It can be seen that the addition of MDM increases the rate constant, causing the curing reac-
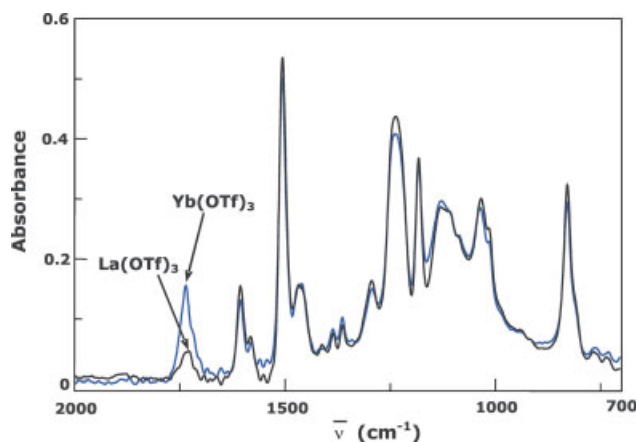
tion to accelerate. Ytterbium triflate leads to higher rate constants, which can be attributed to the higher Lewis acidity of the cation. Figure 5 shows plots of the conversion degree against the temperature for the mixtures with different proportions of MDM initiated by ytterbium and lanthanum triflates. In both cases, the addition of MDM accelerates the curing process in the entire range in comparison with pure DGEBA. However, there are some slight differences between the effects of both initiators. With ytterbium triflate, the increase in the proportion of MDM in the curing mixture leads to a slightly progressive acceleration in the entire range. On the other hand, lanthanum triflate leads to a different behavior before and after 50% conversion, especially with the mixture containing the highest proportion of MDM. This behavior

Figure 2 MDM conversion degree (965 cm^{-1}) versus the time for the 2 : 1 mol/mol DGEBA/MDM formulation with 0.015 mol of each initiator during curing at 150°C by ATR–FTIR. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 4 ATR–FTIR spectra of the materials obtained after curing at 150°C from DGEBA/MDM mixtures (2 : 1 mol/mol) with 0.015 mol of ytterbium or lanthanum triflates. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Calorimetric Data and Kinetic Parameters of the Curing of Several Formulations Initiated by Lanthanide Triflates

Entry	Formulation[a]	T_g (°C)[b]	ΔH (J/g)[c]	ΔH (kJ/ee)[d]	T_{max} (°C)[e]	E_a (kJ/mol)[f]	$\ln A$ (s^{-1})[g]	$k_{150°C} \cdot 10^3$ (s^{-1})[h]
1	1 : 0.006 DGEBA/Yb	135	519.7	95.6	184	90.7	18.09	0.45
2	3 : 1 : 0.021 DGEBA/MDM/Yb	111	427.6	91.1	175	86.5	17.35	0.70
3	2 : 1 : 0.015 DGEBA/MDM/Yb	107	396.5	90.1	174	87.9	17.74	0.71
4	1 : 1 : 0.009 DGEBA/MDM/Yb	96	325.4	88.2	174	90.1	18.46	0.78
5	1 : 0.006 DGEBA/La	127	513.5	94.4	192	79.8	14.59	0.30
6	3 : 1 : 0.021 DGEBA/MDM/La	110	422.1	89.8	190	81.6	15.40	0.41
7	2 : 1 : 0.015 DGEBA/MDM/La	105	394.1	89.6	188	80.4	15.15	0.44
8	1 : 1 : 0.009 DGEBA/MDM/La	91	308.6	84.8	176	76.6	14.05	0.45

[a] The compositions of the formulations are given as molar ratios.
[b] Glass-transition temperature obtained by DSC in the second scan after dynamic curing.
[c] Enthalpy per gram of mixture.
[d] Enthalpy per equivalent of epoxy groups.
[e] Temperature of the maximum degradation rate calculated by thermogravimetry.
[f] Activation energy evaluated by the isoconversional integral method [eq.(3)] applied at a conversion of 0.5.
[g] Pre-exponential factor for kinetic model R$_3$ in which $g(\alpha) = [1 - (1 - \alpha)^{1/3}]$.
[h] Rate constant at 150°C calculated with the Arrhenius equation:

$$\ln k = \ln A - \frac{E}{RT}.$$

could be explained on the basis of the sublimation process of MDM previously mentioned and by the different extent to which each reaction occurs during curing.

Figure 6 shows the dependence of the activation energy on the degree of conversion calculated with the isoconversional method [eq. (3)][22] for all the samples studied. As we can see, with ytterbium triflate, the higher the proportion is of MDM, the higher the initial activation energy is, but over 40% conversion, the differences among them are slight, and all are lower than that of pure DGEBA, which has been introduced as a reference. However, a different trend

is observed for lanthanum triflate initiated curing. In this case, lower activation energy in the first part of the process is observed for the 1 : 1 mol/mol DGEBA/MDM mixture, whereas similar values are observed for the other samples, possibly because of the sublimation process, which overlaps with curing.
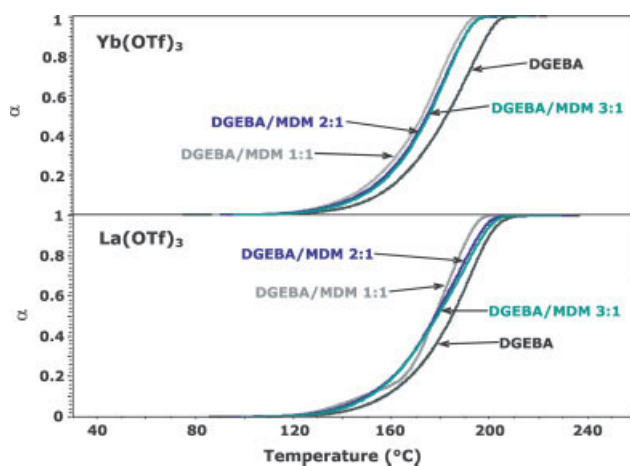
Figure 5 Conversion degree (α) versus the temperature of curing for DGEBA and DGEBA/MDM mixtures with different molar ratios initiated by Yb(OTf)$_3$ or La(OTf)$_3$ from dynamic DSC experiments. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
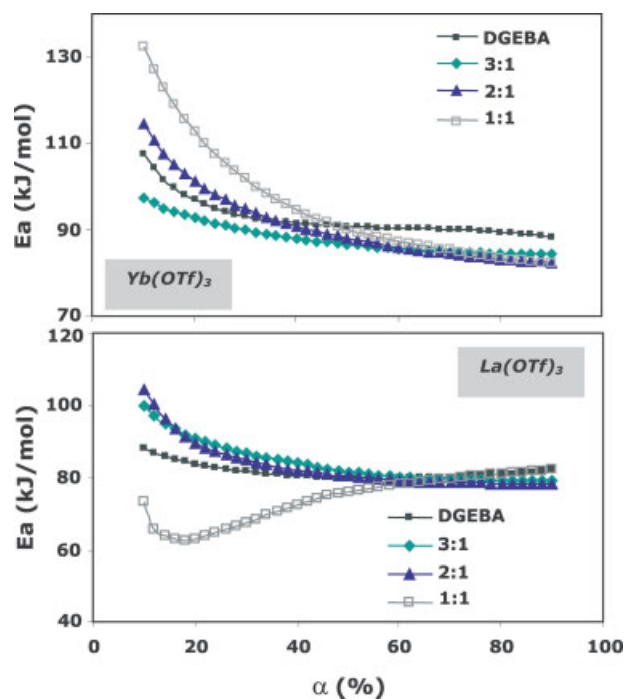
Figure 6 Dependence of the activation energy (E_a) on the degree of conversion (α) for DGEBA and DGEBA/MDM (mol/mol) formulations initiated by Yb(OTf)$_3$ or La(OTf)$_3$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
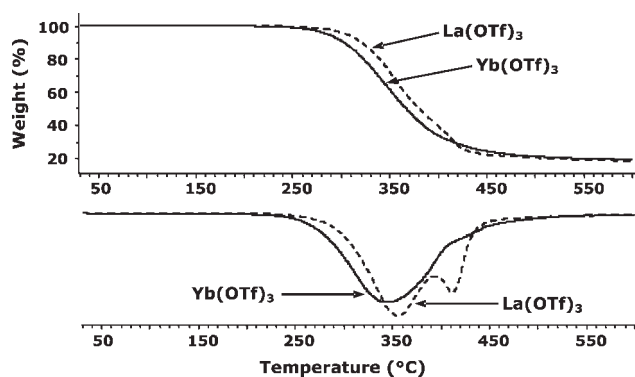
Figure 7 TGA and DTG curves at 10°C/min under an N_2 atmosphere of two thermosetting materials obtained from the 2 : 1 mol/mol DGEBA/MDM formulation initiated by 0.015 mol of ytterbium or lanthanum triflates.

With over 60% conversion, all the samples have similar activation energies. The general decrease observed between degrees of conversion of 10–60% can be related to the autocatalytic effect.

Thermogravimetric studies

In a previous study,[9] we demonstrated the enhanced degradability of thermosets obtained by the copolymerization of DGEBA with MCP due to the formation of tertiary ester groups in the network. From the analysis of the volatiles that evolved on heating, we could detect the rupture of these ester groups and also the breakage of the ether linkages. These ruptures occurred at lower temperatures when ytterbium triflate was used as the initiator.

Figure 7 shows the TGA and differential thermogravimetry (DTG) curves for the degradation of the materials obtained from the 2 : 1 mol/mol DGEBA/MDM formulation initiated with ytterbium and lanthanum salts. The thermal stability of the material obtained with lanthanum triflate is higher, and the

bimodal shape of its DTG curve is most characteristic. In the previous study with MCP,[9] we observed a three-modal DTG curve for the analogous material, with a broad peak at a lower temperature, which is not found in the MDM curves. Therefore, we think that the spiranic structure of MCP facilitated the degradative process.

Table II collects the thermogravimetric data obtained for all the formulations studied. Again, in this work, we can confirm that when the proportion of the lactone is increased, the degradability of the material also increases, and the materials obtained with ytterbium triflate begin their degradation at lower temperatures than those obtained with lanthanum triflate. This fact may be related to the higher content of linear ester groups in the network and also to the catalytic effect of ytterbium in the degradation. The catalytic effect should contribute because the same trend can be observed in samples 1 and 5, in which there are no ester groups. The addition of lactone to DGEBA samples mainly affects the initial steps of the process, and this is worth it to increase the reworkability of the electronic devices. If we compare the temperatures of the initial degradation with those previously published, we can conclude that the spiranic MCP lactone favors degradation.[9]

The kinetic parameters for the degradation (E_a, A, and k) were calculated only for the ytterbium triflate cured materials, which show a unimodal degradation curve, because the appearance of more than one peak for lanthanum triflate cured materials makes the kinetic comparison difficult. Using a procedure similar to that previously described for the curing of DGEBA/ MDM mixtures, we obtained the values collected in Table III. The values of k confirm a quicker degradation of the materials when a higher proportion of MDM is added for the modification of DGEBA. Moreover, the values of k are slightly lower than those obtained from the modification of DGEBA with MCP.

TABLE II
Thermogravimetric Data, Densities, and Shrinkage of the Materials Obtained from the Different Formulations

| Entry | Formulation[a] | T (°C)[b] | T_{max} (°C)[c] | Char yield (%)[d] | Density (g/cm³) | | Shrinkage (%) |
					Initial mixture	Final material	
1	1 : 0.006 DGEBA/Yb	287	345	20	1.158	1.192	2.9
2	3 : 1 : 0.021 DGEBA/MDM/Yb	265	337	19	1.165	1.191	2.2
3	2 : 1 : 0.015 DGEBA/MDM/Yb	262	340	18	1.167	1.190	2.0
4	1 : 1 : 0.009 DGEBA/MDM/Yb	253	355	17	—	—	—
5	1 : 0.006 DGEBA/La	303	354	19	1.158	1.193	3.0
6	3 : 1 : 0.021 DGEBA/MDM/La	286	361	18	1.161	1.192	2.7
7	2 : 1 : 0.015 DGEBA/MDM/La	282	355	18	1.164	1.193	2.5
8	1 : 1 : 0.009 DGEBA/MDM/La	272	373	17	—	—	—

[a] The compositions of the formulations are given as molar ratios.
[b] Temperature of 2% weight loss calculated by thermogravimetry.
[c] Temperature of the maximum degradation rate calculated by thermogravimetry.
[d] At 600°C.

TABLE III
Kinetic Parameters of the Thermal Decomposition of Ytterbium Triflate Initiated Materials

Entry	Formulation[a]	E_a (kJ/mol)[b]	$\ln A$ (s^{-1})[c]	$k_{300°C} \cdot \times 10^3$ (s^{-1})[d]
1	1 : 0.006 DGEBA/Yb	155.4	23.43	0.1016
2	3 : 1 : 0.021 DGEBA/MDM/Yb	160.8	24.83	0.1340
3	2 : 1 : 0.015 DGEBA/MDM/Yb	144.0	21.55	0.1715
4	1 : 1 : 0.009 DGEBA/MDM/Yb	105.2	14.00	0.3016

[a] The compositions of the formulations are given as molar ratios.
[b] Activation energy evaluated by the isoconversional integral method applied at a conversion of 0.5.
[c] Pre-exponential factor for the kinetic model with $n = 3$, in which $g(\alpha) = 2^{-1}[-1 + (1 - \alpha)^{-2}]$.
[d] Rate constant at 300°C calculated with the Arrhenius equation:

$$\ln k = \ln A - \frac{E}{RT}.$$

Shrinkage

In a previous work,[8] we put into evidence the expandable character of MCP in its cationic copolymerization with DGEBA, in which we observed that the higher the proportion was of MCP in the sample, the lower the overall shrinkage was. However, the most important fact is the shrinkage after gelation because it occurs in the gel state when the material lacks mobility and is the cause of the internal stresses in the material, which make its properties as a coating worse.[20] Furthermore, when a monomer with a functionality of two (MCP or MDM) is added to another with a functionality of four (DGEBA), the network's crosslink density decreases, and the degree of conversion at the gelation point increases.[23,24] This fact was experimentally proved in similar systems by thermomechanical analysis.[4]

The expandable character of MCP was proved and attributed to the change in the dipolar moment by the opening of the lactone ring.[8] Moreover, the amount of shrinkage is related to the size of the ring being opened; in general, the larger the ring is, the smaller the shrinkage is.[20] Therefore, six-membered lactones should produce a larger expansion on polymerizing than five-membered lactones. However, as we said before, we cannot discard a possible influence of the spiranic structure. Therefore, the evaluation of the shrinkage during the curing of DGEBA/MDM mixtures could shed light on the origin of the expandable character.

Table II shows the densities of the mixtures before and after curing and the calculated global shrinkage. As we can see, the addition of MDM leads to a higher density of the uncured mixture and to a reduction of the shrinkage, which is more important for the ytterbium salt initiated curing because of the incorporation of a higher proportion of MDM. The lower shrinkage is a result of the higher extent of the polymerization reactions in which SOEs open. It should be mentioned that the formation of SOE, which takes place at the beginning of the curing, occurs with shrinkage, whereas its opening occurs with expansion at the end of the process. In this way, the shrinkage in the gel state is much lower. Because of the reduction of the global shrinkage found experimentally in DGEBA/MDM curing, we could confirm the expandable character of the substituted MA ring, which on opening should reduce the interactions between the polymeric chains because of the change in the dipolar moment. In previous studies with other five-membered lactones,[2,4] we did not observe a reduction of the global shrinkage, but the shrinkage after gelation was reduced when the proportion of lactone was increased in the reactive mixture.

The results obtained in this study allow us to confirm that the copolymerization of DGEBA epoxy resins with functional cyclic monomers is a convenient route to simultaneously improve some properties of epoxy thermosets.

CONCLUSIONS

The modification of DGEBA by copolymerization with MDM using ytterbium and lanthanum triflates as initiators incorporates tertiary linear ester moieties into the network (in higher proportions with ytterbium triflate).

The addition of MDM to the DGEBA resins accelerates the curing process, the curing rate being higher in the ytterbium-initiated samples because of the higher Lewis acidity of the cation.

The addition of MDM to DGEBA slightly reduces T_g of the materials.

The expandable character of MDM has been demonstrated by the reduction of the global shrinkage upon the curing of mixtures of DGEBA and MDM.

The degradability of these materials increases with the proportion of MDM, and ytterbium triflate leads to higher degradability.

References

1. Ivin, J. K.; Saegusa, T. In Ring Opening Polymerization; Ivin, J. K.; Saegusa, T., Eds.; Elsevier Science: New York, 1984; Vol. 1.
2. Mas, C.; Ramis, X.; Salla, J. M.; Mantecón, A.; Serra, A. J Polym Sci Part A: Polym Chem 2003, 41, 2794.
3. Giménez, R.; Fernández-Francos, X.; Salla, J. M.; Serra, A.; Mantecón, A.; Ramis, X. Polymer 2005, 46, 10637.
4. Mas, C.; Ramis, X.; Salla, J. M.; Mantecón, A.; Serra, A. J Polym Sci Part A: Polym Chem 2006, 44, 1711.
5. Wang, L.; Li, H.; Wong, C. P. J Polym Sci Part A: Polym Chem 2000, 38, 3771.
6. Li, H.; Wong, C. P. IEEE Trans Adv Packaging 2004, 27, 165.
7. Chen, J.-S.; Ober, C. K.; Poliks, M. D.; Zhang, Y.; Wiesner, U.; Cohen, C. Polymer 2004, 45, 1939.
8. González, L.; Ramis, X.; Salla, J. M.; Mantecón, A.; Serra, A. J Polym Sci Part A: Polym Chem 2006, 44, 6869.
9. González, L.; Ramis, X.; Salla, J. M.; Mantecón, A.; Serra, A. Polym Degrad Stab 2007, 92, 596.
10. Garcia, S. J.; Serra, A.; Suay, J. J Polym Sci Part A: Polym Chem 2007, 45, 2316.
11. Lanthanides: Chemistry and Use in Organic Synthesis; Kobayashi, S., Ed.; Topics in Organometallic Chemistry; Springer-Verlag: Berlin, 1999.
12. Davidson, D.; Bernhard, A. S. J Am Chem Soc 1948, 70, 3426.
13. Coats, A. W.; Redfern, J. P. Nature 1964, 201, 68.
14. Kissinger, H. E. Anal Chem 1957, 29, 1702.
15. Boey, F. Y. C.; Qiang, W. Polymer 2000, 41, 2081.
16. Xiong, Y.; Boey, F. Y. C.; Rath, S. K. J Appl Polym Sci 2003, 90, 2229.
17. Criado, J. M. Thermochim Acta 1978, 24, 186.
18. Ramis, X.; Salla, J. M.; Cadenato, A.; Morancho, J. M. J Therm Anal Calorim 2003, 72, 707.
19. Bailey, W. J.; Sun, R. L. Polym Prepr (Am Chem Soc Div Polym Chem) 1972, 13, 281.
20. Expanding Monomers: Synthesis, Characterization and Applications; Sadhir, R. K.; Luck, M. R., Eds.; CRC: Boca Raton, FL, 1992.
21. Vyazovkin, S.; Linert, W. J Solid State Chem 1995, 114, 392.
22. Vyazovkin, S.; Lesnikovich, A. Thermochim Acta 1992, 203, 177.
23. Flory, P. J. Principles of Polymer Chemistry; Cornell University Press: Ithaca, NY, 1953.
24. González, S.; Fernández-Francos, X.; Salla, J. M.; Serra, A.; Mantecón, A.; Ramis, X. J Polym Sci Part A: Polym Chem 2007, 45, 1968.