

CATIONIC CROSSLINKING OF SOLID DGEBA RESINS WITH YTTERBIUM(III) TRIFLUOROMETHANESULFONATE AS INITIATOR

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Solid bisphenol-A epoxy resin of medium molecular mass was cured using a Lewis acid initiator (ytterbium(III) trifluoromethanesulfonate) in three different proportions (0.5, 1 and 2 phr). A kinetic study was performed in a differential scanning calorimeter. The complete kinetic triplet was determined (activation energy, pre-exponential factor, and integral function of the degree of conversion) for each system. A kinetic analysis was performed with an integral isoconversional procedure (free model), and the kinetic model was determined both with the Coats–Redfern method (the obtained isoconversional value being accepted as the effective activation energy) and through the compensation effect. All the systems followed the same isothermal curing model simulated from non-isothermal ones. The growth-of-nuclei Avrami kinetic model $A_{3/2}$ has been proposed as the polymerization kinetic model. The addition of initiator accelerated the reaction especially when 2 phr was added. 0.5 and 1 phr showed very few kinetic differences between them.

Keywords: epoxy resin, initiator, kinetics (polym.), ytterbium triflate

Introduction

The formulation of low curing temperatures epoxy powder coatings (using new initiators and cross-linkers) has become one of the main lines of research in industries and related research centres. One of the main objectives of this research is to obtain epoxy 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. Properties of the paints (mechanical, thermal, anticorrosive and so on) are specially influenced by the kind of epoxy network-structure (which depends on the cross-linker and initiator employed in its formulation).

Powder coatings are currently the fastest growing section of industrial paints, because of their favourable environmental attributes and performance advantages. They are well-adapted for the main strategic goals of the paint industry, namely corrosion protection, improved durability, increased transfer efficiency, elimination of organic solvents, reduction of toxic waste, conservation of energy and reduction of costs. Since they are fully solid, and without

volatile organic emissions, powder coatings are considered to be the best alternative for the reduction of the volatile organic contents (VOCs) of solvent-based paints, among the emerging coating technologies (powder coatings, high solid coatings and waterborne ones) [1, 2].

Compared to liquid paints, the film formation process of powder coatings is different since it is occurring in the molten phase. Melting, flow, gel point and cure completion are the principal stages in film formation of powder coatings and determine both the aesthetic and protective properties of the paint. The duration of these stages is directly affected by the paint composition, e.g., type of binder and cross-linker, pigmentation (nature and particle size, packaging and distribution), catalyst, and additives, curing and application conditions. These factors, in turn, determine important coating characteristics such as levelling, adhesion, gloss, chemical resistance and exterior durability [3–12].

Catalysts are important in polymerization processes because they decrease the activation energies and accelerate the reaction. They can be stimulated by heating or photoirradiation but, from the practical point of view, heating is the easier

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option; because of homogeneous heating of reaction mixtures can be achieved without difficulty [13]. In addition, elementary reactions are accelerated and the viscosity of the reaction mixture decreases. This shortens the reaction time, especially for systems in which the curing rate is diffusion-determined. Among the new thermal initiators, those having anions with low nucleophilicity, minimize or prevent the reaction of the growing chain with the anion, being more active their cationic salts and more effective the polymerization [14].

The Lewis acid character and the great oxophilicity of lanthanide compounds is highly improved in the case of lanthanide triflates because of the electron-withdrawing capacity of the anionic group [15]. Thus, the metal can coordinate to the epoxy oxygens weakening the C–O bond. Lewis acids, 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. This fact represents an enormous advantage in their technological application as initiators.

As usual in Lewis acid initiators, ytterbium(III) trifluoromethanesulfonate leads to chain growth polymerization of epoxy compounds, which mainly proceed by the cationic chain end mechanism depicted in Scheme 1, where oxirane group of DGEBA resin is opened by coordination of oxirane oxygen to the initiator and subsequent nucleophilic attack of another oxirane group.

Moreover, the presence of hydroxylic groups can lead to hydroxylic initiated polyetherification processes that can change both the kinetics of the

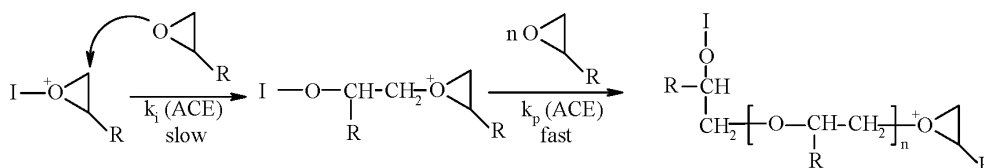
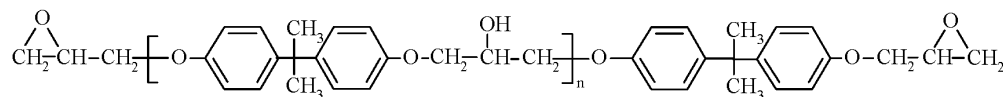
reaction and the properties of the materials (Scheme 2), although this kind of reaction should be less important in extension than the first one, because of the low proportion of hydroxyls. This mechanism is known as activated monomer mechanism.

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 [16, 17].

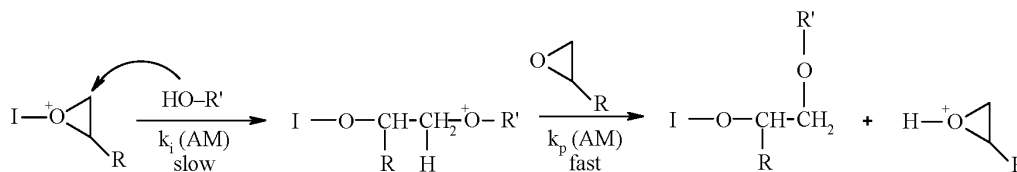
The usefulness of lanthanide triflates as initiators has been proved in other studies [14, 18] with liquid epoxy resins, showing that they highly accelerated the reactions of the system. Nevertheless, the behaviour of these initiators in powder coatings (using epoxy resins in the molten phase) has not been studied until now.

To predict the temperatures and times at which these polymerizations should be performed, one must know the kinetics. Preliminary kinetic studies have been performed using the method described by Kissinger [19]. This procedure, used by many authors because of its simplicity, assumes a reaction mechanism of order n . 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. Here we attempt to establish a

DGEBA resin:



Scheme 1 Activated chain-end mechanism/ACE



Scheme 2 Activated monomer mechanism/AM

method for this type of polymerization that allows the complete kinetic triplet (kinetic model, E and A) to be determined throughout the entire reaction. To analyze exothermic polymerizations, we have adapted a method from earlier studies addressing the kinetics of curing and degradation [20].

Many exothermic polymerizations present 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 works studying the curing kinetics of powder coatings and liquid ones using systems containing epoxy resins and diamines have been published [22–24].

In this work a complete kinetic study of homopolymerization of a medium molecular mass DGEBA resin with ytterbium(III) trifluoromethanesulfonate as initiator has been developed. Isothermal polymerization was simulated with non isothermal data. The reaction model was established from non isothermal data with two different methods and posterior isothermal scans during different times were performed in order to compare conversion–time–temperature data of the chosen kinetic model, experimental data and the isoconversional obtained data. The first method was the Coats–Redfern method [25–27], and the E value obtained isoconversionally was taken as the effective value. The second method used the compensation effect 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, 773 gr eq⁻¹ epoxy (from Huntsman), was homo-polymerized with ytterbium(III) trifluoromethanesulfonate (from Aldrich) added in three different amounts: 0.5, 1 and 2 phr (parts of initiator per hundred of resin, mass/mass).

Samples were premixed and hand-shacked until good mixing was afforded. After that, the material was extruded in a single screw extruder (Haake Rheomex 254), where operating conditions were 80°C 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 cm³ 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 not-cured-samples of epoxy systems using three different ytterbium triflate initiator amounts. The scans were performed at the range of temperature from 25 to 300°C.

Isothermal scans at 120°C were also carried out in order to obtain the experimental isothermal conversion degree. Different samples were maintained at the isothermal temperature for different given times. After each isothermal scan, the sample was cooled until ambient temperature inside the calorimeter and a second dynamic scan was registered in order to obtain the residual enthalpy. With these data and the total enthalpy obtained from a dynamic scan to a non-cured sample, the conversion degree was calculated.

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

Kinetic analysis

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

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

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:

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

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

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

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 .

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:

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

where β is the heating rate.

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

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

For a given kinetic model, the linear representation of $\ln[g(\alpha)/T^2]$ vs. T^{-1} makes it possible to determine E 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 similar to that obtained isoconversionally (considered to be the effective E value) was selected.

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

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

The linear representation of $\ln[\beta/T^2]$ vs. $1/T$ makes it possible to determine E 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[®] Mettler Software uses Eqs (6) and (2) to determine the isoconversional 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:

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

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

The slope $a=1/RT_{\text{iso}}$ is related to the isokinetic temperature (T_{iso}), and the intercept $b=\ln k_{\text{iso}}$ 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 only one mechanism is present, whereas the existence of parameters that do not meet the IKR implies that there are multiple reaction mechanisms [31].

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 increasing amounts of ytterbium triflate in the kinetics of the system has been studied.

Results and discussion

In Fig. 1 we can see the curves corresponding to the heating of three different samples with 0.5, 1 and 2 phr of ytterbium, at a rate of 5°C min^{-1} . The thermograms

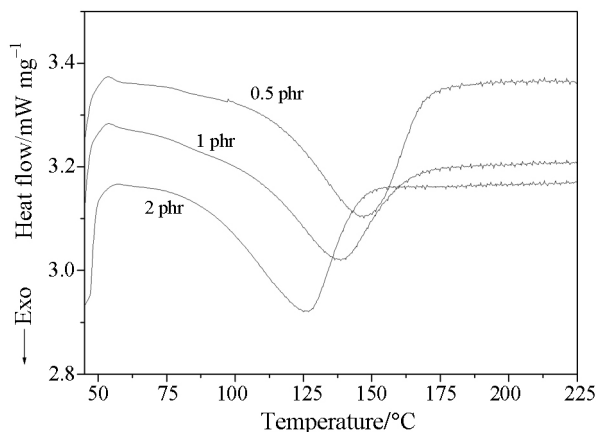


Fig. 1 Non-isothermal DSC curves at 5°C min^{-1} of heating rate for three different epoxy systems containing 0.5, 1 and 2 phr of ytterbium triflate

exhibits a small endothermic peak at 55°C (where the T_g should be detected) related to the physical aging of the DGEBA and an exothermic one at higher temperatures (near 120°C) related to the curing reaction of the epoxy resin. It can be seen that for the three different samples, a similar shape of the curves was obtained. As the content of ytterbium triflate increases, the curve shifts to minor temperatures.

The results of the calorimetric scans were employed to obtain the conversion degree with the temperature, by means of the STAR^o software. Figure 2 shows α vs. T plots for a constant rate of 5°C min⁻¹ for the three samples studied.

It can be seen that the higher the content of ytterbium triflate, the lower the temperature for a given conversion degree is. It could be also pointed out, that for 0.5 phr of initiator the reaction seems faster at high temperatures. On the other hand, when the amount of initiator is 2 phr, there are few differences with the other two samples but the curing was always faster.

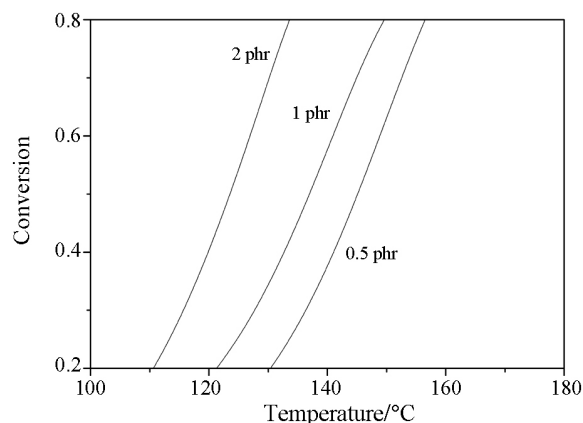


Fig. 2 Conversion degree (α) vs. temperature plots for a heating rate of 5°C min⁻¹ for three different epoxy systems containing 0.5, 1 and 2 phr of ytterbium triflate as initiator

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 1 shows the kinetic parameters of non-isothermal curing obtained from Eq. (6) for the sample prepared at 1 phr of ytterbium triflate. The process was repeated with the other proportions of triflate.

Figure 3 shows the experimental relationship between $\ln[\beta/T^2]$ and the inverse of the temperature, with the adjustment made with Eq. (6). Table 1 shows that E is weakly modified during curing, rising with the advance of the reaction, probably due to the increased viscosity of the reaction medium as the molecular mass increases. The parameters $\ln[AR/g(\alpha)E]$ and the associated A values exhibit the same trend as E . Similar tendencies were obtained for the other two proportions.

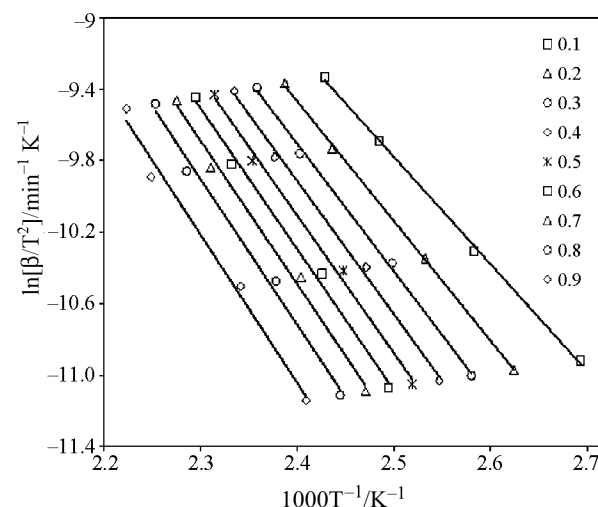


Fig. 3 Correlations between $\ln[\beta/T^2]$ and the inverse of the temperature ($1000/T$) for different values of α of an epoxy sample with 1 phr of ytterbium triflate

Table 1 Kinetic parameters of non-isothermal homopolymerization obtained by Eq. (6), for a sample with 1 phr of ytterbium triflate.

α	^a $E/\text{kJ mol}^{-1}$	^a $\ln[AR/g(\alpha)E]/\text{K}^{-1} \text{ min}^{-1}$	^b $\ln[g(\alpha)/A]/\text{min}$	^c $\ln A/\text{min}^{-1}$	r
0.1	49.9	5.22	-13.91	12.41	0.9994
0.2	55.2	6.49	-15.29	14.29	0.9997
0.3	58.5	7.23	-16.09	15.40	0.9991
0.4	60.9	7.74	-16.64	16.19	0.9984
0.5	62.7	8.10	-17.03	16.78	0.9977
0.6	64.1	8.35	-17.30	17.25	0.9971
0.7	65.2	8.50	-17.46	17.59	0.9965
0.8	66.2	8.58	-17.56	17.88	0.9960
0.9	67.4	8.63	-17.63	18.19	0.9941

^a $\ln[AR/g(\alpha)E]$ and E were calculated on the basis of non-isothermal DSC experiments as the intercept and slope of the isoconversional relationship $\ln[\beta/T^2] = \ln[AR/g(\alpha)E] - E/RT$, ^b $\ln[g(\alpha)/A]$ was calculated on the basis of $\ln[AR/g(\alpha)E]$ and E , ^c $\ln A$ was calculated with kinetic model $A_{3/2}$ and $\ln[g(\alpha)/A]$

Table 2 Algebraic expressions for $f(\alpha)$ and $g(\alpha)$ for the kinetic models used

Models	$f(\alpha)$	$g(\alpha)$
$A_{3/2}$	$(3/2)(1-\alpha)[- \ln(1-\alpha)]^{1/3}$	$[- \ln(1-\alpha)]^{2/3}$
A_2	$2(1-\alpha)[- \ln(1-\alpha)]^{1/2}$	$[- \ln(1-\alpha)]^{1/2}$
A_3	$3(1-\alpha)[- \ln(1-\alpha)]^{2/3}$	$[- \ln(1-\alpha)]^{1/3}$
A_4	$4(1-\alpha)[- \ln(1-\alpha)]^{3/4}$	$[- \ln(1-\alpha)]^{1/4}$
R_2	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
R_3	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
D_1	$(2\alpha)^{-1}$	α^2
D_2	$[- \ln(1-\alpha)]^{-1}$	$(1-\alpha)\ln(1-\alpha)+\alpha$
D_3	$3/2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	$[1-(1-\alpha)^{1/3}]^2$
D_4	$3/2(1-\alpha)^{1/3}[1-(1-\alpha)^{1/3}]^{-1}$	$(1-2/3\alpha)(1-\alpha)^{2/3}$
F_1	$(1-\alpha)$	$-\ln(1-\alpha)$
power	$2\alpha^{1/2}$	$\alpha^{1/2}$
$n+m=2; n=1.9$	$\alpha^{0.1}(1-\alpha)^{1.9}$	$[(1-\alpha)\alpha^{-1}]^{-0.9}(0.9)^{-1}$
$n+m=2; n=1.5$	$\alpha^{0.5}(1-\alpha)^{1.5}$	$[(1-\alpha)\alpha^{-1}]^{-0.5}(0.5)^{-1}$
$n=2$	$(1-\alpha)^2$	$-1+(1-\alpha)^{-1}$
$n=3$	$(1-\alpha)^3$	$2^{-1}[-1+(1-\alpha)^{-2}]$

Table 3 Arrhenius parameters determined by the Coats–Redfern method and isokinetic parameters for a sample with 1 phr of ytterbium triflate at a heating rate of 5°C min^{-1}

Models	Coats–Redfern/1 phr			IKR/1 phr			
	$E/\text{kJ mol}^{-1}$	$\ln A/\text{min}^{-1}$	r	$a/\text{mol kJ}^{-1}$	b/min^{-1}	$T_{\text{iso}}/^\circ\text{C}$	r
$A_{3/2}$	67.17	17.966	0.9992	0.3300	-3.949	91.45	0.9994
A_2	48.67	12.288	0.9991	0.3017	-2.138	125.64	0.9988
A_3	30.17	6.464	0.9989	0.2734	-0.326	166.90	0.9976
A_4	21.01	3.429	0.9987	0.2593	0.579	190.91	0.9968
R_2	86.47	22.840	0.9944	0.3699	-7.791	52.14	0.9994
R_3	92.09	24.202	0.9966	0.3623	-2.287	58.99	0.9989
D_1	149.39	41.560	0.9854	0.4673	-13.773	-15.61	0.9982
D_2	174.73	49.486	0.9924	0.4920	-15.746	-28.53	0.9994
D_3	190.99	52.245	0.9968	0.5231	-18.879	-43.05	0.9999
D_4	175.71	47.527	0.9938	0.5022	-17.785	-33.51	0.9997
F_1	104.17	29.087	0.9993	0.3866	-7.572	38.09	0.9999
power	32.23	6.885	0.9802	0.2794	-0.971	157.43	0.9953
$n+m=2; n=1.9$	131.85	37.948	0.997	0.4249	-9.318	10.04	0.9970
$n+m=2; n=1.5$	70.22	19.863	0.9968	0.3324	-3.077	88.80	0.9997
$n=2$	147.26	42.463	0.9971	0.4481	-10.837	-4.56	0.9961
$n=3$	199.66	58.584	0.9874	0.5238	-14.887	-43.37	0.9838

To establish the kinetic model for the system with an initiator amount of 1 phr, the isoconversional kinetic parameters (Table 1) and the Eq. (7) were used (the same process was done for the other two systems). From the parameters $\ln[AR/g(\alpha)E]$ and E shown in Table 1 and the $g(\alpha)$ functions, A values were calculated for all the different kinetic models used (Table 2). Subsequently, by plotting E vs. $\ln A$,

we determined the IKRs for all the models (Eq. (7)). Table 3 shows the obtained results, as well as the T_{iso} values determined from the slope of the IKRs. Although some models exhibit IKRs (specially $A_{3/2}$ and $m=0.5/n=1.5$ models), the model considered that is the best one describing the homopolymerization is the nucleation growth type $A_{3/2}$ because this model shows a good regression and T_{iso} values closer to the

Table 4 Arrhenius parameters determined by the Coats–Redfern method for samples with 0.5 and 2 phr of ytterbium triflate at a heating rate of $5^{\circ}\text{C min}^{-1}$

Models	Coats–Redfern/1 phr			IKR/1 phr		
	$E/\text{kJ mol}^{-1}$	$\ln A/\text{min}^{-1}$	r	$E/\text{kJ mol}^{-1}$	$\ln A/\text{min}^{-1}$	r
$A_{3/2}$	59.17	15.242	0.9997	66.71	18.626	0.9999
A_2	42.65	10.210	0.9997	48.39	12.809	0.9999
A_3	26.14	5.016	0.9996	30.07	6.837	0.9999
A_4	17.88	2.284	0.9996	20.91	3.726	0.9999
R_2	76.93	19.621	0.9997	86.26	23.809	0.9989
R_3	81.78	20.739	0.9999	91.69	25.173	0.9995
D_1	134.40	36.543	0.9975	149.64	43.373	0.9957
D_2	157.40	43.729	0.9992	174.20	51.262	0.9982
D_3	170.46	45.465	0.9999	189.94	54.113	0.9995
D_4	157.26	41.408	0.9996	175.18	49.388	0.9987
F_1	92.20	25.094	0.9997	103.34	30.056	0.9999
power	28.43	5.516	0.9964	32.49	7.403	0.9943
$n+m=2; n=1.9$	115.54	32.583	0.9947	129.57	38.769	0.9965
$n+m=2; n=1.5$	61.12	16.808	0.9942	69.07	20.346	0.9962
$n=2$	129.14	36.521	0.9978	144.70	43.369	0.9965
$n=3$	173.87	50.216	0.9871	194.81	59.362	0.9899

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 same conclusion was reached for the systems with 0.5 and 2 phr of ytterbium triflate.

To confirm the methodology used, we determined E and $\ln A$ for each tested model with the Coats–Redfern method (Eq. (5)). The results obtained at the heating rate of $5^{\circ}\text{C min}^{-1}$ for the sample with 1 phr of ytterbium triflate when Eq. (5) was applied to conversions between 0.2 and 0.8 are shown in Table 3 (other tested rates showed similar results). The same process was applied to the other two samples. 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 mean value of E obtained isoconversionally ($61.12 \text{ kJ mol}^{-1}$; Table 1). This value of E is considered the effective value because it was obtained without the necessity of determining the model. In addition to exhibiting a good regression, the correct kinetic model must also possess a value of E similar to the effective value. According to these criteria, model $A_{3/2}$ with $r=0.9992$ and $E=67.17 \text{ kJ mol}^{-1}$, is considered the correct one. The F1 model also presents a good regression but its E is too much higher than that obtained isoconversionally, so it is not considered an appropriate model.

In Table 4 it can be seen the Coats–Redfern results for the other two samples and how the kinetic

Table 5 Variation of the activation energy with the conversion of samples with 0.5, 1 and 2 phr of ytterbium triflate

Conversion	$E/\text{kJ mol}^{-1}$		
	0.5 phr	1 phr	2 phr
0.1	47.9	59.5	59.0
0.2	60.0	60.9	62.2
0.3	62.0	61.9	61.3
0.4	62.9	62.4	61.0
0.5	63.5	63.0	61.1
0.6	63.9	63.4	61.5
0.7	64.2	64.0	61.7
0.8	64.6	64.7	61.7
0.9	64.9	66.0	61.3

model chosen ($A_{3/2}$) is valid for all the systems. In both cases the model F1 could be possible from the point of view of the regression but the obtained E is much higher than the isoconversional one (Table 5). Thus, the model $A_{3/2}$ was chosen and considered appropriate for all the systems. These results were also confirmed by the so-called method of the reduced master curves proposed by Criado [33, 34], and results showed that the kinetic model chosen ($A_{3/2}$) fitted very well with experimental data.

All the samples have shown that the two methodologies (IKR and Coats–Redfern) produce the same result, and in both cases, it is necessary to know

the effective E (isoconversional) value to determine the complete kinetic triplet (E_a , A and $f(\alpha)$).

If we compare the activation energies (Table 5), a simple analysis would conclude that the fastest system is that with the minor E_a , but this is not always true because it exists a compensation effect between E and $\ln A$. Then, to know which system is the most efficient it should be compared the conversion rate r . Equation 8 shows the Arrhenius relation between k (rate constant), A and E .

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

From Eq. (1),

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

Introducing in this equation values of E , A and α with the chosen kinetic model $A_{3/2}$ and for a given conversion degree ($\alpha=0.5$) we can obtain a graphic like Fig. 4 ($\ln r=f(1/T)$). In this figure it can be observed that, the higher the proportion of initiator the faster the system is. This graphic shows that when initiator is added in proportions of 0.5 and 1 phr there are almost no changes in the reaction rate, so the system is not too much accelerated when 1 phr is added. Nevertheless, when the initiator amount is 2 phr the curing gets faster than in the other two samples, especially at high temperatures. When 0.5 and 1 phr are used, straight lines are observed, it can be seen that at high temperatures there is almost a crossing between both reaction rate lines, meaning that some little differences in E were obtained. These results corroborate that in order to know which system is the fastest it is appropriate to consider not only E_a but also the parameter $\ln A$ if they fit the same kinetic model.

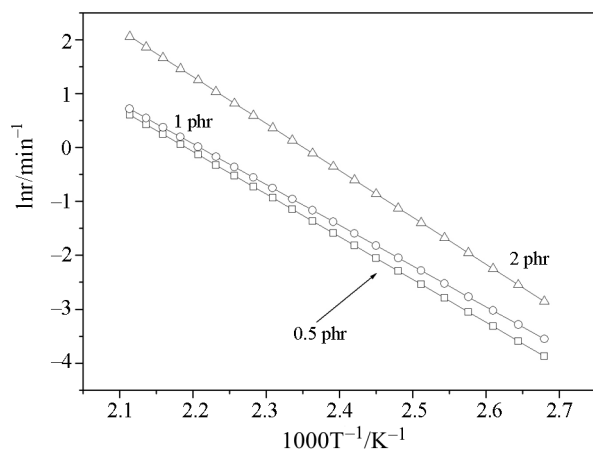


Fig. 4 Conversion rate ($\ln r$) vs. the inverse of the temperature ($1000/T$) for samples with 0.5, 1 and 2 phr of ytterbium triflate

In order to investigate whether the kinetic model chosen and isoconversional data obtained by the STAR software fitted the experimental data a comparison between conversion–time graphics for a given temperature was made. Because 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 was lost.

The experimental conversion degree (α) data were obtained doing a first isothermal test during a given time in a DSC, and then a scan from 25 to 300°C at 10°C min⁻¹ was performed for each isothermal test. With Eq. (10) and the residual enthalpies obtained, the different conversion values were calculated.

$$\alpha_{\text{exp}} = \frac{\Delta H_{\text{total}} - \Delta H_{\text{residual}}}{\Delta H_{\text{total}}} \quad (10)$$

where, $\Delta H_{\text{total}}=73.3$ kJ eq⁻¹ epoxy obtained from non-isothermal data.

Figure 5 represents the three curves obtained: kinetic model data, isoconversional data obtained by the STAR software and finally experimental data, for a sample with 0.5 phr of ytterbium triflate.

It can be observed that the three curves show a similar trend. The experimental data almost show the same conversion–time values than those obtained theoretically by the kinetic model. Only some few variations were found at low conversions.

The isoconversional data given by the STAR software were a bit different to those obtained by the kinetic model and experimentally.

Those little differences between the data could be due to the experimental limits of the DSC device.

Nevertheless, as the curves are very similar it can be pointed out that the kinetic model chosen fits quite

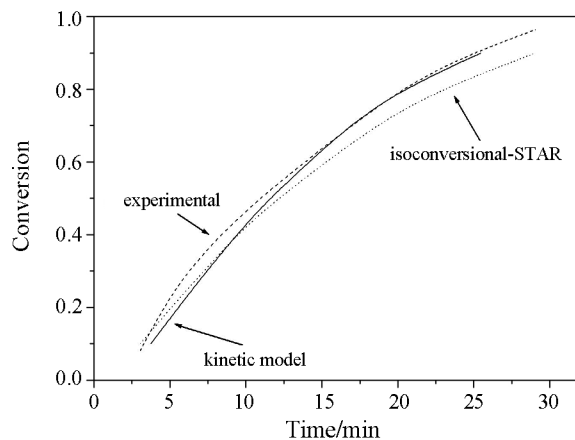


Fig. 5 Conversion vs. time graphics of data obtained experimentally (isothermally at 120°C), isoconversionally with the STAR software and from the chosen kinetic model for a sample with 0.5 phr of ytterbium triflate

well with the isoconversional data obtained with the STAR software and with the experimental data. So, with the appropriate kinetic model it has been possible to obtain easily the time–temperature–conversion triplet.

Conclusions

In order to reduce the curing temperature and time of powder coatings, and thus obtain production benefits, a Lewis acid as initiator has been proposed. The kinetics of reaction using ytterbium(III) trifluoromethanesulfonate in three different proportions has been studied.

To compare kinetic results, it is necessary to know the complete kinetic triplet (E , A , $g(\alpha)$) because of the existence of a compensation effect between E and $\ln A$. The use of E as a unique comparative parameter can introduce errors.

Two methods that allow the determination of the complete kinetic triplet have been shown, 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 (free model).

An epoxy system composed by a DGEBA resin and a Lewis acid initiator (ytterbium(III) trifluoromethanesulfonate with applications in the formulation of low curing powder coatings) was studied. Three different amounts of initiator were studied: 0.5, 1 and 2 phr. 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 $A_{3/2}$ grain growth model, showing no dependence on the initiator amount.

Reaction rates for all the systems were obtained. Results showed that the more the initiator is added the faster the reaction rate is, but adding 0.5 or 1 phr of initiator shows almost no differences in the reaction rate. An amount of 2 phr should be added in order to observe important changes in the acceleration of the system.

A simulation of the isothermal curing to a reasonably accurate degree has been obtained using a non-isothermal method. In this way it has been possible to obtain the isothermal curing degree vs. temperature and time without any isothermal tests (that in fast catalyzed curing systems are experimentally difficult to perform) but only with four DSC dynamic scans at different rates.

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