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INFLUENCE OF THE PROPORTION OF YTTERBIUM TRIFLATE AS INITIATOR ON THE MECHANISM OF COPOLYMERIZATION OF DGEBA EPOXY RESIN AND γ-BUTYROLACTONE

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Non-isothermal differential scanning calorimetry (DSC) experiments were performed to study the kinetics of the curing process of mixtures of diglycidylether of bisphenol A (DGEBA) and γ-butyrolactone (γ-BL) with ytterbium triflate as an initiator. It can be deduced that the cured material consists of epoxide homopolymers with incorporated poly(ether-ester) unities, which come from the lactone incorporated into the network. The kinetic parameters, obtained using the non-isothermal isoconversional procedure, show not only the importance of the proportion of initiator but also the influence of γ-butyrolactone on the polymerization of DGEBA. The homopolymerization of DGEBA catalyzed by ytterbium triflate has an activation energy of 85.3 kJ mol^{-1}, which decreases to 68.2 kJ mol^{-1} in the presence of γ-butyrolactone forming copolymers. Analysis from DSC and FTIR data showed that, when the proportion of ytterbium triflate was increased, the reaction process accelerated and the mechanism of the cationic non-linear polymerization named activated monomer (AM) became more evident than the activated chain-end mechanism (ACE). Finally, the activation energies and the pre-exponential factors were determined for both mechanisms.

Keywords: *cationic polymerization, DSC, epoxy resins, FTIR, lactones*

Introduction

Cationic ring-opening polymerization has made a considerable contribution to the development of new polymer syntheses. These include the large-scale production of polyketals, polytetrahydrofurans, polysiloxanes and polyphosphazenes [1]. Cationic polymerization can be initiated by protonic acids, carbenium and onium ions, covalent initiators and Lewis acids. Among Lewis acids, the most commonly used are BF_3 and its complexes with ether or amines. However, Lewis acids are moisture sensitive and easily decomposed or deactivated in the presence of even a small amount of water.

Kobayashi *et al.* [2–4] were the first to describe lanthanide triflates to be effective as catalysts and stable in water. They are still active in the presence of many Lewis bases that contain nitrogen, oxygen, phosphorous and sulfur atoms. These catalysts are regarded as environmentally friendly because of their low toxicity and their ability to be reused. Because of its smaller ionic radius, ytterbium triflate has the highest Lewis acidity of the lanthanide triflates and, therefore, the highest catalytic activity. In previous studies we have demonstrated the effectiveness of using lanthanide triflates as cationic catalysts in the curing of DGEBA [5] and cycloaliphatic epoxy resins [6] by a ring-opening mechanism.

Our recent research has focused on achieving two main goals: 1) the preparation of new thermally- or chemically-reworkable three-dimensional materials for the electronic industry with high reliability and long term usability and 2) the reduction of shrinkage during curing in order to reduce the formation of microvoids and microcracks and facilitate the adhesion to the substrate, which increases the durability of the material [7, 8]. These two objectives led us to use ytterbium triflate to catalyze the copolymerization reactions of DGEBA epoxy resins with γ-butyrolactone [9, 10]. It has been reported that epoxy compounds and lactones produce spiroorthoester (SOE) intermediates in the presence of a Lewis acid [7] and that when SOEs polymerize they expand in volume. Mixtures of DGEBA and γ-BL cure with little contraction after gelation, because the polymerization of SOE is the principal process during the final stages of curing, as has been observed by FTIR studies [9]. As a consequence of the polymerization of the in-situ formed SOEs, ester groups are incorporated into the network, which makes the thermoset more readily reworkable as well [11].

The present paper focuses on the overall kinetics of curing of mixtures of DGEBA epoxy resin with

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different proportions of γ-butyrolactone and varying the proportion of ytterbium triflate used as an initiator. The influence of the variation of these proportions was analyzed by studying FTIR data and the kinetic parameters obtained with DSC.

Experimental

Materials

Diglycidylether of bisphenol A (DGEBA n=0.12) (epoxy equiv.=187 g eq^{-1}), γ-butyrolactone (γ-BL) and phenylglycidylether (PGE) (Aldrich) were used as received. Ytterbium(III) trifluoromethanesulfonate (Aldrich) was used without purification. Solvents were purified by standard methods.

Synthesis of 2-phenoxymethyl-1,4,6-trioxaspiro[4.4]nonane (SOE)

This product was synthesized by a previously described procedure [12] from phenylglycidylether and γ-butyrolactone with $BF_3{\cdot}OEt_2$ as catalyst. Results were similar when ytterbium triflate was used as the catalyst.

Preparation of the curing mixtures

The mixtures were prepared by dissolving the selected proportion of ytterbium triflate in the corresponding amount of γ-BL and adding the required proportion of DGEBA with magnetic stirring. Mixtures with SOE needed to be heated at 80°C (above fusion temperature) before the appropriate proportion of ytterbium triflate was added. The proportion of ytterbium triflate is given in phr (parts per hundred parts of resins, *w*/*w*). The prepared samples were kept at –18°C before use.

Methods

Calorimetric studies were carried out on a Mettler DSC-821^e thermal analyzer in covered Al pans under N_2 at heating rates of 2, 5, 10 and 15°C min^{-1}. 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.

The T_g's were calculated when curing was complete, by means of a second scan at 10°C min^{-1}, as the temperature of the half-way point of the jump in the heat capacity when the material changed from the glassy to the rubbery state.

In order to identify the different elemental processes that take place in the curing of the system under study, samples were cured isothermally at 150°C in a FTIR Bomem Michelson MB 100 spectrophotometer, with a resolution of 4 cm^{-1} in the absorbance mode. An attenuated total reflection accessory with thermal control and a diamond crystal (Golden Gate Heated Single Reflection Diamond ATR, Specac-Teknokroma) was used in order to determine the FTIR spectra. Details on the calculation of the conversion of the significant reactive groups are shown elsewhere [9].

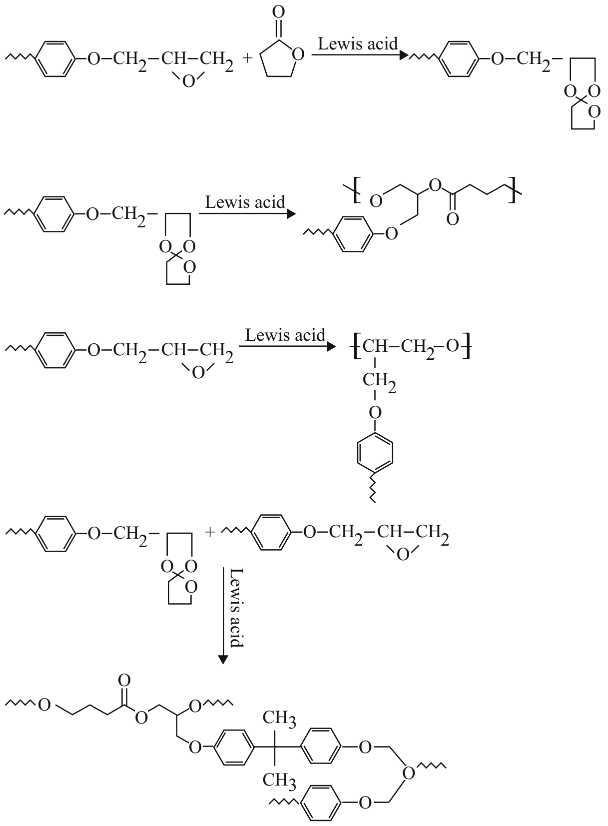
Results and discussion

The kinetic study of a reactive system is a valuable tool for ascertaining the mechanism that provides the final product. It can also give information about the degree of conversion and how it is affected by the immediate environment. Differential scanning calorimetry (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 [13].

In thermosetting materials, the reactive process is inseparable from the application of the material. Thus, kinetic information enables us to find out how the degree of conversion varies as a function of time for the set of operating temperatures.

It is not easy to study the isothermal cationic curing of epoxy systems. At high temperatures the curing is so fast that some heat is evolved before the device stabilizes, and at low temperatures the heat cannot be properly registered by the calorimeter at the start and at the end of the reaction because the reaction rate is so low that it falls below the sensitivity of the device. The non-isothermal DSC method at a controlled heating rate is the most suitable procedure for obtaining the kinetic parameters of reactive systems such as the one proposed in this work [10]. The system under study consists of DGEBA epoxy resin and γ-butyrolactone (γ-BL) initiated by ytterbium triflate as a Lewis acid. It must be noted that DGEBA has a functionality of four and γ-BL is bifunctional. Thus, a higher proportion of DGEBA leads to a higher density of cross-linking, while a higher proportion of γ-BL leads to a higher molecular mass between cross-links.

Scheme 1 shows the four reactive processes that can take place during curing: the first is the formation of SOE from epoxide and lactone groups; the second is the homopolymerization of SOE, which leads to the formation of linear ether-esters in the network; the third is the homopolymerization of epoxide groups; and the fourth is the reaction of SOE with epoxide groups. Because some of these four processes can



Scheme 1 Copolymerization of DGEBA with γ-BL

take place simultaneously, it is not possible calorimetrically to separate them for individual analysis, and a complementary technique such as FTIR is needed in order to identify the different reactions.

Figure 1 shows DSC plots of mixtures of DGEBA and γ-BL in two different molar ratios with 1 phr of ytterbium triflate. For purposes of comparison, the calorimetric curve of DGEBA with the same initiator has been included. As can be seen, the presence of γ-BL significantly influences the curing process of DGEBA promoted by ytterbium triflate. Adding γ-BL accelerates the reactive process and therefore the curve is shifted to lower temperatures.

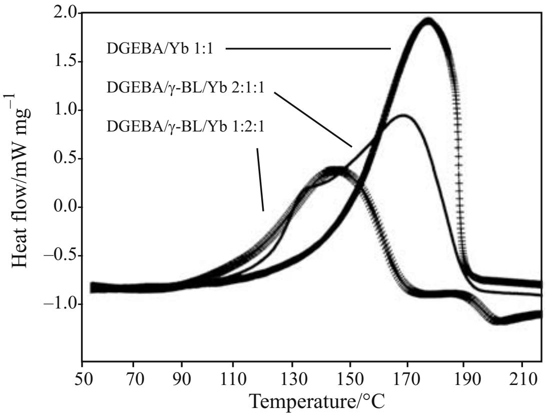


Fig. 1 DSC curves of DGEBA, DGEBA/γ-BL 2:1 and DGEBA/γ-BL 1:2 with 1 phr of ytterbium triflate at a heating rate of 10°C min^{-1}

Table 1 collects the compositions of the mixtures studied, the reaction enthalpies by mass and by equivalent of epoxy groups and the glass transition temperatures of the final materials. It can be seen that the heat evolved by the epoxy equivalent is practically the same as that evolved by pure DGEBA, which indicates that the reaction heat comes from the opening of the most strained epoxy ring. In general, an increase in the proportion of γ-BL reduces the T_g due to the fact that the γ-BL increases the flexibility of the network via SOE formation and subsequent polymerization. The isothermal curing in the IR proved that the band at 915 cm^{-1} of the epoxide group had disappeared, that the lactone band at 1773 cm^{-1} had decreased and that a new band had appeared at 1736 cm^{-1}, which indicated that lactone had indeed been introduced into the network through formation and polymerization of SOE. FTIR spectra of the curing of the DGEBA/γ-BL mixtures using ytterbium triflate as initiator are shown in previous works [9, 10]. It can be noticed that the T_g value of the network of the mixture of entry 2, with stoichiometric proportions of reactants, is significantly lower than the others, indicating that a certain amount of γ-BL re-

Table 1 Calorimetric parameters of the reaction processes of the systems studied initiated by ytterbium triflate

Entry	Formulations[a]	Eq. initiator/eq. epoxide	Δh/J g^{-1}	Δh^b/kJ ee^{-1}	T_g/°C
1	DGEBA/Yb 1:1	0.0030	500	93.5	111
2	DGEBA/γ-BL/Yb 1:2:1	0.0040	330	93.8	54
3	DGEBA/γ-BL/Yb 2:1:1	0.0034	445	94.1	98
4	DGEBA/γ-BL/Yb 2:1:2	0.0062	450	96.1	91
5	DGEBA/γ-BL/Yb 2:1:3	0.0093	447	96.4	93
6	DGEBA/SOE/Yb 2:1:1	0.0040	368	93.8	74
7	SOE/Yb 1:1	–	89	21.1	–40

[a] The compositions of the formulations are given in molar ratios with the exception of the proportion of initiator, given in phr;
[b] Enthalpies are expressed by equivalent of epoxy groups with the exception of entry 7 in which are expressed by equivalent of SOE

mains unreacted in the network and acts as a plasticizer [9]. This fact can be attributed to homopolymerization of epoxy groups and copolymerization of epoxy with SOE, which would obviously produce incomplete lactone reaction.

In order to acquire information about the different reactive processes, we homopolymerized SOE samples using ytterbium triflate as the initiator (entry 7 in Table 1), which allowed us to characterize this reaction calorimetrically and kinetically. We also used the same catalyst to study the copolymerization of SOE with DGEBA (entry 6 in Table 1). Figure 2 shows the calorimetric curves obtained for these two systems and those obtained from the homopolymerization of DGEBA (entry 1, Table 1) and from the copolymerization of DGEBA/γ-BL in proportion 2:1:1 (entry 3, Table 1). In the figure, we can clearly observe that homopolymerization of SOE takes place at higher temperatures and evolves less heat (21.1 kJ eq^{-1}) than the other processes, while the reaction of DGEBA with SOE takes place in a broad range of temperatures with a reaction heat similar to that of the homopolymerization of DGEBA.

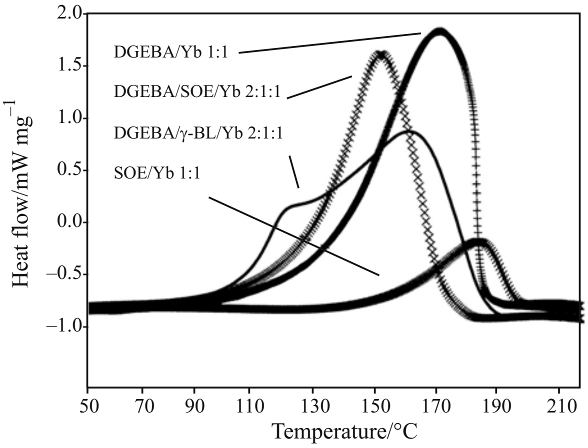


Fig. 2 DSC curves of DGEBA, DGEBA/SOE 2:1 DGEBA/γ-BL 2:1 and SOE with 1 phr of ytterbium triflate at a heating rate of 10°C min^{-1}

We used non-isothermal DSC experiments to study how the proportion of γ-BL affected the kinetics of the curing process. The kinetics of the heterogeneous condensed phase reactions in non-isothermal conditions is described by the basic equation:

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

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

To interpret the kinetic results we used the isoconversional method [14]. This method presupposes that the reaction rate at a constant conversion is only a function of temperature. For each conversion, the activation energy E_α is related to the rate of conversion and temperature by:

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

In the systems under study, the reaction rate not only depends on the functional groups that react in multistep processes, but also on the active initiator, which in turn depends on the previous thermal history. This should result in E_α varying with conversion [15, 16].

If the reaction mechanism is known, for every α it is also possible to calculate the corresponding pre-exponential factor A_α for every E_α. In this paper, in order to assign a reaction mechanism to the system studied, we used the master curves procedure of Criado [17, 18], which is described elsewhere [19].

Instead of using the differential equation (Eq. (2)) the E_α and A_α were obtained from the Kissinger–Akahira–Sunose (KAS) equation [20, 21]:

$$\ln\frac{\beta}{T^2} = \ln\frac{A_\alpha R}{E_\alpha g(\alpha)} - \frac{E_\alpha}{RT} \qquad (3)$$

where

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

is the so-called integral function. This equation can be deduced integrating Eq. (1) and using the Coats–Redfern approximation [22] and considering that $2RT/E$ is much lower than 1 to solve the so-called temperature integral.

For each α=const. and for the set of heating rates used, the plot $\ln(\beta/T^2)$ *vs.* $1/T$ should be a straight line, whose slope can be used to evaluate the activation energy. From the intercept, the pre-exponential factor A_α is obtained using Eq. (3) if the kinetic model is known. Table 2 shows the activation parameters for α=0.5, the best kinetic models found for the various reactions analyzed and the form of the $g(\alpha)$ function.

Figure 3 shows the dependence of the activation energy against the degree of conversion for the reaction of DGEBA/Yb 1:1, DGEBA/γ-BL/Yb 2:1:1 and DGEBA/γ-BL/Yb 1:2:1 in the range 0.1<α<0.9. At first, the activation energy decreases. Then it remains practically constant between 30 and 70% of conversion

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

Entry	Formulations[a]	E^b/kJ mol^{-1}	A^c/s^{-1}	k^d/s^{-1}	Kinetic model, $g(\alpha)$ function[e]
1	DGEBA/Yb 1:1	85.3	$4.36\cdot10^7$	$1.28\cdot10^{-3}$	R_3, $g(\alpha)=1-(1-\alpha)^{1/3}$
2	DGEBA/γ-BL/Yb 1:2:1	74.1	$5.34\cdot10^6$	$3.80\cdot10^{-3}$	R_3, $g(\alpha)=1-(1-\alpha)^{1/3}$
3	DGEBA/γ-BL/Yb 2:1:1	68.2	–		–
4	DGEBA/γ-BL/Yb 2:1:2	70.5	–		–
5	DGEBA/γ-BL/Yb 2:1:3	75.3	–		–
6	DGEBA/SOE/Yb 2:1:1	64.2	$4.08\cdot10^5$	$4.85\cdot10^{-3}$	A_2, $g(\alpha)=[-\ln(1-\alpha)]^{1/2}$
7	SOE/Yb 1:1	94.9	$2.28\cdot10^8$	$4.39\cdot10^{-4}$	R_3, $g(\alpha)=1-(1-\alpha)^{1/3}$

[a] The compositions of the formulations are given in molar ratios with the exception of the proportion of initiator given in phr.
[b] The values of activation energies have been taken for α=0.5.
[c] The values of pre-exponential factor have been taken for α=0.5 considering the kinetic model.
[d] Values of rate constant at 150°C calculated using the Arrhenius equation.
[e] The selected model was the one that best correlate the experimental results

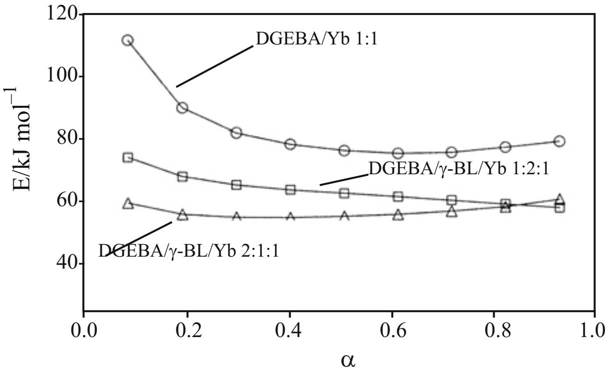


Fig. 3 Dependence of activation energy on the degree of conversion for DGEBA, DGEBA/γ-BL 2:1 and DGEBA/γ-BL 1:2 with 1 phr of ytterbium triflate

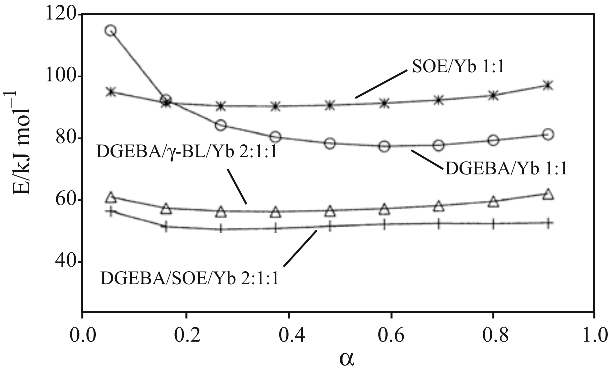


Fig. 4 Dependence of activation energy on the degree of conversion for DGEBA, DGEBA/SOE 2:1 and DGEBA/γ-BL 2:1 and SOE with 1 phr of ytterbium triflate

and finally it increases slightly. In the initial steps of the reaction, the higher activation energy can be attributed to the initiation process, while during the propagation this value remains practically constant. This behavior is characteristic of autocatalytic processes [16, 23]. For α=0.5, the activation energy for the homopolymerization of DGEBA is about 85.3 kJ mol^{-1}. Adding γ-BL to the reactive mixture lowers the activation energy. It must be noted that mixtures containing γ-BL lead to simultaneous processes that contribute to the activation energy. The higher proportion of γ-BL facilitates the final step of the reaction, since the activation energy even decreases (formulation DGEBA/γ-BL/Yb 1:2:1). This may happen because the unreacted lactone acts as a plasticizer and makes the diffusion easier. The values of the rate constants in Table 2 clearly show the accelerative effect of the γ-BL on the curing of the DGEBA.

Figure 4 plots activation energy *vs*. conversion degree for systems containing SOE and compares them to the homopolymerization of DGEBA and its copolymerization with lactone. It must be noted that the homopolymerization of SOE is the less kinetically favored reaction, because its activation energy is higher (about 95 kJ mol^{-1}). It can also be observed that the activation energy of the reaction of the DGEBA/SOE system is the lowest, possibly because copolymerization is the most favorable reaction.

The activation energies, the pre-exponential factors and the rate constants for these reactive systems are collected in Table 2. It is interesting to observe that the pre-exponential factors of the homopolymerization of DGEBA and SOE are the highest, but this effect is compensated for the highest activation energies. This is why homopolymerization of SOE shows the lesser rate constant value. We could not calculate the pre-exponential factors and rate constants for the formulations in entries 3–5, since the complex shape of the exotherms (Fig. 5) does not match any theoretical kinetic models.

We further studied how the proportion of initiator influenced the curing and the individual reactive processes. Figure 5 shows the DSC calorimetric curves of the curing of mixtures of DGEBA/γ-BL 2:1 with different proportions of ytterbium triflate (1, 2 and 3 phr). First of all, we can observe that the curing process accelerates when the proportion of initiator increases, since the exotherms are shifted to lower temperatures.

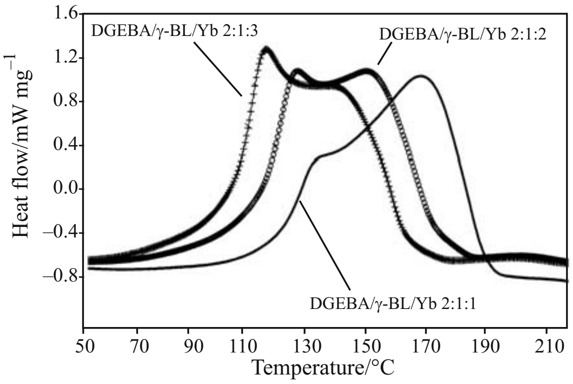


Fig. 5 DSC curves of DGEBA/γ-BL 2:1 with 1, 2 and 3 phr of ytterbium triflate at a heating rate of 10°C min^{-1}

It is also noticeable that the shapes of the peaks change with the initiator content. Table 1 shows the reaction enthalpies for these systems. In all cases, the enthalpy by epoxy equivalent is similar so we can conclude that all DGEBA has polymerized. The T_g values confirm that the obtained networks are similar. Consequently, differences in the shape of the DSC curves should not be attributed to differences in the extent of the four different processes (Scheme 1) [9, 10].

A possible explanation for the different shapes on changing the amount of initiator can be found in a previous study reported by Matejka *et al.* [24], who analyzed the cationic polymerization of DGEBA in the presence of γ-BL with BF_3·4-methoxyaniline as initiator. They suggested that there are two different propagation mechanisms, the activated chain-end (ACE) and the activated monomer (AM), which are described for cationic ring-opening polymerization [25, 26]. These authors reported that the AM mechanism is preferred in the presence of a relatively high content of the initiator and hydroxylic groups. In the cationic polymerization of heterocycles proceeding by ACE mechanism, propagation involves nucleophilic attack of the heteroatom of the monomer to the growing chain end, which is a cationic species. In the polymerization that proceeds by AM mechanism there are no active species at the growing chain end, and the monomer is in this case activated by the initiator and undergoes the nucleophilic attack on the uncharged growing chain end. The ACE mechanism is characterized by back-biting processes that lead to oligomeric species. However, when ring-opening polymerization is applied to the formation of thermosetting materials, the ACE mechanism produces inter- or intramolecular chain transfers which do not lead to relevant changes in the network structure.

Matejka *et al.* [24] proposed that protons coming from the BF_3·4-methoxyaniline system coordinates oxirane oxygen, which originates the active species (AM mechanism). In our case, ytterbium would play the same role as the protons in the activation of the monomer, but in a previous study [9] IR spectroscopy showed that ytterbium coordinates in both the oxirane oxygen and the carbonylic oxygen of the lactone. Thus, the AM mechanism should involve two different active species in our reactive system, and it is hypothesized that a lactone-ytterbium complex is formed that may enhance the activity of the initiator.

From the above, it seems that the change in the relative intensity of the two peaks in the exotherm when the proportion of initiator is varied must be the result of the competition between the two propagation mechanisms. When the proportion of initiator increases, the exotherm at lower temperatures becomes more important. Therefore, this exotherm must be related to the propagation by the AM mechanism and the second exotherm by the ACE mechanism. This hypothesis has been confirmed by adding a little proportion of ethanol to the reactive mixture. Its calorimetric curve shows an increase of the exotherm at lower temperatures, similarly to the one observed previously by us on adding alcohol in cycloaliphatic epoxy photocuring [27].

It is known that cationic polymerization of oxiranes leads to the formation of a certain amount of hydroxyl-containing molecules through the conversion of activated epoxy monomers to vinylethers and hydroxyl terminated chains [28, 29]. Evidences on the existence of the AM mechanism in the curing of DGEBA/γ-BL system initiated with ytterbium triflate have been observed by FTIR. The appearance of an absorption band between 3200 and 3600 cm^{-1} when the proportion of initiator increases confirms that a certain amount of hydroxyl groups is formed, thus favoring AM mechanism. In previous works [27, 30] we have detected evidences of competence between AM and ACE mechanism in cationic thermal and photocuring of epoxy systems. These works show the schemes of AM and ACE mechanisms, which are expected to occur for the studied systems.

To make a kinetic study of both propagation processes, we used the isoconversional method. Figure 6 shows the variation in activation energies *vs.* conversion degree. As can be seen, the activation energies increase as the proportion of initiator increases, but in all cases they are lower than those determined for the homopolymerization reaction of DGEBA (Fig. 3), which confirms that lactone plays a kinetic role. If we assume that propagation by the AM mechanism is predominant at higher proportions of initiator we can conclude that the AM propagation mechanism must have a higher activation energy than the ACE mechanism. Moreover, the competition between the two mechanisms depends on the conversion degrees.

Table 3 Apparent activation energies, pre-exponential factors and kinetic models for the separated exotherms of the curing of DGEBA/γ-BL 2:1 with different proportion of ytterbium triflate

Formulations[a]	First exotherm				Second exotherm			
	E^b/kJ mol^{-1}	A^c/s^{-1}	k^d/s^{-1}	kinetic model[e]	E^b/kJ mol^{-1}	A^c/s^{-1}	k^d/s^{-1}	kinetic model[e]
DGEBA/γ-BL/Yb 2:1:1	79.8	$6.63\cdot10^{7}$	$9.30\cdot10^{-3}$	$n+m=2$, $n=1.5$	65.6	$1.47\cdot10^{5}$	$1.16\cdot10^{-3}$	R_3
DGEBA/γ-BL/Yb 2:1:2	71.6	$1.21\cdot10^{8}$	0.174	$n+m=2$, $n=1.5$	69.6	$1.11\cdot10^{6}$	$2.82\cdot10^{-3}$	R_3
DGEBA/γ-BL/Yb 2:1:3	73.7	$3.59\cdot10^{8}$	0.284	$n+m=2$, $n=1.5$	64.4	$3.92\cdot10^{5}$	$4.04\cdot10^{-3}$	R_3

[a] The compositions of the formulations are given in molar ratios with the exception of the proportion of initiator given in phr

[b] Values of activation energies associated to the conversion of the exotherm

[c] Values of pre-exponential factor associated to the conversion of the exotherm taking into account the kinetic model

[d] Values of rate constant at 150°C calculated using the Arrhenius equation

[e] The selected models were the ones that best correlate the experimental results

For model $n+m=2$, $n=1.5$ (autocatalytic model) $g(\alpha)=[(1-\alpha)\alpha^{-1}]^{-0.5}(0.5)^{-1}$

For model R_3 $g(\alpha)=1-(1-\alpha)^{1/3}$.

In order to make a kinetic analysis of the two processes separately, we used a mathematical software package (Peak Fit from Jandel Scientific Software, with the so-called 'log normal-4-area' function) to separate the two peaks of the curves in Fig. 5. The kinetic parameters associated to the set of curves obtained for each exotherm were obtained by applying KAS procedure to the temperature of the maximum of the exotherm, T_p.

$$\ln\frac{\beta}{T_p^2}=\ln\frac{AR}{Eg(\alpha_p)}-\frac{E}{RT_p} \qquad (4)$$

Equation (4) becomes the well-known Kissinger equation [20] if we use an *n* order reaction mechanism. i.e. $g(\alpha_p)\approx 1$. The results obtained by applying this equation to both peaks are summarized in Table 3. As we can see, the apparent activation energies associated to the first exotherm (overall value, 75.0 kJ mol^{-1}) are slightly higher than those associated to the second one (66.6 kJ mol^{-1}). It must be noted that these energies correspond to the apparent activation energies associated to the reactive processes that take place simultaneously (Scheme 1). The same table also shows the pre-exponential factors for the three systems studied. We can observe that the values associated to the first exotherm are appreciably higher, which explains why the reactive processes associated to the first exotherm (and consequently the process of curing in a whole) accelerate when the proportion of initiator is increased (Fig. 5).

The differences in activation energies and pre-exponential factors between both exotherms favor the preponderance of the AM mechanism rather than the ACE mechanism when the proportion of initiator is increased, which increases the overall activation energy (Table 2). Because of the compensation effect between the activation energy and the pre-exponential factor, it would be more accurate to analyze the reaction rate using the rate constant that include both parameters. Table 3 shows that an increase in the initiator content produced a big increase in *k* values. It can also be seen that values of rate constant corresponding to first exotherm (AM mechanism) are higher that those corresponding to second exotherm (ACE mechanism).

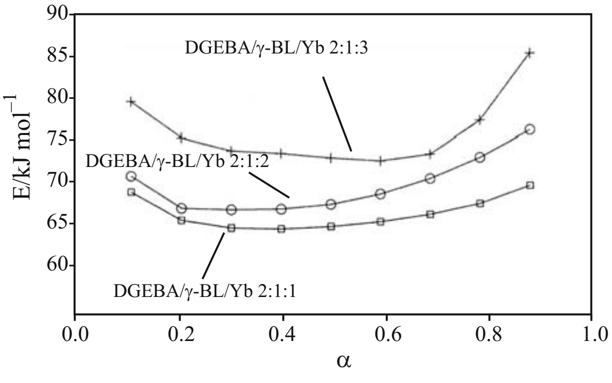


Fig. 6 Dependence of activation energy on the degree of conversion for DGEBA/γ-BL 2:1 with 1, 2 and 3 phr of ytterbium triflate

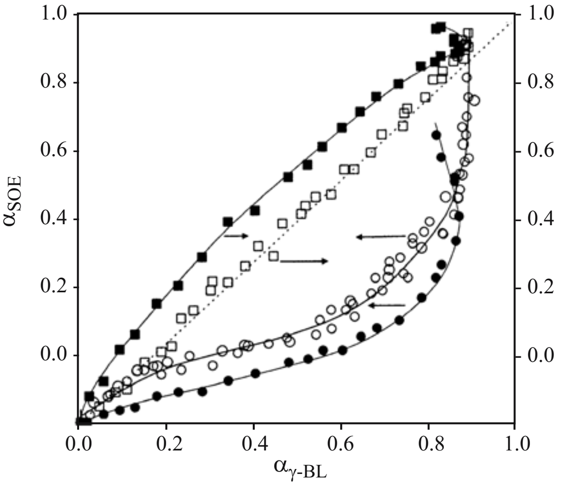


Fig. 7 Conversion profiles of epoxy and SOE groups *vs.* lactone conversion for DGEBA/γ-BL 2:1 with 1 phr (open symbols) and 3 phr (filled symbols) of ytterbium triflate cured at 150°C

Figure 7 shows epoxy conversion plotted *vs.* lactone conversion for 2:1:1 and 2:1:3 formulations, cured isothermally at 150°C under FTIR/ATR. In formulation 2:1:1 the profile of epoxy conversion is almost diagonal, which means that epoxy homopolymerization and epoxy copolymerization with lactone groups are almost identical processes from the kinetic point of view. In contrast, formulation 2:1:3 reveals that epoxy conversion is enhanced at the beginning of the curing process, and that lactone conversion is incomplete, resulting in γ-BL molecules trapped in the network and even some depolymerization of SOE back to γ-BL and epoxy. Increasing the content of initiator clearly favors epoxy homopolymerization at the beginning, which can be attributed to an enhancement of the AM mechanism in detriment of ACE mechanism.

Conclusions

The calorimetric analysis of the reactive processes of the DGEBA/ytterbium triflate in the presence of γ-BL or SOE allowed us to find a reaction enthalpy of about 94 kJ eq^{-1} of epoxide. This value, in addition to the T_g values of the materials obtained after curing and the FTIR results, allowed us to conclude that the four possible processes (the reaction of γ-BL with epoxide to give SOE, the reaction of DGEBA with SOE, the homopolymerization of DGEBA and the homopolymerization of SOE) overlap during curing.

Kinetic analysis made possible the assignment of activation energies to the different processes. Using the isoconversional method we found that, in a conversion range between 30 and 70%, the apparent activation energy of the process is practically constant. We assigned an activation energy of 85.3 kJ mol^{-1} to the homopolymerization of DGEBA catalyzed by ytterbium triflate. We observed that this activation energy is considerably lower in the presence of γ-BL. For the homopolymerization of SOE we found an activation energy of 94.9 kJ mol^{-1}.

The appearance of two partially overlapped exotherms that change in shape when the proportion of initiator increases made us aware of the competition between two propagation mechanisms related to epoxy homopolymerization: AM and ACE. The kinetic analysis made possible the assignment of apparent activation energies, pre-exponential factors and rate constants to both propagation mechanisms. The obtained values of rate constants explain why an increase in the proportion of initiator accelerates the curing process, despite the apparent increase in activation energy.

FTIR analysis showed that copolymerization of DGEBA with γ-BL occurred, and that the in situ formed SOEs subsequently polymerized. The presence of some hydroxylic groups in the cured sample should account for the existence of the AM mechanism related to DGEBA homopolymerization. Isothermal FTIR experiments showed that an increase in the proportion of initiator not only accelerated the curing process but also favored homopolymerization of DGEBA, which can be attributed to a different balance between the AM and ACE competitive mechanisms.

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