

MICROWAVE ACCELERATE POLYMERIZATION OF 2-PHENOXYMETHYL-1,4,6-TRIOXASPIRO [4,4] NONANE WITH DIGLYCIDYL ETHER OF BISPHENOL A

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Abstract

We studied for the first time the cationic copolymerization of the SOE: 2-phenoxyethyl-1,4,6-trioxaspiro [4,4] nonane with diglycidyl ether of Bisphenol A (DGEBA) under microwave irradiation using ytterbium and lanthanum triflates as initiators. A comparison with thermal heating showed a great enhancement in the reaction rates and a higher SOE incorporation in the network. The double ring-opening of SOE reduces the usual shrinkage of epoxy resins on curing, and it was lower under microwave irradiation. Moreover, the ytterbium triflate initiator leads to a higher incorporation of linear ester moieties in the network than lanthanum triflate.

Keywords: cationic polymerization; crosslinking; microwave; spiroorthoester; epoxy resins; lanthanide triflate

INTRODUCTION

The curing of thermoset polymers such as epoxy resins has become increasingly important, arising from their application as coatings, adhesives and encapsulants in

microelec-tronic applications. In particular, the requirement for higher performing systems has also led to unacceptably long cure times

become the bottleneck of the whole production process.

The incentive for using alternative non thermal curing methods is typically to accelerate the curing process and thus reduce the time of cure. These include the use of ultraviolet (UV) light, gamma rays and electron beams. UV and electron beam curing have limited application due to their poor penetration ability and limited dose rate. Gamma rays have enormous radiation hazards and environmental issues. In many cases, the use of microwave irradiation appears to be a more selective and much faster approach to the synthesis and also leads to higher yields for a number of organic and polymer reactions compared to classical thermal heating.¹⁻³ Micro-wave curing has been also found to be a viable alternative method for the curing of thermoset polymers, with a significant increase in the rate of reaction.⁴⁻⁶

Another disadvantage that epoxy resins present is their shrinkage during curing that can cause poor adhesion to a substrate, delamination, microvoids and microcracks, which in turn can reduce the durability of the materials. A number of different techniques have been employed to reduce shrinkage, such as the addition of fillers and also curing at lower temperatures. However, these methods are not totally efficient as the shrinkage is due to the crosslinking reaction

rather than as a consequence of production methods. One way of solving this problem is to copolymerize the epoxy resins with the so-called "expanding monomers",⁷ which are monomers that lead to zero shrinkage or even positive expansion during polymerization. Some kinds of bicyclic monomers such as spiroorthoesters (SOEs), spiroorthocarbonates (SOCs), and bicycloorthoesters (BOEs) have been reported to maintain their volume or actually expand during the double ring-opening polymerization.⁷⁻¹⁰ SOEs can be readily synthesized from epoxides and lactones^{11,12} and undergo cationic ring-opening polymerization by Lewis acid catalysts.

This work focuses on the first reported copolymerization of the SOE: 2-phenoxyethyl-1,4,6-trioxaspiro [4,4] nonane with diglycidyl ether of Bisphenol A (DGEBA) under micro-wave conditions and a comparison is made with conventional thermal conditions. Furthermore, we depict the influence of SOE incorporation in the network on shrinkage during curing.

EXPERIMENTAL

Materials

Diglycidyl ether of bisphenol A (Epikote Resin 827, Shell Chemicals; epoxy equiv. = 182.08 g/equiv), phenyl glycidyl ether (PGE; Aldrich) and γ -butyrolactone

(γ -BL; Aldrich) were used as received. Ytterbium (III) and lanthanum (III) trifluoromethanesulfonates (Aldrich) and boron trifluoride diethyl etherate ($\text{BF}_3 \cdot \text{OEt}_2$; Aldrich) were used without purification.

Instrumentation

Microwave irradiation was performed in a CEM microwave, model Discover, with IR temperature sensor and power control.

The FTIR analysis was monitored with a FTIR-680PLUS spectrophotometer with a resolution of 4 cm^{-1} in the absorbance mode.

Calorimetric studies (DSC) were carried out on a Mettler DSC-821e thermal analyzer in covered Al pans under N_2 at scan rate of $10 \text{ }^\circ\text{C}/\text{min}$ to determine the degree of conversion (α) and at a heating rate of $20 \text{ }^\circ\text{C}/\text{min}$ to determine the glass transition temperatures (T_g 's).

TGAs were carried out with a Mettler TGA/SDTA 851e thermobalance. Cured samples with an approximate mass of 10 mg were degraded between $30 \text{ }^\circ\text{C}$ and $800 \text{ }^\circ\text{C}$ at a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$ in atmosphere of N_2 or air.

Thermodynamomechanical analysis (DMTA) were carried out with a TA DMA 2928, working with a three point bending clamp from $30 \text{ }^\circ\text{C}$ to

$150 \text{ }^\circ\text{C}$ with heating rate of $3 \text{ }^\circ\text{C}/\text{min}$.

Table 1. Curing and Postcuring conditions for DGEBA/SOE-PGE system Yb(OTf)₃ and La(OTf)₃ under microwave and thermal conditions.

Assay	Curing Conditions		Postcuring Conditions	
	Temperature (°C)	Time (min)	Temperature (°C)	Time (min)
Yb-MW	60	6	100	8
Yb-OVEN	120	60	140	90
La-MW	60	8	100	10
La-OVEN	120	100	140	140

The densities of materials were measured with a Micromeritics Accu-pyc 1330 TC gas pycnometer at $30 \text{ }^\circ\text{C}$.

Preparation of the curing mixtures

The mixtures were prepared by mixing 2 g (5.4 mmol) of DGEBA and 0.64 g (2.7 mmol) of SOE-PGE with 1 phr (1 part per 100 of mixture weight/weight) of the selected triflate.

Curing procedure

The sample was placed into a 5 mm (internal diameter) glass tube inside the microwave reactor vial (10 mL) and subjected to MW irradiation using a power of 50 W. Overheating of reaction mixtures was avoided by cooling with compressed air. The reaction mixtures without

microwave irradiation were heated in a standard oven. The curing conditions are listed in table 1.

The determination of the extent of polymerization was as follows: after a time of heating the sample under mi-

as catalyst. Mixtures of SOE-PGE and DGEBA reacted using lanthanide triflates as initiator.

We found that the reaction of SOE-PGE and DGEBA with lanthanide triflates as initiators takes place under microwave irradiation and thermo-sets can be obtained in a

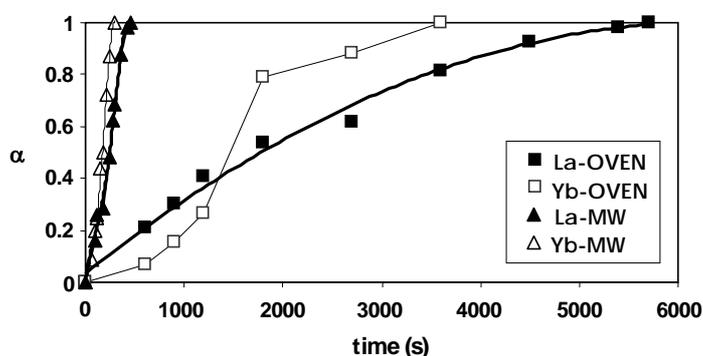


Figure 1. Plot of the conversion against the cure time for the DGEBA/SOE-PGE system initiated by Yb(OTf)₃ and La(OTf)₃ for microwave and thermal curing.

crowave or thermal conditions, it was quickly cooled by liquid nitrogen quench to stop the polymerization. The extent of polymerization was determined by DSC and the conversion of the reactive species was determined by FTIR measurements.

RESULTS AND DISCUSSION

The synthesis of 2-phenoxyethyl-1,4,6-trioxaspiro [4,4] nonane (SOE-PGE) was carried out by a previously described procedure¹¹ from PGE and γ -BL using BF₃·OEt₂

significantly shorter reaction time in comparison to conventional heating. Figure 1 shows the reaction conversion against curing times. After curing at different times the residual enthalpy ($\Delta H_{residual}$) was calculated by dynamic DSC. The degree of conversions were calculated by the following equation:

$$\alpha_t = \frac{\Delta H_{total} - \Delta H_{residual}}{\Delta H_{total}}$$

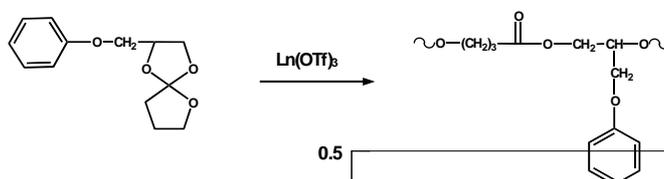
where ΔH_{total} is the heat of reaction obtained in a dynamic DSC of the initial mixture. As can be seen,

thermal and microwave initiated reactions with ytterbium triflate are faster. However, the most significant difference lies in the reaction conditions, that is, the reaction under microwave irradiation is much faster than conventional thermal heating with both initiators. Thus, only 250-

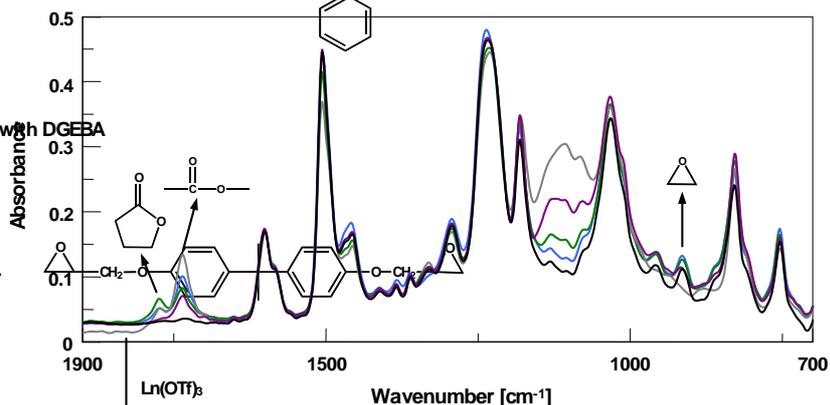
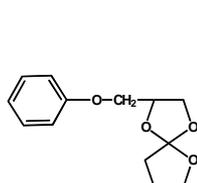
300 seconds are necessary to reach the total conversion under microwave irradiation against 3600-5700 seconds under thermal conditions.

In Scheme 1 are represented the

a) Homopolymerization of SOE-PGE



b) Copolymerization of SOE-PGE with DGEBA



c) Homopolymerization of DGEBA

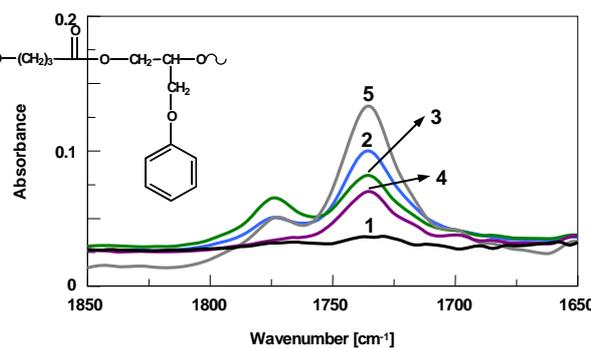
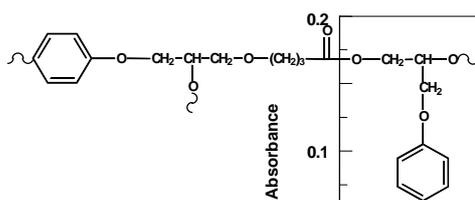


Figure 2. FTIR spectra of the initial mixture without initiator (1), just after add 1phr of Yb(OTf)₃ (2), after 300 s reaction (3), after 2100 s reaction (4), and at the end of curing (5) of DGEBA/SOE-PGE : 2/1 (mol/mol) under thermal conditions.
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Scheme 1

different processes for the cationic copolymerization of DGEBA/SOE-PGE, which are usually expected: a) homopolymerization of SOE-PGE; b) copolymerization of SOE-PGE and DGEBA; and c) homopolymerization of DGEBA.

To follow the evolution of the different reactive species the FTIR was used. Figure 2 shows the FTIR spectra of the 2/1 (mol/mol) DGEBA/SOE-PGE mixture initiated by 1 phr of Yb(OTf)₃ at different times of reaction under thermal conditions: without initiator (1); just after addition the initiator (2); at two intermediate curing times, 300 sec (3) and 2100 sec (4); and after completely curing (5).

As can be seen, the initial mixture (*spectrum 1*) shows an oxirane band at 914 cm⁻¹, due to the ring deformation, and does not show any carbonyl signals. Just after addition of the initiator (*spectrum 2*) two carbonyl signals appear, one at 1734 cm⁻¹ attributable to the linear ester moieties formed in the double ring-opening of the SOE, and another at 1770 cm⁻¹. This later band corresponds to the carbonyl group of γ -lactones¹³ which could be formed by the reversion of SOE to a γ -butirolactone (γ -BL) and epoxide (Scheme 2). The reversibility of SOEs was previously reported in the literature.¹⁴ The appearance of these two carbonyl bands implies that the SOE-PGE is very reactive at ambient temperature. After 300 sec (*spectrum 3*) a decrease of the band of linear ester and an increase

of the band of γ -BL is observed. This could be explained by a back biting process.¹⁵ The band of the γ -BL decreases in the next steps of the reaction, arising to zero at 2100 sec (*spectrum 4*), indicating that γ -BL completely reacts with glycidyl to form SOE groups. These SOE groups must homo-polymerize or copolymerize with DGEBA because an increase of the linear ester band was observed in the following steps. At the end of the curing (*spectrum 5*), the glycidyl band disappears indicating that the epoxide completely polymerizes. Furthermore, the band of γ -BL is newly formed, which seems to indicate that some degree of depolymerization by back biting takes place at the last steps of the curing, giving γ -BL which now cannot react with epoxy groups because they are not present, and γ -BL does not homopolymerize by thermodynamical reasons.^{16,17}

The evolution of these three species, SOE, lactone and epoxy, was followed by recording the FTIR spectrum of the samples after different curing times. The conversion of SOE groups was calculated from the variation of the carbonyl linear ester band at 1734 cm⁻¹, the conversion of γ -BL from the variation of the carbonyl band at 1770 cm⁻¹, and the conversion of epoxides from the decrease of the band at 914 cm⁻¹.

The absorbances were calculated in terms of peak areas. The

$$\alpha_{epoxy} = 1 - \left(\frac{\overline{A}_{914}^t}{\overline{A}_{914}^0} \right)$$

$$\overline{A}_{914}^t = \frac{A_{914}^t}{A_{1603}^t} = \left(\frac{\overline{A}_{1734}^t}{\overline{A}_{1734}^0} \right) = \frac{A_{914}^0}{A_{1603}^0}$$

$$\overline{A}_{1734}^t = \frac{A_{1734}^t}{A_{1603}^t} \quad \overline{A}_{1734}^\infty = \frac{A_{1734}^\infty}{A_{1603}^\infty}$$

conversions were determined by the Lambert-Beer Law from the normalized changes in absorbance respect to the band at 1603 cm^{-1} corresponding to the phenyl group in DGEBA and using the following equations:

$$\alpha_{\gamma\text{-BL}} = \left(\frac{\overline{A}_{1770}^t}{\overline{A}_{1770}^\infty} \right)$$

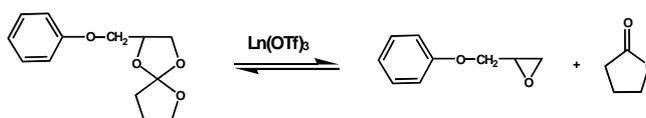
$$\overline{A}_{1770}^t = \frac{A_{1770}^t}{A_{1603}^t} \quad \overline{A}_{1770}^\infty = \frac{A_{1770}^\infty}{A_{1603}^\infty}$$

where:

$\overline{A}_{1734}^\infty = \frac{A_{1734}^\infty}{A_{1603}^\infty}$: is the highest value obtained for all the systems.

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different evolution in function of the reaction conditions and the initiator used. With ytterbium triflate, initially the linear ester content decreases, being higher under microwave conditions. This diminution of the ester band and a similar increase in the conversion of γ -BL could be associated to the back biting process, which forms γ -BL and diminishes the proportion of linear ester groups. When lanthanum triflate was used some differences were observed. A decrease of ester band also occurred in the first reaction stages, being more pronounced under thermal conditions. However, with this initiator, the higher amount of formed γ -BL could not be only explained by the back biting process above mentioned. Thus, other factors have been considered. An explanation could be the reversion of SOE groups to yield an epoxide and a lactone, therefore the epoxide absorption should increase in a similar proportion than the lactone band. However, this fact was not observed, maybe because of the homo-polymerization of



Scheme 2

Figures 3 and 4 show the conversion of SOE and γ -BL, respectively against time. As we can see, the two species follow a

epoxide reduces the proportion of the epoxy groups formed in this reversion reaction. Another possibility that could contribute to

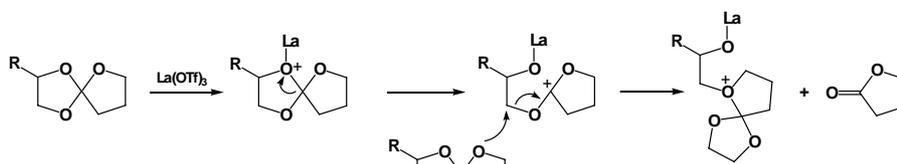
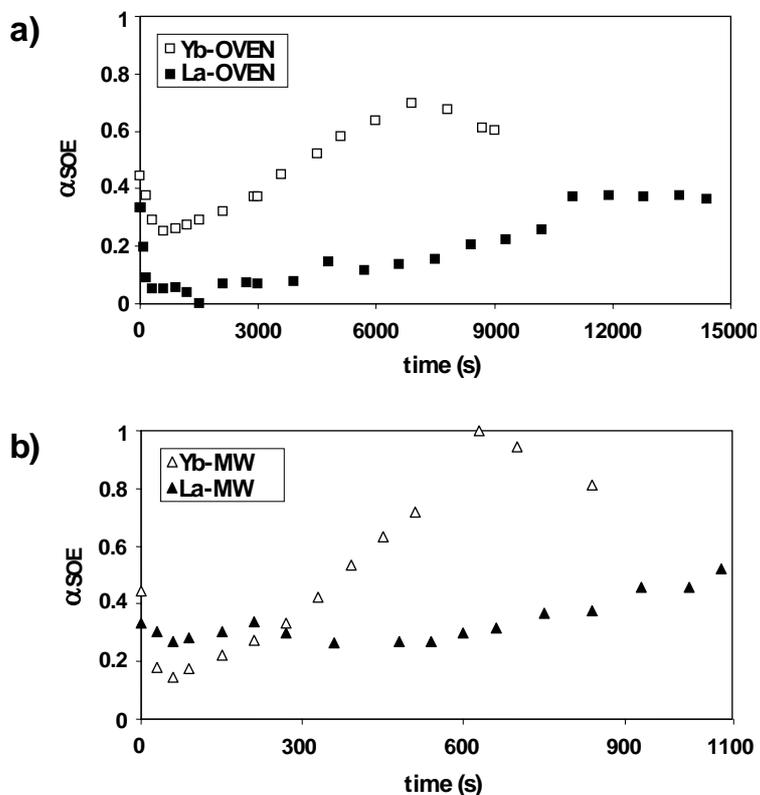


Figure 3. Plot of SOE conversion against the cure time for the DGEBA/SOE-PGE system initiated by Yb(OTf)₃ and La(OTf)₃ under thermal (a) and microwave (b) conditions.



the γ -BL formation lies in a different mechanism pathway in the ring-opening of SOEs (Scheme 3). The ring-opening of SOEs has been described⁷ that starts by a coordination of the Lewis acid to the ether oxygen of the SOE to form an oxonium cation, followed by isomerization into a carbonium cation stabilized by the two adjacent oxygen atoms. The propagation reaction is a nucleophilic attack by another monomer. Different pathways are possible in the ring-

opening of SOEs,¹⁸ leading some of them to the formation of γ -BL, being the most probable of these pathways represented in Scheme 3. The γ -BL generated in this reaction may in turn reacts with epoxy to get a new SOE group, what agrees with the decrease of the γ -BL conversion observed for all the systems studied. Some differences were observed related to curing conditions. Under conventional heating, the conversion of γ -BL beco-

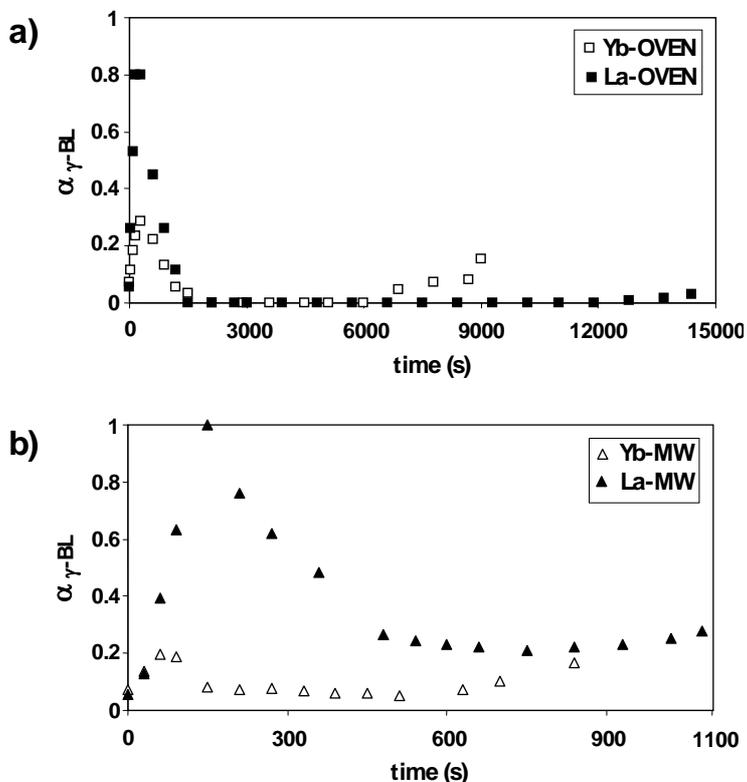


Figure 4. Plot of γ -BL conversion against the cure time for the DGEBA/SOE-PGE system initiated by $\text{Yb}(\text{OTf})_3$ and $\text{La}(\text{OTf})_3$ under thermal (a) and microwave (b) conditions.

mes to zero with both initiators at similar times. However, under microwave irradiation some amount of γ -BL remains unreacted. This difference could be explained by the faster reaction, which not allows the complete formation of SOE groups. The initial SOE and the SOE formed from γ -BL and epoxides can homopolymerize or copolymerize with DGEBA, thus, an increase of the conversion of SOE was observed.

At longer reaction times, clear differences between the two initiators and curing conditions were observed. With $\text{Yb}(\text{OTf})_3$ the incorporation of SOE to yield a poly(ether-ester) is higher than with $\text{La}(\text{OTf})_3$, what can be attributed to the higher Lewis acidity of $\text{Yb}(\text{OTf})_3$ which favours the reaction. We also observed that the conversion is higher under microwave conditions than in thermal conditions for both initiators.

SOEs takes place without shrinkage

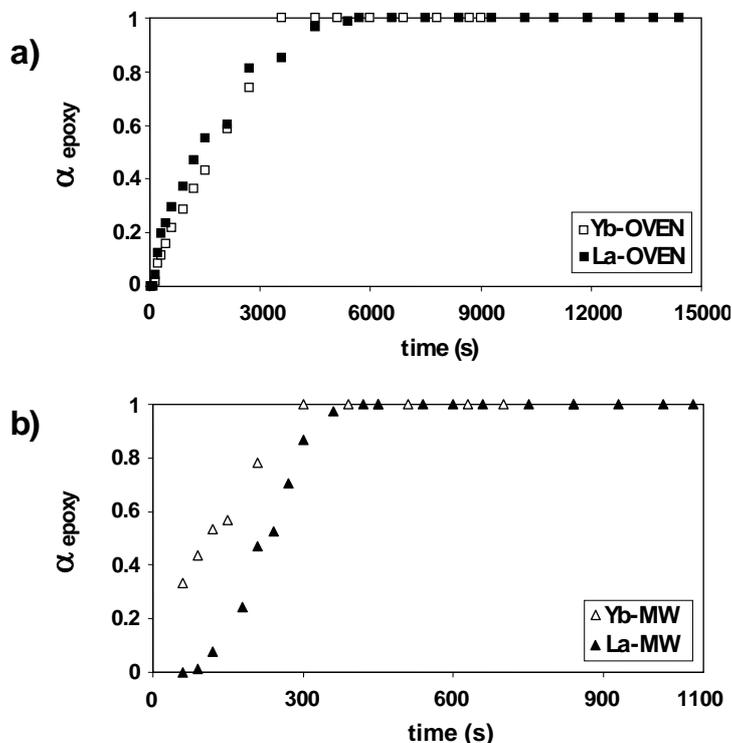


Figure 5. Plot of epoxy conversion against the cure time for the DGEBA/SOE-PGE system initiated by Yb(OTf)₃ and La(OTf)₃ under thermal (a) and microwave (b) conditions.

At the end of the curing process, a low diminution of the ester band was detected, being higher with Yb(OTf)₃ and under microwave irradiation, which indicates that the depolymerization process takes place in a higher extent.

Figure 5 depicts the conversion of epoxy groups, which in all cases is complete at relatively short times.

It has been reported that the cationic double ring-opening of

or even with expansion.^{19,20} Therefore, the volume changes in the crosslinking reaction of the mixtures DGEBA/SOE-PGE were evaluated by density measurements with a Micromeritics helium pycnometer at 30 °C before and after crosslinking (Table 2). The volume change was calculated with the following equation:

$$\Delta V (\%) = \frac{d_{\text{crosslinked polymer}} - d_{\text{initial mixture}}}{d_{\text{initial mixture}}} \times 100$$

where $d_{\text{crosslinked network}}$ is the density of the crosslinked material and d_{initial}

is also observed under conventional heating.

Table 2. T_g s of crosslinked polymers and densities before and after crosslinking and volume change upon crosslinking.

ASSAY	T_g (°C) ^a	Tan Delta (°C)	Density at 30 °C (g/cm ³)		Volume Change (%)
			Initial mixture	Crosslinked	
Yb-MW	70	79	1.178	1.192	1.1
Yb-OVEN	71	80	1.178	1.204	2.2
La-MW	64	77	1.178	1.197	1.6
La-OVEN	67	80	1.178	1.209	2.6

d_{mixture} is the density of the initial mixture of comonomers.

Although typical crosslinking of epoxy resins are generally accompanied by a significant volume shrinkage (above 3%, depending on the crosslinking mechanism),^{21,22} in all mixtures of glycidyl compounds with SOEs studied, the observed positive values, between 1.1-2.6, are lower than those observed in the crosslinking of pure DGEBA with lanthanide triflates (about 3%).^{23,24} This lower shrinkage on curing must be attributed to the expanding character of SOE moieties. Moreover, we observed a lower shrinkage under microwave irradiation than under conventional heating and it is lower with ytterbium triflate than with lanthanum triflate. This can be attributed to the higher SOE conversion at the end of the curing with Yb(OTf)₃. This later behaviour

The same table 2 collects the T_g values of the crosslinked materials obtained by DSC and Tan δ . T_g s as well as Tan δ are similar for all the samples. The materials obtained with ytterbium triflate, under both microwave and thermal conditions and lanthanum triflate under conventional heating showed similar shape of Tan δ plots, whereas the Tan δ plot of the material obtained with lanthanum triflate by microwave irradiation is broader, indicating a higher number of branching modes which produces a wider distribution of structures.

By TGA experiments we observed that the materials obtained under microwave conditions initiate the degradation at lower temperatures. Thus, the weight loss of 5% under nitrogen, was observed at 232 °C (with ytterbium triflate) and 238 °C (with lanthanum triflate). The thermally obtained materials start the degradation at 271 °C and 273

°C with ytterbium triflate and lanthanum triflate respectively. This higher de-gradability can be associated to a higher ester content in the network. In air, the degradations start at slightly lower temperatures. The temperature of the maximum rate degradation was similar for all materials, about 360° C under nitrogen atmosphere, and about 350° C under air.

CONCLUSIONS

It can be concluded from the above-described results that in all cases, the curing time was considerably shortened by microwave irradiation. Under these reaction conditions materials with a higher content of ester groups in the network, from SOE incorporation, were obtained and showed a lower shrinkage than conventional epoxy resins. Moreover, the ytterbium triflate initiator led to a higher incorporation of linear ester moieties in the network than lanthanum triflate.

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