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# Kinetic analysis by DSC of the cationic curing of mixtures of DGEBA and 6,6-dimethyl (4,8-dioxaspiro[2.5]octane-5,7-dione)

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## Abstract

The kinetics of the thermal cationic cure reaction of mixtures in different proportions of diglycidylether of bisphenol A (DGEBA) with 6,6-dimethyl (4,8-dioxaspiro[2.5]octane-5,7-dione) (MCP) initiated by ytterbium or lanthanum triflates or using a conventional initiator, $BF_3\cdot$MEA was investigated. The non-isothermal differential scanning calorimetry (DSC) experiments at a controlled heating rate was used for obtaining the kinetic parameters of the reactive systems. $BF_3\cdot$MEA and lanthanide triflates initiated curing systems follow a complete different kinetic model. Among lanthanide triflates, ytterbium is the most active initiator.

*Keywords:* Epoxy resins; Kinetics; Thermosets; Cationic polymerization; Calorimetry

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## 1. Introduction

The extraction of the maximum relevant information from non-isothermal data obtained by differential scanning calorimetry (DSC) techniques and the modelling of the kinetic process are common tasks in calorimetric data treatments. DSC is an experimental technique that can be used to evaluate the kinetics of a reactive system. The results of the kinetic study can be used for various purposes, i.e. to analyze how an initiator or different proportions of a co-reactant can affect a reactive system or how the temperature can affect the evolution of the reaction [1].

The cure reaction of thermosetting polymers have been studied extensively [2,3], among them epoxy resins studies are relevant because of their industrial applications [4–6]. However, most of the studies have been performed on epoxy-amine traditional systems and few studies are based on cationic systems [7,8].

The present study deals with the kinetics of the copolymerization reaction of diglycidylether of bisphenol A (DGEBA) with 6,6-dimethyl (4,8-dioxaspiro[2.5]octane-5,7-dione) (MCP) mixtures in several proportions using ytterbium and lanthanum triflates or boron trifluoride monoethylamine ($BF_3\cdot$MEA) as initiators. The materials obtained with lanthanide triflates have been demonstrated to be more degradable than conventionally crosslinked DGEBA materials [9] and that their curing takes place with a lower shrinkage [10]. The cationic copolymerization reaction between DGEBA and lactones are scarcely studied from the point of view of the kinetics [11–14]. As has been previously demonstrated [9] the copolymerization mechanism is rather complex, because lactones and epoxides react to form spiro orthoesters (SOEs) intermediates, which can polymerize or copolymerize with epoxies to form poly(ether-ester) structures. Moreover, epoxides can homopolymerize leading to polyether structures. In addition to these four elemental processes, cationic ring-opening polymerizations of cyclic monomers can occur by the activated chain end (ACE) or by the activated monomer (AM) mechanisms and also back-biting processes can take place [15]. All these processes overlap during curing and therefore only the global kinetic parameters of curing can be calculated. Moreover, physical processes also take place during curing (gelation and vitrification) that can affect not only the curing process but also the physical properties of the material.

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## 2. Experimental

### 2.1. Materials

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

6,6-Dimethyl-(4,8-dioxaspiro[2.5]octane-5,7-dione) (MCP) (Aldrich) was used as received.

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

### 2.2. Preparation of the curing mixtures

The samples were prepared by mixing the selected initiator in the corresponding amount of MCB and adding the required proportion of DGEBA with manual stirring. The prepared mixtures were kept at −18 °C before use. Lanthanide triflates are added in a proportion of 0.006 mol/mol of DGEBA and 0.03 mol/mol of MCB. Previous experiments showed that with $BF_3$·MEA it was necessary to add 0.096 mol/mol of DGEBA and 0.048 mol/mol of MCB to reach the complete curing.

### 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 2, 5, 10 and 15 °C/min. The calorimeter was calibrated using an indium standard (heat flow calibration) and an indium–lead–zinc standard (temperature calibration). The samples weighed approximately 5 mg.

## 3. Results and discussion

In a previous work [9] we studied the curing of mixtures of DGEBA/MCP initiated by ytterbium and lanthanum triflates and $BF_3$·MEA as Lewis acids. The proportions of DGEBA/MCP were 3:1, 2:1 and 1:1. We observed a moderate decrease of the $T_g$ values on increasing the proportion of MCP in the material in addition to a decrease in the global shrinkage during curing, which put into evidence the nature of MCP as expandable monomer. By FTIR spectroscopy we could prove the formation of linear ester linkages in the network and the complete curing of the mixtures. We observed the total disappearance of the epoxy absorption band, although several proportion of the intermediate SOE remained unreacted in the material.

In previous works [16,17] we observed that the higher the Lewis acidity of the lanthanide triflates (from lanthanum to ytterbium) the higher the curing rate. However, the $BF_3$ complex usually follows a different trend than lanthanide triflates because of the formation of the initiating active specie, $HBF_4$. Moreover, lanthanide triflates lead to the consumption of epoxide before the disappearance of MCP whereas with $BF_3$·MEA, MCP and epoxide react completely at the same time. Thus, a higher proportion of the boron initiator is always needed to reach the total curing and the materials showed a higher $T_g$, which seems to indicate that the curing proceeds by a different way. The differences in the structure of the cured materials could be proved by the degradation behavior by thermogravimetric analysis (TGA) [9,10].

In the present work we studied the kinetic of the curing process of these materials. Many exothermic polymerizations have difficulties for the determination of the heat of reaction trough isothermal experiments and the subsequent deduction of the kinetic from these values. When reactions are performed at high temperatures, some of the heat may be lost during the stabilization of the apparatus, whereas at low temperatures, the heat is released slowly and can fall below the sensitivity of the calorimeter. Another problem arises when a physical phenomenon (e.g. vitrification) takes place. One alternative in both cases is to simulate isothermal curing with non-isothermal data [18]. Thus, in this work we used the non-isothermal differential scanning calorimetry experiments at a controlled heating rate as the most suitable procedure for obtaining the kinetic parameters of the reactive systems.

Thermal data obtained from non-isothermal DSC for all the samples studied are collected in Table 1. As can be seen the total enthalpy per gram of the curing strongly decreases as the pro-

Table 1
Calorimetric and thermogravimetric data of all systems studied

| Entry | Formulation[a] | $T_g$ (°C) | $\Delta H$[b] (J/g) | $\Delta H$[c] (kJ/ee) | $T$[d] (°C) | $T_{max}$[e] (°C) |
|---|---|---|---|---|---|---|
| 1 | DGEBA/Yb 0.006 | 135 | 519.7 | 95.6 | 287 | 345 |
| 2 | DGEBA/MCP/Yb 3:1:0.021 | 117 | 430.3 | 91.5 | 241 | 335 |
| 3 | DGEBA/MCP/Yb 2:1:0.015 | 110 | 388.0 | 88.2 | 230 | 332 |
| 4 | DGEBA/MCP/Yb 1:1:0.009 | 105 | 314.4 | 84.4 | 214 | 319 |
| 5 | DGEBA/La 0.006 | 127 | 513.5 | 94.4 | 303 | 354 |
| 6 | DGEBA/MCP/La 3:1:0.021 | 105 | 418.6 | 89.1 | 250 | 350 |
| 7 | DGEBA/MCP/La 2:1:0.015 | 100 | 386.8 | 87.7 | 233 | 348 |
| 8 | DGEBA/MCP/La 1:1:0.009 | 95 | 307.4 | 83.4 | 216 | 344 |
| 9 | DGEBA/$BF_3$·MEA 0.096 | 160 | 460.0 | 86.6 | 332 | 360–433 |
| 10 | DGEBA/MCP/$BF_3$·MEA 3:1:0.336 | 156 | 391.0 | 84.5 | 296 | 333–429 |
| 11 | DGEBA/MCP/$BF_3$·MEA 2:1:0.240 | 147 | 337.1 | 78.0 | 288 | 330–425 |

[a] The compositions of the formulations are given in molar ratios.
[b] Enthalpies of curing per gram of mixture.
[c] Enthalpies of curing expressed by the equivalent of epoxy groups.
[d] Temperature of a 2% of weight loss calculated by thermogravimetry.
[e] Temperature of the maximum degradation rate calculated by thermogravimetry.

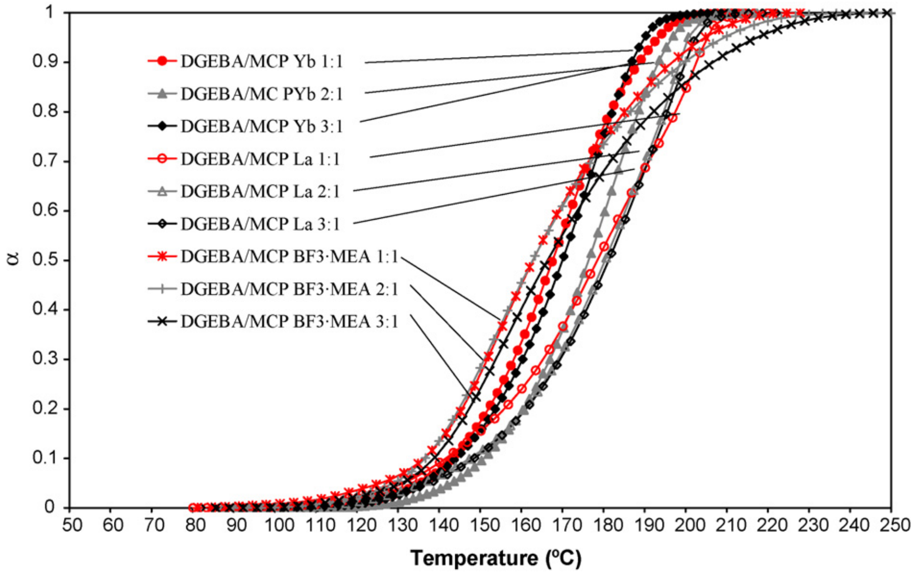

Fig. 1. Conversion degree against temperature for the curing of several DGEBA/MCP (mol/mol) formulations initiated by different Lewis acids obtained through dynamic DSC experiments.

portion of MCP increases. However, if we consider the enthalpy per epoxy equivalent this diminution is lower. We should take into account that the heat release is mainly due to the opening of the strained epoxy ring. If we consider the heat evolved during curing for the DGEBA/MCP samples cured with the different initiators, we observed that the ytterbium salt leads to the maximum heat and boron trifluoride to the lowest, which can be related to the proportion of the unreacted SOE remaining in the final material as observed by FTIR [9]. Moreover, when a higher proportion of MCP is present in the mixture the higher the proportion of unreacted SOE is. Figs. 1 and 2 show the variation of the conversion degree and the rate of conversion against the temperature of these formulations studied at a heating rate of 10 °C/min. Fig. 1 shows that all curing processes are activated above 80 °C and they are completed at 220 °C for lanthanide salts and even higher for the $BF_3$·MEA initiated systems. The most reactive systems at low temperatures are those initiated by $BF_3$·MEA and the ytterbium triflate systems are more active than the ones initiated by the lanthanum salt in all the range of temperatures. Similar trends are observed in Fig. 2. Moreover, the plots show that $BF_3$·MEA initiated systems have a very different kinetic behavior. Thus, these systems reach the maximum curing rate at low conversions, whereas lanthanide triflates lead to the highest curing rate at high conversions. Moreover a broad exotherm appears at low temperatures (100–130 °C), which is due to the formation of the initiating active species [19,20]. By increasing the amount of $BF_3$·MEA an important increase in this exotherm is observed. Moreover, by FTIR of the $BF_3$·MEA at 120 °C has been observed the conversion of $BF_3$ to $HBF_4$ which are the true initiator species. This conversion has been shown

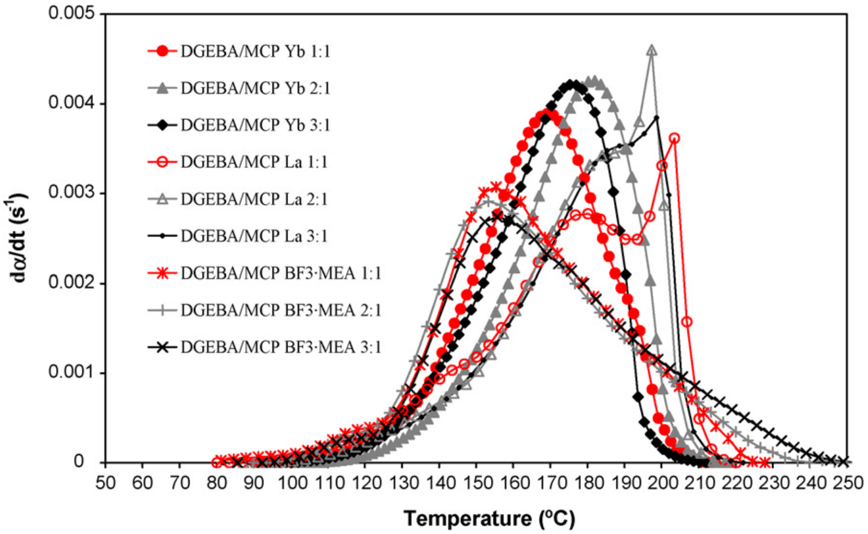

Fig. 2. Variation of the rate of conversion with the temperature of several DGEBA/MCP (mol/mol) formulations initiated by different Lewis acids obtained through dynamic DSC experiments.

by the appearance of an absorption band at 1034 $\text{cm}^{-1}$ caused by $BF_4^-$ (asymmetric B–F stretch) and for the decrease of the bands caused by B–F asymmetric and symmetric stretching in $BF_3$. Fig. 2 also shows that the samples with lanthanum triflate present a bimodal curve of curing with the higher peak at higher temperatures. This fact could be attributed to the SOE homopolymerization that takes place at higher temperatures [21]. This explanation has also been demonstrated in these DSC experiments by recording FTIR spectra of partially cured samples. The lowest reactivity of the lanthanum triflate in comparison to the ytterbium salt could explain the appearance of a second exotherm which appears overlapped in the ytterbium initiated curing.

The isoconversional dynamic procedure was used to obtain the kinetic parameters, given by the following equation:

$$\frac{d\alpha}{dt} = \beta\frac{d\alpha}{dT} = kf(\alpha) = Af(\alpha)\exp\left(-\frac{E}{RT}\right) \quad (1)$$

where $\alpha$ is the degree of conversion, determined from the fractional areas of the DSC exotherm, $T$ the absolute temperature, $t$ the time, $\beta$ the linear heating rate, $k$ the constant rate, $A$ the pre-exponential factor, $E$ the activation energy, $R$ the gas constant, and $f(\alpha)$ is the differential conversion function (reaction model).

The isoconversional method presupposes that the reaction rate at a constant conversion is only a function of temperature. For each conversion, the activation energy $E_\alpha$ is related to the rate of conversion and temperature by [22,23]:

$$\left[\frac{d(\ln(\beta\, d\alpha/dT))}{d(1/T)}\right]_\alpha = -\frac{E_\alpha}{R} \quad (2)$$

From the calorimetric curves at different heating rates and applying Eq. (2), we obtained the activation energy for each degree of conversion in all the formulations studied. Fig. 3 shows the apparent activation energy and conversion rates against of degree of conversion (10 °C/min) for the DGEBA/MCP 3:1 (mol/mol) formulation with the three initiators tested. We can observe that lanthanide initiated systems have a similar activation energy with the exception of the last part of the curve (over 70% of conversion) in which lanthanum triflate leads to an increase, which could be related to the homopolymerization of SOE groups in the second maximum observed in Fig. 2. This result is supported by the activation energy (94.9 kJ/mol) calculated for the homopolymerization of SOE groups in a previous study [21].

In Fig. 3 we can also observe that the activation energy for the curing with $BF_3{\cdot}MEA$ is higher than with lanthanides in the main range of the conversion and slightly increases in all the range. The relative low values in the initial stage can be attributed to the formation of initiating active species. This fact produces that at low temperatures the samples initiated by $BF_3{\cdot}MEA$ reacts faster than samples initiated by triflates.

In spite of the multi-stage cure mechanisms, the isoconversional analysis of all the samples reflects, for an important part of the reaction process, that the apparent activation energy varies slightly with the conversion degree, as can be seen in Fig. 3. We have used this fact to obtain and average single kinetic triplet ($E$, $A$, $f(\alpha)$) for each mixture in order to compare and to better understand the differences between the analyzed samples. The most representative numerical values of this analysis are collected in Table 2. To obtain them, the following steps were necessary.

To calculate the frequency factor from the activation energies obtained from the isoconversional procedure, firstly we determined the kinetic model which better fits with the experimental results. We used the differential reduced master curves procedure [24,25] that consist in comparing the experimental curves with the theoretical calculated for the different models like $n$th reaction-order, autocatalytic, diffusion, Avrami-Erofeev and contraction. These models have not been described here because they are widely documented in the literature [13,24].

Using as a reference point $\alpha = 0.5$, the following differential master equation is easily derived from Eq. (1):

$$\frac{f(\alpha)}{f(\alpha_{0.5})} = \frac{d\alpha/dt}{d(\alpha_{0.5})/dt}\exp\left(\frac{E_{\alpha_{0.5}}}{R}\left(\frac{T_{\alpha_{0.5}} - T}{T_{\alpha_{0.5}}T}\right)\right) \quad (3)$$

where $d(\alpha_{0.5})/dt$, $T_{\alpha_{0.5}}$ and $f(\alpha_{0.5})$ are, respectively, the reaction rate, the temperature reaction and the differential conversion

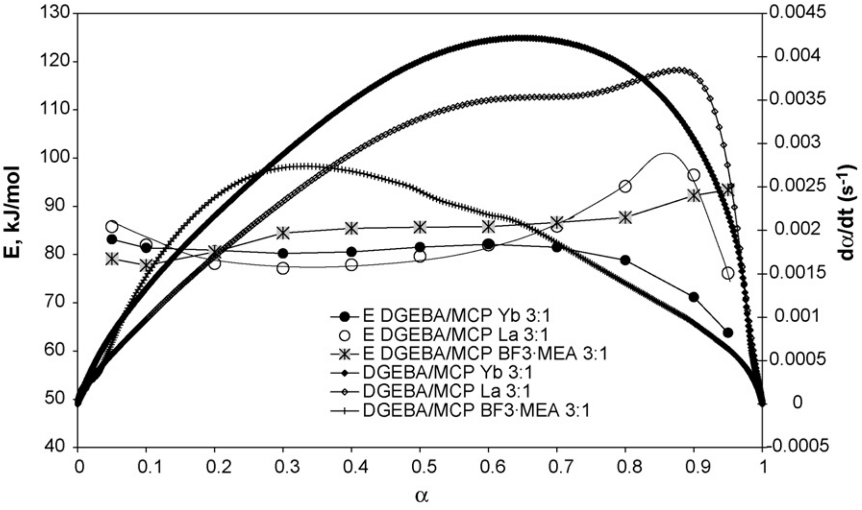

Fig. 3. Apparent activation energies and conversion rates against degree of conversion (10 °C/min).

Table 2
Apparent activation energies, pre-exponential factors and kinetic models for the systems studied

| Entry | Formulation[a] | $E$[b] (kJ/mol) | $A$[c] ($s^{-1}$) | $k_{423\,K}$[d] ($s^{-1}$) | Kinetic model, $f(\alpha)$ function[e] |
|---|---|---|---|---|---|
| 1 | DGEBA /MCP/Yb 3:1:0.021 | 75.8 | $5.4 \times 10^{6}$ | $2.4 \times 10^{-3}$ | $n_1, f(\alpha) = (1-\alpha)$ |
| 2 | DGEBA/MCP/Yb 2:1:0.015 | 79.4 | $1.0 \times 10^{7}$ | $1.6 \times 10^{-3}$ | $n_1, f(\alpha) = (1-\alpha)$ |
| 3 | DGEBA/MCP/Yb 1:1:0.009 | 68.8 | $7.0 \times 10^{5}$ | $2.3 \times 10^{-3}$ | $n_1, f(\alpha) = (1-\alpha)$ |
| 4 | DGEBA/MCP/La 3:1:0.021 | 89.0 | $1.2 \times 10^{8}$ | $1.3 \times 10^{-3}$ | $n_1, f(\alpha) = (1-\alpha)$ |
| 5 | DGEBA/MCP/La 2:1:0.015 | 87.6 | $8.8 \times 10^{7}$ | $1.4 \times 10^{-3}$ | $n_1, f(\alpha) = (1-\alpha)$ |
| 6 | DGEBA/MCP/La 1:1:0.009 | 77.1 | $4.5 \times 10^{6}$ | $1.3 \times 10^{-3}$ | $n_1, f(\alpha) = (1-\alpha)$ |
| 7 | DGEBA/MCP/$BF_3$·MEA 3:1:0.336 | 77.7 | $1.7 \times 10^{7}$ | $4.4 \times 10^{-3}$ | Autocatalytic, $f(\alpha) = \alpha^{0.15}(1-\alpha)^{1.85}$ |
| 8 | DGEBA/MCP/$BF_3$·MEA 2:1:0.240 | 84.8 | $7.4 \times 10^{7}$ | $2.5 \times 10^{-3}$ | Autocatalytic, $f(\alpha) = \alpha^{0.15}(1-\alpha)^{1.85}$ |
| 9 | DGEBA/MCP/$BF_3$·MEA 1:1:0.144 | 89.8 | $6.7 \times 10^{8}$ | $5.4 \times 10^{-3}$ | Autocatalytic, $f(\alpha) = \alpha^{0.15}(1-\alpha)^{1.85}$ |

[a] The compositions of the formulations are given in molar ratios.
[b] The values of activation energies have been taken for an interval $0.1 < \alpha < 0.9$.
[c] The values of pre-exponential factor have been calculated considering the kinetic model.
[d] Values of rate constant at 423 K calculated using the Arrhenius equation.
[e] The selected model was the one that best correlate the experimental results.

function at $\alpha = 0.5$. $E_{\alpha_{0.5}}$ is the activation energy calculated by the isoconversional method for a degree of conversion $\alpha = 0.5$. It was assumed $E_{\alpha_{0.5}}$ and the pre-exponential factor constant.

The left-hand side of Eq. (3) is a reduced theoretical curve which is characteristic of each kinetic function. The right-hand side of the equation is associated with the reduced rate and can be obtained from experimental data if the activation energy is known. The comparison of both sides of Eq. (3) tells us which kinetic model describes an experimental reaction process.

Fig. 4 represents the $f(\alpha)/f(\alpha_{0.5})$ function for the usual kinetic models in addition to the experimental data obtained at 10 °C/min for the different formulations studied. We can observe that no formulation perfectly fits any kinetic model in all the conversion range. The formulations initiated by lanthanide triflates follow similar kinetic models, but different from those followed by the $BF_3$·MEA initiated systems. In basis of these results, we selected an autocatalytic model $f(\alpha) = \alpha^{0.15}(1-\alpha)^{1.85}$ for the curing of the samples initiated with $BF_3$·MEA and a $n = 1$ model for the samples containing lanthanide triflates. Although these models do not fit perfectly with our experimental values, we selected them because they are the most applied in the curing of epoxy resins [19,20]. Thus, the frequency factors and constant rates will be comparable for all the systems initiated by lanthanide triflates but not with those initiated by $BF_3$·MEA.

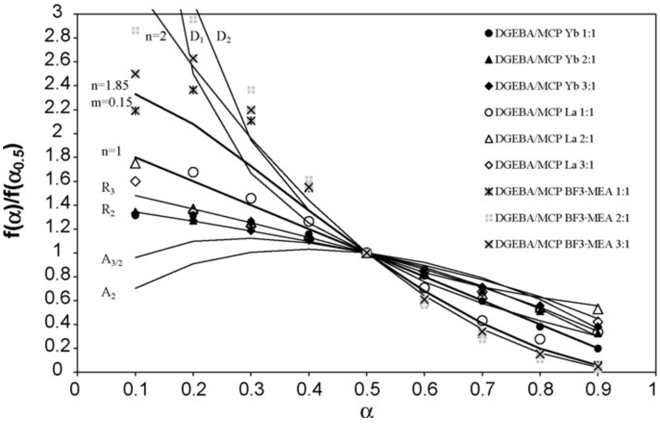

Fig. 4. Comparison of the theoretical differential master plots of $f(\alpha)/f(0.5)$ vs. $\alpha$ with the experimental master curve. The symbols correspond to the experimental values determined for the curing of the reactive mixtures studied.

Known the activation energy and the kinetic model and using Eq. (1) we can obtain the frequency factor $A_\alpha$ for each conversion through the following equation:

$$A_\alpha = \left(\frac{\mathrm{d}\alpha/\mathrm{d}t}{f(\alpha)}\right) \exp\left(\frac{E_\alpha}{RT_\alpha}\right) \tag{4}$$

where $\mathrm{d}\alpha/\mathrm{d}t$ and $T_\alpha$ are obtained experimentally and $E_\alpha$ is the activation energy calculated by the isoconversional procedure. The obtained values of $A_\alpha$ are not reproduced because they reflect the same behavior than $E_\alpha$ which has already represented in Fig. 3.

The different kinetic model obtained for $BF_3$·MEA and lanthanide triflates initiated systems can be related with the formation of different active species in both cases. When we used lanthanide triflates the kinetic model is of $n$ order being the maximum curing rate at zero conversion. When the reaction progresses, there are less active species in the reaction medium and the topological hindrance increases. However, when we use $BF_3$·MEA, the need to form the true active species ($HBF_4$) at the beginning of the curing process [19,20], might explain the different behavior with regard to the lanthanide triflate initiation and, in accordance with Fig. 3, this process better fit with an autocatalytic model than to one of order $n$. After the highest curing rate is reached (about $\alpha = 0.2$) the curing declines as it occurs in the case of lanthanide triflates.

To obtain a single pair ($E$, $A$) for each reactive system, we used the so-called reduced constant rate defined by the following equation:

$$k_r = \left(\frac{\beta(\mathrm{d}\alpha/\mathrm{d}T)}{f(\alpha)}\right) \tag{5}$$

By comparing Eqs. (1) and (5), extracting logarithms and rearranging terms the following equation can be obtained:

$$\ln k_r = \ln A - \frac{E}{RT} \tag{6}$$

In Eq. (6) the subscript $\alpha$ does not appear to mean that if the activation energy and $A$ are independent of the conversion degree

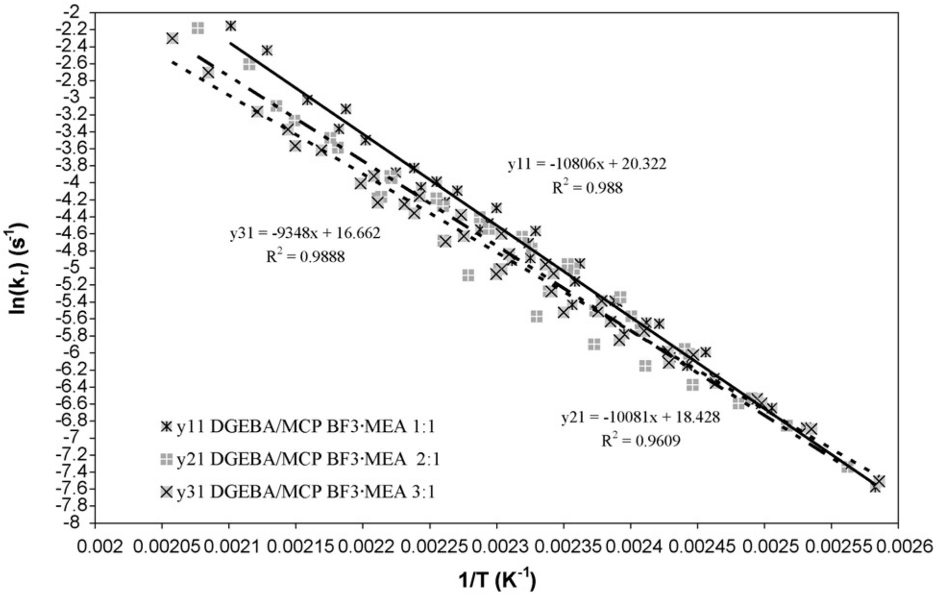

Fig. 5. Analysis by the reduced rate constant of the DGEBA/MCP formulations initiated by $BF_3$·MEA.

then the reduced constant rate turns into the actual constant rate that only depends on the temperature.

If the plot of the ln $k_r$ values (obtained from experimental data and using the selected kinetic model) against $1/T$ fits a straight line, the kinetic process is well defined by the kinetic triplet ($f(\alpha)$, $E$ and $A$) being $E$ and $A$ the values obtained from the slope and the intercept, respectively, of the regression line.

Fig. 5 shows, as an example, the comparative analysis made with the constant rates of the $BF_3$·MEA catalytic systems, using all the heating rate values (2, 5, 10 and 15 °C/min) and all conversions between 0.1 and 0.9. The correlations obtained are good enough to consider the activation energies and pre-exponential factors, collected in Table 2, as representative average values for these systems. From Fig. 5 it could be put into evidence the different accelerative effect that an increase in the proportion of MCP causes in the different stages of the curing. The amount of MCP in the samples makes to increase the rate constant, but this influence is not the same at the beginning of the reaction (at low temperatures is practically unappreciable) than later.

An analogous analysis was made for the formulations initiated by lanthanide triflates. In Fig. 6 are represented the results for the formulation DGEBA/MCP 3:1 (mol/mol) for both initiators. We can observe the greater catalytic effect of the ytterbium triflate. Similar behavior was observed for the DGEBA/MCP 2:1 and 1:1 (mol/mol) formulations.

From the average values collected in Table 2 we can see that the activation energies are lower for the systems initiated by the ytterbium salt. As commented earlier, these differences probably reflects the different ability of the initiators to produce copolymerization of SOE and epoxy with the consequence that the remaining SOE homopolymerizes at higher temperatures. For both lanthanide triflate initiators, the increase of MCP in the reactive mixture reduces the activation energies and pre-exponential factors. These results show that the differences cannot be explained exclusively by the changes produced by the combined effect of temperature and medium viscosity when the amount of MCP is increased. The contrary trend is observed when the amount of MCP increases in the samples with the boron initiator. It is difficult to explain this behavior only on the basis of the kinetic processes. For these samples, the pre-exponential factor increases with MCP addition but not enough to compensate the increment of the activation energy so there is not appreciable effect on the constant rate. The differences of pre-exponential factors and constant rate values for lanthanide triflates and $BF_3$·MEA initiated samples in Table 2 are not comparable because they were obtained from different kinetic models.

All these facts put into evidence the complexity of the cationic curing of these systems. Although the kinetic analysis performed allowed to find out differences between the samples with different initiators and proportions of MCP, we must accept that the results obtained are not enough to explain

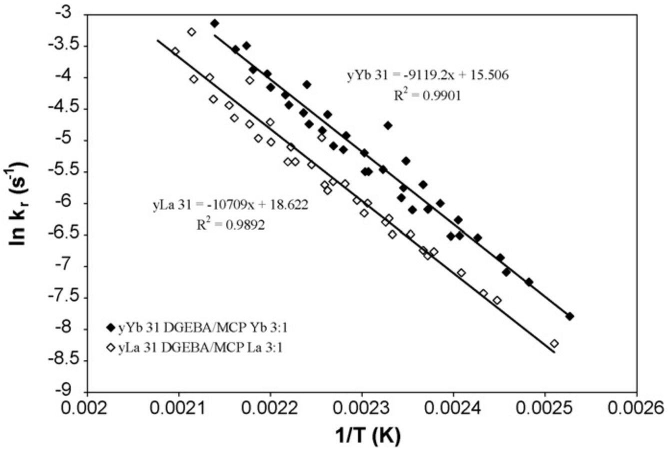

Fig. 6. Analysis by the reduced rate constant of the DGEBA/MCP (3:1, mol/mol) formulations initiated by lanthanum and ytterbium triflates

in detail the curing behavior and the properties of the cured materials. The competitive reaction processes, whose extension depends on the initiator and on the composition of the mixtures, are only a partial cause of the cure kinetics and the final structure of the material. In addition, the formation of intermediate SOEs, the possibility of separated phases, the amount of poly(ether-ester) and polyether structures depending on homopolymerization–copolymerization extensions, produce a physical change of the substrate that plays a relevant role as a complementary cause in the explanation of the complex kinetics and the final properties of the cured samples [9,10].

## 4. Conclusions

This work shows that the kinetics of the thermal cationic cure process of mixtures of DGEBA with MCP must be analyzed as a multi-stage cure mechanisms highly dependent on the initiator system (conventional $BF_3{\cdot}MEA$ or lanthanide triflates). Based on the results of DSC isoconversional kinetic analysis, the apparent activation energy of the $BF_3{\cdot}MEA$ systems is higher than those of lanthanide triflates systems in the most range of conversion. The lower reactivity of the mixtures initiated by $BF_3{\cdot}MEA$ correlates well with the higher activation energy obtained for this system in comparison to those obtained for lanthanide triflates systems.

The analysis of reduced constant rate allows to obtain a single kinetic triplet ($E$, $A$, $f(\alpha)$) for each mixture in order to a better understanding of the effect of the initiator and the amount of MCP in the DGEBA/MCP mixtures. In all the samples analyzed, the reactivity increases with the proportion of MCP. The increase in the amount of MCP produces an acceleration effect that is notorious in advanced steps of the reaction but not in the initial stage. Although the kinetic of mixtures initiated by ytterbium and lanthanum triflates are very similar, the ytterbium triflate is more active than lanthanum triflate due to the higher Lewis acidity of the ytterbium cation.

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