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INFLUENCE OF THE ADDITION OF ERBIUM AND YTTERBIUM TRIFLATES IN THE CURING KINETICS OF A DGEBA/*o*-TOLYLBIGUANIDE POWDER MIXTURE

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Solid bisphenol-A epoxy resin (DGEBA) of medium molecular mass was cured using *o*-tolylbiguanide (TBG) as cross-linking agent. In order to improve the kinetics of the reactive system, two Lewis acid catalysts (erbium(III) and ytterbium(III) trifluoromethanesulfonates) were added in proportions of 1 phr. The kinetic study was performed by dynamic scanning calorimetry (DSC) and the complete kinetic triplet (E, A and $g(\alpha)$) determined. The kinetic analysis was performed with an integral isoconversional procedure (model-free), and the kinetic model was determined by the Coats–Redfern method and through the compensation effect (IKR). All the systems followed the m=1.5/n=0.5 isothermal curing model simulated from non-isothermal experiments. The addition of a little proportion of ytterbium or erbium triflates accelerated the curing process. In order to extract further information about the role of the lanthanide triflates added to epoxy/TBG systems, the kinetic results were compared with our previous kinetic studies made on DGEBA/lanthanide triflates initiated systems.

Keywords: *catalyst, epoxy, erbium triflate, kinetics (polym.), ytterbium triflate*

Introduction

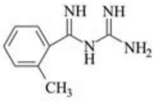
Powder coatings are currently the fastest growing section of industrial paints, because of their favourable environmental attributes (less than 4% of volatile organic contents) and performance advantages [1]. Apart from their clear advantages, powder coatings, show some limitations, like the difficulty of application on thermo-sensible substrates like wood or plastic [2]. Nowadays, the most used powder coating systems are those based on epoxy resins cured with dicyandiamide (DICY) or its derivatives, which are used in proportions of 4 to 6 phr and the curing temperature is above 448 K [3]. For this reason, the formulation of new epoxy powder coatings (using new catalysts and cross-linkers) capable to cross-link at lower temperatures has become one of the main lines of research in industries and related research centres.

In Scheme 1 it can be observed the structure of the cross-linker used in the present work. *o*-Tolylbiguanide (TBG) is structurally related to DICY, which is a typical latent curing agent. This curing agent was reported to be effective in the curing of DGEBA epoxy resins [4] and in liquid crystalline epoxy resins [5] but no studies were reported on the reaction mechanism.

Barton [6] reported the mechanism followed by the curing of epoxy resins with DICY, in which the amine groups react with epoxides leading to the formation of four new C–N linkages. TBG should react similarly to DICY with epoxy groups, but from its structure, a functionality of five can be predicted (Scheme 2). Thus, one mol of TBG reacts with five equivalents of epoxy resin.

One of the main objectives of this research was to obtain epoxy powder systems with low curing temperatures so that they can be applied on different substrates sensitive to temperature (mainly different types of organic ones, like plastics), and of course to reduce energetic costs in the curing process.

Catalysts are important in polymerization processes because they decrease the activation energies (when comparing systems with the same reaction mechanism process) and accelerate the reaction. They can be stimulated by heating or photoirradiation but, from the practical point of view, heating is the easier option, be-



Scheme 1 Structure of the cross-linking agent, TBG

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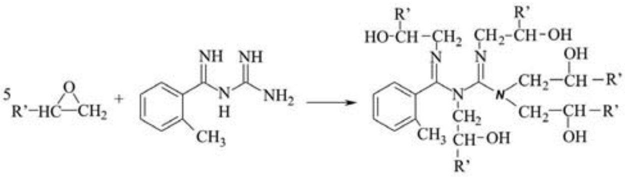


Scheme 2 Chemical structure of the network using TBG as cross-linking agent

cause homogeneous heating of reaction mixtures can be achieved without difficulty [7] and because the curing is not too much influenced by the pigments, like in UV paints happens [8]. Among the new cationic thermal initiators, those having anions with low nucleophilicity minimize or prevent the reaction of the growing chain with the anion, being more actives their cationic salts and more effective the polymerization [9].

Lewis acids used as initiators or catalysts, such as $AlCl_3$, BF_3 or $TiCl_4$ are moisture sensitive and easily decompose in the presence of humidity. On the contrary, lanthanide triflates are stable and act as Lewis acids in water or humid environments. This fact represents an enormous advantage in their technological applications as catalysts. The lanthanide cations (Ln(III)) have a very high coordination capacity and a great oxophilicity, thus, weakening the C–O bond [10], and favouring the cationic mechanisms of reaction. This process is improved by the electron-withdrawing capacity of the anionic group, TfO^- [10].

As usual in Lewis acid initiators, erbium(III) and ytterbium(III) trifluoromethanesulfonates (here on, $Er(TfO)_3$ and $Yb(TfO)_3$ respectively), lead to chain growth polymerization of epoxy compounds, which mainly proceed by the cationic chain end mechanism depicted in Scheme 3, where oxyrane groups of DGEBA resin are opened by coordination of oxyrane oxygen to the initiator and subsequent nucleophylic attack of another oxyrane group. This mechanism is known as activated chain end mechanism (ACE).

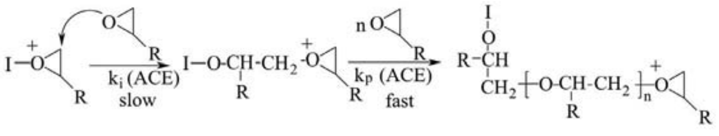
Moreover, the presence of hydroxylic groups can lead to hydroxylic initiated polyetherification processes that can change both the kinetics of the reaction and the properties of the materials (Scheme 4), although this kind of reaction should be less important in extension than the first one, because of the low proportion of hydroxyls. This mechanism is known as activated monomer mechanism (AM).

Thus, the proportion of hydroxylic groups can influence the global propagation rate. In addition to these competitive chain growth mechanisms, inter and intra molecular transfer processes can occur and also termination reactions. All these processes lead to changes in the network structure and difficult the study of the kinetics of each separated process. Thus, the kinetics of a cationic cure should be studied taking the process as a whole [11, 12].

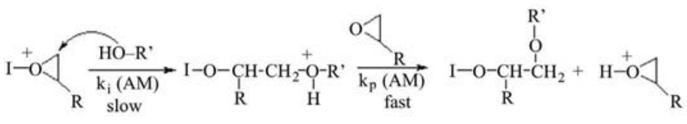
The usefulness of lanthanide triflates as initiators has been proved in other studies [9, 13] with liquid epoxy resins, showing that they highly accelerated the reactions of the system. Their effect in powder coatings has also been studied for systems using DGEBA resin with lanthanide triflates as initiator [14, 15], proving that they offer very good improvements in curing kinetic processes. However, no research has been published about their effect in the curing kinetics of a powder system DGEBA resin-DICY derivative where a triflate is added as a catalyst.

Several authors described the ability of lanthanide triflates to catalyze the reaction of epoxides and nitrogen heterocycles [16] or amines [17, 18] to give β-aminoalcohols. It seems that the coordination of oxirane oxygen to lanthanide facilitates the nucleophylic attack of the nitrogen to the oxirane ring by weakening the C–O bonds of the epoxide groups and making more electrophylic the carbon atoms of this group. Therefore, the use of lanthanide triflates could also catalyze the reaction of DGEBA with TBG facilitating the cure at lower temperatures.

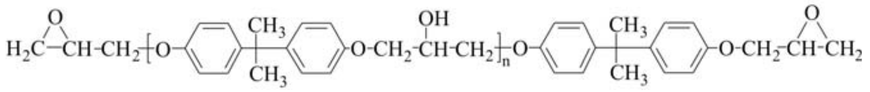
Nevertheless, when using a Lewis acid catalyst we are promoting the homopolymerization where the nucleophylic agent is the oxirane oxygen instead of the amine, especially when hydroxylic groups are origi-



Scheme 3 Activated chain-end mechanism/ACE



Scheme 4 Activated monomer mechanism/AM



Scheme 5 DGEBA epoxy resin structure

nated during curing. In this case, the Lewis acid acts as initiator, because it remains attached to the polymeric chain. However, nitrogen compounds are generally more nucleophylic than oxiranes or hydroxylic groups and therefore the competitive homopolymerization processes should be, in principle, less important. On the other hand, the reaction of TBG with the epoxy resin originates hydroxylic groups, which favours the homopolymerization of oxirane by an AM mechanism (Scheme 4). These facts prompted us to investigate the role of lanthanide triflates in the curing of DGEBA resins with TBG.

The difference in the reaction mechanisms gives rise to differences in the structure of the network and in the reaction enthalpies. In order to know if the network formed is different or not we used infrared spectroscopy (FTIR) because it could give significant structural information. Moreover, some degradation tests (such as TG measurements) were performed, because the stability of the network could be slightly affected by the chemical structure of the network.

To predict the temperatures and times at which these polymerizations should be performed, one must know the kinetics. Preliminary kinetic studies have been done using the method described by Kissinger [19]. This procedure, used by many authors because of its simplicity, assumes an *n* order mechanism. However, this assumption is not correct in many cases and leads to incorrect values of pre-exponential factor *A*. In addition, kinetic methods that only use the maximum of the velocity curve to determine the kinetic parameters do not allow an assessment of whether these parameters vary during polymerization or not. In the present study we attempt to establish a method for this curing that allows the complete kinetic triplet (kinetic model, *E* and *A*) to be determined throughout the entire reaction. To analyze exothermic polymerizations, we have used a method from earlier studies addressing the kinetics of curing and degradation [20].

Many exothermic polymerizations have difficulties for the determination of the heat of reaction through isothermal experiments and the subsequent deduction of the kinetics 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. fusion) overlaps with the polymerization. One alternative in both cases is to simulate isothermal polymerization with non isothermal data [21]. Different studies on the curing kinetics of liquid [22–24] and powder coatings [14, 15] using systems containing epoxy resins and diamines have been published.

In this work, a complete kinetic study of polymerization of a medium molecular mass DGEBA resin cured with TBG and little proportions of erbium(III) or ytterbium(III) trifluoromethanesulfonates has been developed. The reaction model was established from non isothermal data by two different methods. The first was the Coats–Redfern method [25–27], where the *E* value obtained isoconversionally (with the STAR^e software) was taken as the effective value, E_{ef}, and used to obtain the apparent *E* value from Coats method (E_{ap}). The second method used the compensation effect (IKR) existing between *E* and *A* at the change in the degree of conversion (α) [20, 28].

Experimental

Materials

Solid bisphenol-A based epoxy resin of medium molecular mass (Scheme 5), 733 g eq^{-1} epoxy (from Huntsman), was polymerized in the ratio given by the producer with a Huntsman DICY derivative, TBG (with an H$^+$ active equivalent mass of 37 g eq^{-1}), and adding 1 phr of erbium(III) and ytterbium(III) trifluoromethanesulfonates (from Aldrich) (one part of lanthanide triflate per hundred of resin, mass/mass). Two samples of epoxy resin were homopolymerized with 1 phr of erbium(III) and ytterbium(III) trifluoromethanesulfonates. The compositions of the samples are detailed in Table 1.

Table 1 Composition of the samples studied and glass transition temperature after curing

Sample	Epoxy resin	TBG/phr	$Er(TfO)_3$/phr	$Yb(TfO)_3$/phr	T_g/K
1	100	4.8	–	–	369
2	100	4.8	1	–	373
3	100	4.8	–	1	370
4	100	–	1	–	382
5	100	–	–	1	382

Samples were pre-mixed and hand-shacked until good pre-mixing was afforded. After that, the material was extruded in a single screw extruder (Haake Rheomex 254), where operating conditions were 352 K along the extruder and 60 rpm. After extruding, the material was grinded in an ultra-centrifugal mill ZM 100 and sieved at 100 micron.

Testing methods and equipment

Differential scanning calorimeter (DSC)

A Perkin Elmer DSC 7 differential scanning calorimeter was employed for dynamic scans in order to study the non-isothermal curing process and to obtain the kinetic model parameters. The samples were analyzed in covered aluminium pans, using high purity indium sample for calibration. A flow of 20 cm^3 min^{-1} of argon was used as purge gas. The mass of the samples was between 9 and 10 mg. Non-isothermal tests were performed at rates of 2.5, 5, 10 and 15 K min^{-1} to the not-cured-samples showed in Table 1. The scans were performed in the temperature range from 298 to 573 K.

DSC was also employed to measure the midpoint T_g of the samples after curing them at 423 K for 25 min, reaching the total cure. DSC scans were performed at 10 K min^{-1}.

STAR^e Mettler-Toledo software was used in order to calculate conversion degrees and kinetics of the process. Kinetic analysis, using Coats–Redfern and IKR methods, were used to calculate the kinetic triplet (A pre-exponential factor, E effective activation energy, and $g(\alpha)$ integral function of the degree of conversion or kinetic model).

Kinetic analysis

If we accept that the dependence of the rate constant (k) on the temperature follows the Arrhenius equation, then the kinetics of the reaction is usually described as follows:

$$r=\frac{\mathrm{d}\alpha}{\mathrm{d}t}=A\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{1}$$

where t is the time, T is the absolute temperature, R is the gas constant, and $f(\alpha)$ is the differential conversion function. Kinetic analysis has generally been performed with an isoconversional method. The basic assumption of such method is that the reaction rate at a constant conversion is solely a function of temperature [29].

Isothermal methods

By integrating the rate equation (Eq. (1)) under isothermal conditions, we obtain:

$$\ln t=\ln\left(\frac{g(\alpha)}{A}\right)+\frac{E}{RT} \tag{2}$$

where $g(\alpha)$ is the integral conversion function and is defined as follows:

$$g(\alpha)=\int_0^\alpha \frac{\mathrm{d}(\alpha)}{f(\alpha)} \tag{3}$$

According to Eq. (2), E and the constant $\ln[g(\alpha)/A)]$ can be obtained from the slope and the intercept, respectively, of the linear relationship $\ln t=f(T^{-1})$ for a constant value of α.

Isothermal methods require long times to be performed and give problems with the data acquisition. Firstly, as isothermal reactions of these systems took place very fast, the DSC equipment was not able to detect the initial calorimetric signal because stabilization time is needed and the initial part of the cure is lost (meaning that the curing reaction begins before reaching the isothermal temperature). Secondly, when the isothermal test finishes the cooling of the sample in the calorimeter is not immediate, so again some time is needed to decrease the temperature and the reaction process continues until ambient temperature is reached, probably non-isothermal data could give more accurate results than those given by isothermal experiments.

Non-isothermal methods

When non-isothermal methods are applied, the integration of rate equation (Eq. (1)) and its reordering gives place to the so-called temperature integral:

$$g(\alpha)=\int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)}=\frac{A}{\beta}\int_0^T \mathrm{e}^{-(E/RT)}\mathrm{d}T \tag{4}$$

where, α is the heating rate.

By using the Coats–Redfern [25] approximation for the resolution of Eq. (4) and considering $2RT/E<<1$, we can rewrite this equation as follows:

$$\ln\frac{g(\alpha)}{T^2}=\ln\left(\frac{AR}{\beta E}\right)-\frac{E}{RT} \tag{5}$$

For a given kinetic model, the linear representation of $\ln[g(\alpha)/T^2]$ *vs.* T^{-1} makes it possible to determine E_{ap} and A from the slope and the ordinate at the origin.

In this work, the kinetic model that had the best linear correlation in the Coats–Redfern equation and that had an E value (E_{ap}) similar to that obtained isoconversionally (considered to be the effective E value, E_{ef}) was selected.

By reordering Eq. (5), we can write:

$$\ln\frac{\beta}{T^2}=\ln\left[\frac{AR}{g(\alpha)E}\right]-\frac{E}{RT} \tag{6}$$

The linear representation of $\ln[\beta/T^2]$ *vs*. $1/T$ makes it possible to determine E_{ap} (apparent E value) and the kinetic parameter $\ln[AR/g(\alpha)E]$ for every value of α.

The constant $\ln[AR/g(\alpha)E]$ is directly related by the R/E to the constant $\ln[g(\alpha)/A]$ of the isothermal adjustment. Thus, taking the dynamic data $\ln[AR/g(\alpha)E]$ and E from Eq. (6), we can determine the isothermal parameters of Eq. (2) and simulate isothermal curing without knowing $g(\alpha)$ [24, 30].

The STAR^e Mettler-Toledo software uses Eqs (2) and (6) to determine the isonconversional activation energy and the isothermal times, respectively.

Compensation effect and isokinetic relationship (IKR)

Complex processes are characterized by the dependences of E on A and α. This generally reflects the existence of a compensation effect through the following equation:

$$\ln A_\alpha=aE_\alpha+b=\frac{E_\alpha}{RT}+\ln\left[\frac{(\mathrm{d}\alpha/\mathrm{d}t)_\alpha}{f(\alpha)}\right] \tag{7}$$

where a and b are constants and the subscript α represents the degree of conversion that produces a change in the Arrhenius parameters.

The slope $a=1/RT_{iso}$ is related to the isokinetic temperature (T_{iso}), and the intercept $b=\ln k_{iso}$ is related to the isokinetic rate constant (k_{iso}). Equation (7) represents an IKR and can be deduced by the reordering of Eq. (2). The appearance of the IKR shows that there is only one model, whereas the existence of parameters that do not meet the IKR (meaning that for a given α the relation between A and E changes) implies that there are several models [31], because $f(\alpha)$ is not constant in all the process.

In this study, the kinetic model whose IKR had the best linear correlation between E and A and in which the associated T_{iso} value was near the experimental temperature range was selected [32]. The influence of the addition of erbium and ytterbium triflates in the kinetics of the epoxy/TBG system has been studied.

Infrared spectroscopy (FTIR)

The FTIR spectra were taken using a 680Plus Jasco with a resolution of 4 cm^{-1} in the absorbance mode. The samples were put on an attenuated reflection accessory with thermal control and diamond crystal (Golden Gate Heated Single Reflection Diamond ATR, Specac-Teknokroma) and were registered at room temperature.

Thermogravimetric analysis (TG)

A Setaram thermogravimetric analyzer (TG) was used. Cured samples (25 min at 423 K, so total curing was afforded) between 15 and 20 mg were scanned up to 1173 K at 10 K min^{-1}. All scans were performed with an argon flow of 50 cm^3 min^{-1}.

Results and discussion

Figure 1 shows the DSC curves registered at a heating rate of 5 K min^{-1} for the five different samples studied. The curves exhibit a small endothermic peak at 328 K (where the T_g should be detected) related to the physical aging of the DGEBA. All the curves show a big exothermic peak at high temperatures (with its minimum between 403 and 433 K) related to the curing reaction of the epoxy resin. It can be seen, that when ytterbium and erbium triflate are used the exotherm shifts to minor temperatures compared to the reference sample DGEBA/TBG, demonstrating the acceleration effect of these Lewis acids. Moreover, when ytterbium and erbium triflates are used alone as initiators the exotherm appears at lower temperatures. Samples containing TBG and lanthanide triflates show a second exothermic peak at 498 K in the curing, due to some secondary or residual reactions. This secondary peak has been observed in curves registered at different heating rates (Fig. 2) but when the rate is very low (2.5 K min^{-1}) this peak has almost disappeared. The interpretation of this secondary peak is difficult because the complexity of the curing process [6].

The calorimetric scans at different heating rates were used to obtain the dependence of the conversion

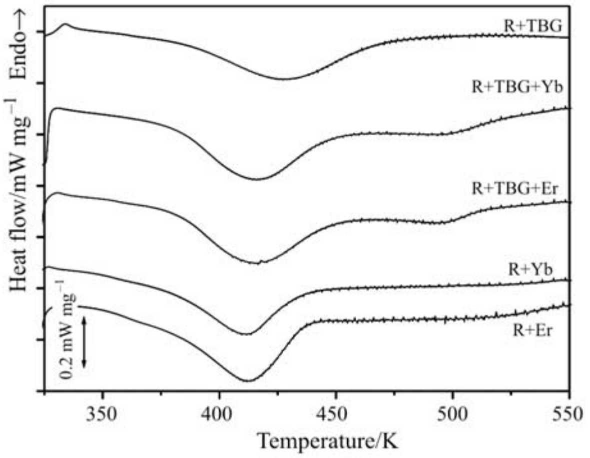


Fig. 1 Non-isothermal DSC curves at 5 K min^{-1} of heating rate for mixtures epoxy resin/TBG, epoxy resin/TBG/erbium triflate, epoxy resin/TBG/ytterbium triflate, epoxy resin/erbium triflate, and epoxy resin/ytterbium triflate

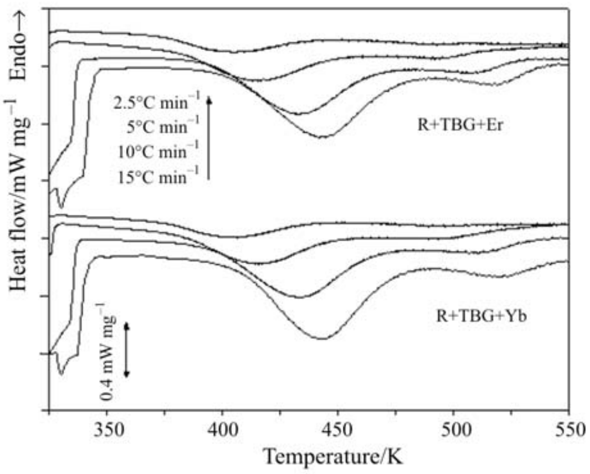


Fig. 2 Non-isothermal DSC curves at 2.5, 5, 10 and 15 K min^{-1} of heating rate for mixtures epoxy resin/TBG/erbium triflate and epoxy resin/TBG/ytterbium triflate

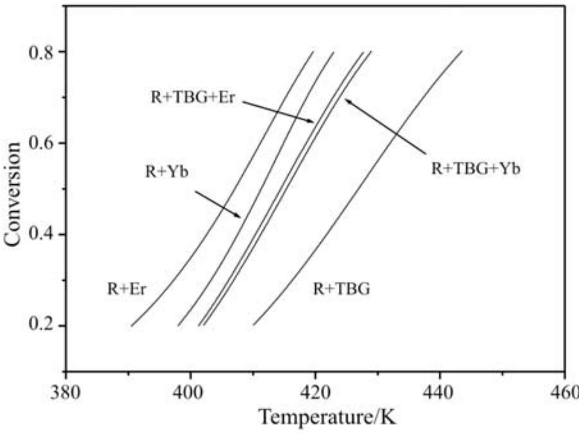


Fig. 3 Conversion degree (α) *vs*. temperature plots for a heating rate of 5 K min^{-1} for epoxy resin/TBG, epoxy resin/TBG/erbium triflate, epoxy resin/TBG/ytterbium triflate, epoxy resin/erbium triflate, and epoxy resin/ytterbium triflate mixtures

degree with the temperature, by means of the STAR^e software. Figure 3 shows α *vs*. T plots for a heating rate of 5 K min^{-1} for all the samples studied. Almost no differences are detected in systems cured with both TBG and ytterbium or erbium triflates. Nevertheless, larger differences are observed when lanthanide triflates are used alone as initiators. In this case, erbium triflate allows performing the curing at lower temperatures than with ytterbium. In all samples containing lanthanide triflates a displacement towards lower temperatures was observed.

The non-isothermal isoconversional kinetic parameters were calculated from the α–T curves by the application of Eq. (6) to different conversions, and from these, the isothermal parameter $\ln[g(\alpha)/A]$, with which the studied curing process would subsequently be simulated. Table 2 collects the E_{ef} values of non-isothermal curing obtained from Eq. (6) for the samples prepared using TBG and TBG with lanthanide triflates. It can be seen that the introduction in the reactive mixture of an initiator, which can promote the cationic homopolymerization reaction, produces a rise of the E values of the system. This could be due to the fact that the homopolymerization of the epoxy resin has higher E values than those obtained for systems cured only with nitrogen compounds, as Barton observed previously [33]. In previous papers we reported the E_{ef} values obtained for DGEBA/lanthanide triflate mixtures, which are, in general, higher [14, 15]. Table 2 shows that E_{ef} is weakly modified during curing due to the complex reaction mechanism.

Figure 4 shows the experimental relationship between $\ln[\beta/T^2]$ and the inverse of the temperature, with the adjustment made with Eq. (6) for the sample DGEBA/TBG/erbium triflate.

To establish the kinetic model for these systems, the isoconversional kinetic parameters obtained for each sample and the Eq. (7) were used (IKR method). From the parameters $\ln[AR/g(\alpha)E]$ and E_{ef}, and the $g(\alpha)$ functions [20], A values were calculated for all

Table 2 Variation of the effective activation energy with the conversion of epoxy resin/TBG, epoxy resin/TBG/erbium triflate and epoxy resin/TBG/ytterbium triflate samples

Conversion	E_{ef}/kJ mol^{-1}		
	R+TBG	R+TBG+Er(TfO)$_3$	R+TBG+Yb(TfO)$_3$
0.2	66.0	80.6	80.6
0.3	64.9	77.7	78.6
0.4	64.3	76.3	77.8
0.5	63.8	75.6	77.5
0.6	63.4	75.3	77.7
0.7	62.9	75.2	78.0
0.8	62.3	74.7	78.2
average	63.9	76.5	78.3

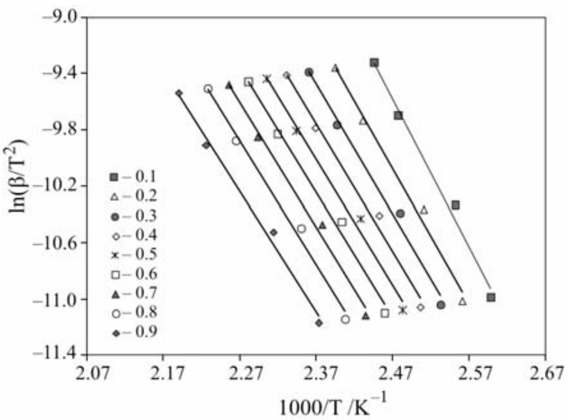


Fig. 4 Correlations between $\ln(\beta/T^2)$ and the inverse of the temperature (1000/T) for different values of α for a sample epoxy resin/TBG/erbium triflate

the different kinetic models. Subsequently, by plotting E *vs*. ln$A$, we determined the IKRs for all the models (Eq. (7)). Table 3 shows the obtained results for a sample epoxy resin/TBG, where T_{iso} values were determined from the slope of the IKRs. Although some models exhibit IKRs (especially $A_{3/2}$ and m=0.5/n=1.5), the best model, which describes the polymerization of the sample is the m=0.5/n=1.5 because it shows a good regression and T_{iso} values in the range of the experimental temperatures. In agreement with Vyazovkin and Linert [32], a T_{iso} value close to the range of experimental temperatures indicates that the kinetic model accurately describes the reactive process. The samples using triflates as catalysts showed similar results, and thus, similar conclusion, being the kinetic model the same.

To confirm the methodology used with the IKR, we determined E_{ap} and ln$A$ for each tested model with the Coats–Redfern method (Eq. (5)). The results obtained for the sample epoxy resin/TBG when Eq. (5) was applied to conversions between 0.2 and 0.8, are shown in Table 3 (similar results were obtained for the other two samples using TBG). Some of the models exhibit very good regressions, and so from these data alone, it is not possible to establish the reaction mechanism. To determine the kinetic model, it was also used the average value of E_{ef} obtained isoconversionally shown in Table 2. This value of E is considered the effective value because it was obtained without the necessity of determining the model. In addition to the good regression, the correct kinetic model must also possess a value of E similar to the effective value. According to these criteria model m=0.5/n=1.5, with good regression and E value closer to the E_{ef} in the three samples, is considered the correct one for samples with TBG, although model $A_{3/2}$ could also be possible. Samples initiated by lanthanide triflate fit the kinetic model $A_{3/2}$ [14, 15]. The fact that samples with TBG and lanthanide triflate fit a kinetic model closer to that obtained for samples with TBG alone seems to suggest that the main reaction could be the nucleophilic attack of the biguanide nitrogens to the oxirane rings catalyzed by the lanthanide salt and not the homopolymerization of epoxides initiated by lanthanide triflates.

In order to corroborate this hypothesis the FTIR spectra of all the samples containing TBG were registered. All these spectra showed an identical pattern, in which the most characteristic absorption is the associated hydroxylic bands between 3600 and 3300 cm^{-1}. This absorption confirms the total reaction of TBG with epoxides and the no-homopolymerization of epoxides, because TBG and epoxides are mixed in stoichiometric proportions. Figure 5 shows, as an example, the spectrum of the DGEBA/TBG/Yb(TfO)$_3$ sample after curing.

Table 1 collects the glass transition temperature of the materials obtained from all the samples. First of all, it can be stated that there is only one T_g in all the materials, even in those containing TBG and lanthanide triflates together, which seems to indicate that the network is completely homogeneous for all the systems. Moreover, the T_g values obtained for the

Table 3 Arrhenius parameters determined by the Coats–Redfern method and isokinetic parameters for the curing of an epoxy resin/TBG mixture obtained at a heating rate of 5 K min^{-1}

Models	Coats–Redfern			IKR			
	E_a/kJ mol^{-1}	ln$A$/min^{-1}	r	a/mol kJ^{-1}	b/min^{-1}	T_{iso}/K	r
$A_{3/2}$	52.1	12.59	0.9981	0.318	–3.938	378.2	0.9980
A_2	37.3	8.17	0.9983	0.394	–8.685	305.8	0.9980
A_3	22.5	3.57	0.9977	0.469	–13.432	256.7	0.9976
A_4	15.1	1.13	0.9970	0.507	–15.806	237.6	0.9973
n+m=2; n=1.9	104.4	28.36	0.9995	0.051	13.587	2342.3	0.6632
n+m=2; n=1.5	54.8	14.38	0.9994	0.304	–2.007	395.9	0.9959
n=2	116.8	31.85	0.9995	–0.012	17.527	–10191.9	0.1717
n=3	159.5	44.64	0.9959	–0.235	32.391	–512.0	0.7953

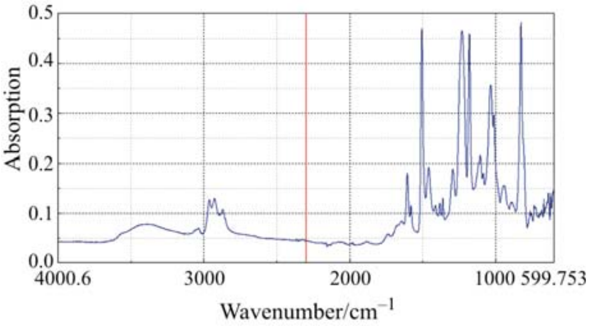


Fig. 5 FTIR spectrum of the cured material from a sample epoxy resin/TBG/ytterbium triflate

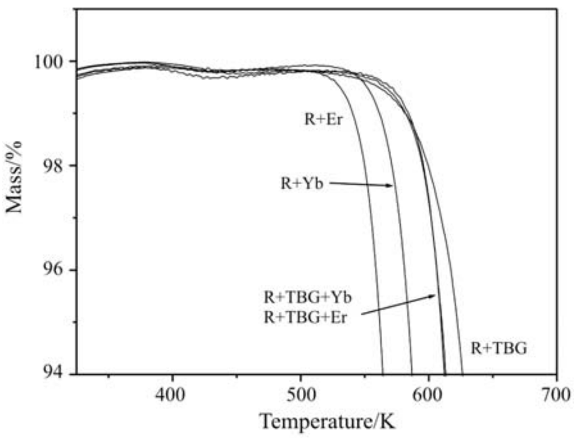


Fig. 6 TG curves of epoxy resin/TBG, epoxy resin/TBG/erbium triflate, epoxy resin/TBG/ytterbium triflate, epoxy resin/erbium triflate and epoxy resin/ytterbium triflate cured samples in argon atmosphere

materials with TBG and lanthanide triflates are very close to those obtained for the system DGEBA/TBG. This fact indicates that the chemical structure of the network should be similar for the three systems using TBG, as well as the achieved curing degree.

Since the thermal stability is influenced by the chemical structure of the networks, some degradation tests were also carried out. In Fig. 6, we can see that the degradation curve of samples containing TBG and lanthanide triflate are closer to that obtained for the systems using TBG alone. This fact again confirms that the network must have a similar chemical structure to that obtained for DGEBA/TBG mixtures.

The obtained kinetic results were also confirmed by the so-called method of the reduced master curves proposed by Criado [34, 35] and showed that the kinetic model chosen (m=0.5/n=1.5) fitted very well with the experimental data.

All the samples investigated showed that the two methodologies (IKR and Coats–Redfern) lead to the same result, and in both cases, it is necessary to know the effective E (isoconversional) value to determine the complete kinetic triplet (E_{ap}, A and $f(\alpha)$).

If we compare the activation energies (Table 2), a simple analysis would conclude that the fastest system is that with the minor E_{ef}, but this is not always true because a compensation effect between E and ln$A$ exists. Then, to know which is the most efficient system it should be compared the conversion rate constant (because samples fit the same kinetic model $g(\alpha)$, if not, r should be compared instead of k). Equation (8) shows the Arrhenius relation between k (rate constant), A and E.

$$k = A\exp\left(-\frac{E}{RT}\right) \rightarrow \ln k = \ln A - \frac{E}{RT} \qquad (8)$$

From Eq. (1),

$$\ln r = \ln A - \frac{E}{RT} + \ln f(\alpha) \qquad (9)$$

Introducing in Eq. (8) values of E, A and α with the chosen kinetic model (m=0.5/n=1.5) and for a given conversion degree (α=0.5) we can obtain a graphic like Fig. 7 (ln$k$=f(1/T)). In this figure it can be observed that the addition of lanthanide triflate give rise to an acceleration of the reaction rate of systems cured with TBG. It can also be observed that there are no differences when using Yb or Er in systems with TBG. However, when ytterbium and erbium triflates were used alone as initiator differences in constant rates were observed between both lanthanide salts [14, 15]. These results corroborate that in order to know which system could be cured at lower temperature it is appropriate to consider not only E_{ef} but also the parameter ln$A$ if they fit the same kinetic model.

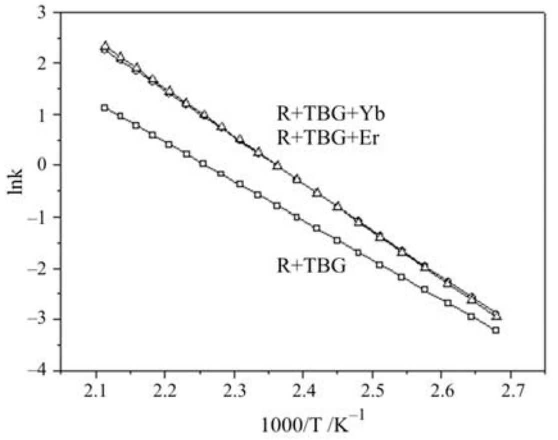


Fig. 7 Conversion rate (ln$k$) *vs*. the inverse of the temperature (1000/T) for □ – epoxy resin/TBG, ○ – epoxy resin/TBG/erbium triflate and △ – epoxy resin/TBG/ytterbium triflate

Conclusions

In order to reduce the curing temperature and time of powder coatings based on DGEBA/TBG mixtures, and thus obtain production benefits, erbium(III) and ytterbium(III) trifluoromethanesulfonates have been proposed as catalysts. The kinetics of the curing processes has been studied.

Two methods that allow the determination of the complete kinetic triplet (E, A, $g(\alpha)$) have been applied, as well as the simulation of the curing. Both methods require the effective E value to be known, which can be determined with an isoconversional procedure (model-free), for which STAR^e software has been used.

A kinetic study by means of non-isothermal tests in a DSC was carried out and a posterior iso-kinetic study was developed. All systems showed that the reaction mechanism followed an $m=0.5/n=1.5$ model, showing no dependence on the initiator used.

Reaction rates for all the systems were obtained. Results showed that adding lanthanide triflates accelerate the reaction of the system, but no differences were observed between ytterbium and erbium triflates.

Both FTIR and TG studies confirm that the main reaction, which takes place in systems cured with TBG alone or TBG with 1 h of lanthanide triflate is the nucleophilic reaction between nitrogen and oxirane ring.

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