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Isoconversional kinetic analysis of a carboxyl terminated polyester resin crosslinked with triglycidyl isocyanurate (TGIC) used in powder coatings from experimental results obtained by DSC and TMDSC

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Abstract

Isoconversional kinetic analysis has been applied to the non-isothermal curing experiments of powder samples used in thermoset powder coatings. The work compares different experimental values obtained from different sets of heating rates by DSC and TMDSC in order to establish how much the experimental process affects the kinetic parameters and the simulated kinetic curves derived from them.

The experimental results that were processed by the differential and integral procedures for each set of rates have proved useful in finding the compensation effect between A, the frequency factor, and E, the activation energy in the form $\ln A = aE + b$ and the kinetic triplet ($E, A, f(\alpha)$). The compensation curves found indicate that the kinetic parameters vary with the set of heating rates used and with the extent of the reaction. In the case of the system under study, it was found that once $f(\alpha)$, is fixed, there are a pair of values [E, A] that are singular and independent of the set of rates used for the determination of the kinetic triplet and degree of conversion α.

Keywords: Triglycidyl isocyanurate; Polyester resin; Isoconversional kinetics; Power coating

1. Introduction

The kinetic study of a reactive system may originate from a desire to find out the mechanisms that lead the reactive system to convert itself into products or in interest in ascertaining the degree of conversion and the influence of immediate environment on it. In the latter case, the kinetic study is mainly aimed at obtaining the so-called kinetic parameters, which allow the reactive process to be reproduced and simulated under any condition [1].

For reactions in heterogeneous systems in condensed phases, in many cases the kinetic study consists of obtaining the so-called kinetic triplet ($A, E, f(\alpha)$ or $g(\alpha)$), where A is the frequency factor, E is the activation energy and the functions $f(\alpha)$, $g(\alpha)$ are functions of the degree of conversion, α, used by the differential, $f(\alpha)$, and integral, $g(\alpha)$, procedures [2].

Differential scanning calorimetry (DSC), and more recently temperature modulated DSC (TMDSC), are experimental techniques that are often used to obtain kinetic parameters, both for physical processes and

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reactions in condensed phases. This is due to the fact that they combine, ease of sample preparation and performance of experiments with suitable monitoring of progress of the reaction by detecting the heat involved in the reactive process. One way of proceeding is by performing experiments at a constant temperature and detecting the changes in reaction heat as a function of time. Another procedure is by means of dynamic experiments carried out at different heating rates.

The results of the kinetic study can be applied to various objectives: analysing the influence of a catalyst, examining the effect of an inhibitor, knowing the effect of pressure and temperature, etc. In thermosetting materials or thermoset powder coatings, the reactive process is inseparable from the application of the material. In these cases, knowledge of kinetic information enables us to find out how the degree of conversion varies as a function of time for the set of operating temperatures.

The best way to obtain kinetic information is by using isothermal experiments that can be carried out by submitting the material to, e.g. four different temperatures, and making the experiment last long enough for the complete reactive process to take place. However, doing isothermal experiments directly using DSC can present insurmountable difficulties: heat detection by the apparatus is not ensured in slow processes or in very fast processes, where the reactive process starts before the instrument can detect the heat correctly. An alternative is to proceed indirectly; instead of detecting the heat of the isothermal process, we can detect the residual heat dynamically once the sample has been submitted to a given temperature for a certain time. In both cases, the procedure is slow and, when carried out indirectly, is costly due to the samples that must be prepared. Other drawbacks when doing isothermal experiments arise from the nature of the material to be analysed. In reactions of materials in the condensed phase and thermosetting materials, excessively long times are needed to reach complete conversion. Furthermore, the reactive process can mask other physical processes caused by the advance of the reaction itself (for example vitrification) which hinder the heat detection process and precise knowledge of the advance of the reaction as a function of time [3,4].

The advantage of obtaining kinetic parameters using dynamic DSC experiments at a controlled heating rate is that it reduces the time needed to do the experiments and to prepare the samples. Another advantage is that it avoids some of the drawbacks already mentioned in connection with isothermal processes. However, at very low or very high heating rates, the reaction heat may not be correctly read by the instrument. The complexity of reactive processes or the possibility that there are physical or chemical effects that overlap as a function of the scanning velocity make subsequent calculation of the reaction heat involved difficult.

Although the system under study in this work does not present a complex reactive process, the reaction of carboxylate polyester with triglycidyl isocyanurate (TGIC) [5], this does not mean that the kinetic analysis is simple. Fig. 1 shows the experimental curves obtained for four different heating rates. It can be seen that two endothermal peaks appear before the exothermal curing process. The first is associated with the glass transition and ageing of the polyester, and the second with fusion. The fact of working with the material as it is applied means that the exothermal reaction effect is relatively small (the total reaction heat is of the order of 40 J/g). In addition, at high temperatures the material can undergo degradation, which, from an experimental point of view, means that it is not easy to separate the reactive process under study from other physical and chemical processes that accompany it.

Furthermore, due to the low reaction heat and the conditions in which it is applied (only a few minutes are needed to cure the sample at 180 °C), it is practically impossible to study the kinetics of this system by using direct isothermal experiments. Nor is the indirect isothermal procedure advisable, as it is difficult to quantify the residual heat when the material conversion is high. The dynamic method is seen to be the most suitable means to study this system using DSC and to obtain the kinetic information needed to predict the behaviour of the material under the conditions of use.

The aim of the present study is to show the procedure used and the results obtained when the dynamic isoconversional method is applied to curing a thermoset powder coating of the polyester carboxylate-TGIC type. The experimental results have been studied using differential and integral isoconversional methods and have enabled the location of a kinetic triplet [A, E $f(\alpha)$], i.e. coherent with experimental results. Analysis

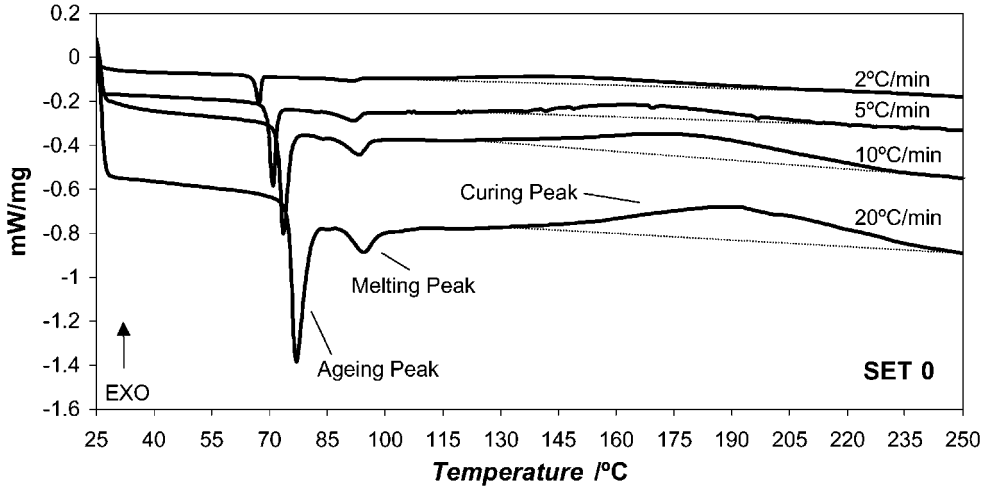


Fig. 1. Experimental DSC curves corresponding to set 0 (2, 5, 10 and 20 °C/min).

of the $\ln A = aE + b$ compensation effect enables detection of the influence of the set of rates used to obtain the kinetic parameters. A pair of isokinetic values, $[E, A]$, were found for the system under study that are independent of the degree of conversion and the set of heating rates used. The procedure described in this study aims to keep the cost of the kinetic analysis as low as possible in terms of both time and experimental work, and to ensure that it is applicable both to the case under study and to other kinetic processes of a similar nature.

2. Experimental

The powder coating system under study is a physical mixture of a slightly branched carboxylate polyester with a functionality of 2.3, an acidity index of 33 and $M_n = 3910$ g/mol, with triglycidyl isocyanurate (TGIC), with a functionality of 3 and $M_n = 297$ g/mol and a weight proportion of 93/7. Fillers and pigments were also used in its preparation. The thermal history of the samples tested, a consequence of the preparation process, consists of: grinding the polyester, physically dry-mixing the components, extruding the mixture at temperatures between 80 and 110 °C and grinding the mixture to obtain a particle size between 60 and 90 μm.

A Mettler-Toledo DSC-30 differential scanning calorimeter (DSC) was used. The dynamic tests were done at rates of 0.5, 2, 3, 3.5, 4, 5, 6, 7.5, 9, 10, 12, 15 and 20 °C/min in the DSC calorimeter. A set of heating rates of 2–5 °C/min were performed using a Mettler 821 TMDSC with alternating DSC (ADSC) software. The heating rates in this case are mean heating rates with a temperature amplitude of 0.5 °C and a period of 1 min. The information from the experimental tests was grouped into several sets of rates, in such a way that sets were formed containing both very low and very high rates, only very low rates and only very high rates. In the case of TMDSC, only the set of low rates was explored; it is not of interest to work at higher rates, due to temperature modulation. The kinetic parameters were analysed for each set. The correspondence between the number of sets of the article and the series of rates used in each set is shown in Table 1.

3. Theoretical considerations

As the theoretical considerations that we wish to discuss and the equations that they are based on are very well known, most of them are summarised in Table 2. They are referred to in the text, by the number that figures beside them.

The starting point to establish the kinetics of a reactive system from calorimetric information consists of, firstly, accepting that for a reaction state associated with a conversion process (α), the conversion rate

Table 1
Heating rates used for the determination of kinetic parameters

Set	Heating rate (°C/min)	Instrument
Set 0	0.5, 2, 3, 3.5, 4, 5, 6, 7.5, 9, 10, 12, 15, 20	DSC
Set 1	2, 6, 10, 20	DSC
Set 2	10, 12, 15, 20	DSC
Set 3	0.5, 2, 3.5, 5	DSC
Set 4	9, 10, 12, 15	DSC
Set 5	6, 7.5, 9, 10	DSC
Set 6	2, 3, 4, 5	DSC
Set 7	2, 3, 4, 5	TMDSC
Set 8	0.5, 2, 3, 4	DSC
Set 9	0.5, 2, 15, 20	DSC
Set 10	2, 3, 12, 15	DSC
Set 11	3, 4, 10, 12	DSC
Set 12	3.5, 5, 9, 15	DSC

$(d\alpha/dt)$, is proportional to the heat flow associated with the reactive process that can be obtained experimentally by DSC. Secondly, $(d\alpha/dt)$ is related to a kinetic equation composed of a temperature rate function constant $k(T)$ and another term which is a function of the degree of instantaneous conversion and the kinetic model $f(\alpha)$ (Eq. (1)). In Eq. (1), Q_{tot} is the total specific heat (per unit of mass) of the reactive process and dQ/dt is the flow of specific heat, both obtained using the DSC signal. It is also commonly accepted that the rate constant $k(T)$ is related to temperature through the Arrhenius equation. In Eq. (2), A is known as the pre-exponential factor, E is the activation energy and R is the gas constant.

Although not lacking in controversy (Eq. (3)) [6,7], a combination of Eqs. (1) and (2) is used as a starting point, both for the kinetic study of isothermal experiments and for different heating rates. In the last case, we accept the validity of Eq. (4), which derives from Eq. (3) simply by replacing $d\alpha/dt$ with $\beta\, d\alpha/dT$, where β is the linear heating rate ($\beta = dT/dt$).

The basic assumption of isoconversional methods or model-free isoconversional methods [8,9] is that the reaction rate at a constant conversion rate is only a function of temperature. This premise supposes the fact that it is accepted to different effective reaction with kinetics parameters E_α, A_α, for each α, over the entire reaction range.

For a given extent of reaction, the direct use of logarithm form of Eq. (3) or Eq. (4) to isothermal as well as to non-isothermal data, Eqs. (5) and (6), produces a set of linear relationships between the ln of the reaction rate or time versus $1/T$. Fig. 2 shows the linear relationships $\ln(d\alpha/dt) - 1/T$ obtained from the set of rates in Fig. 1. According to Eq. (6), E_α and the constant $A_{\alpha,dif} = \ln[A_\alpha f(\alpha)]$ can be determined from the slope and the intercept of each α line.

The integral method uses the integral form of the reaction model, $g(\alpha)$ defined by Eq. (7). Integration of Eq. (3) at constant temperature for α and time t gives Eq. (8). Rearrangement of Eq. (8) yields Eq. (9), which makes it possible to evaluate E_α from the slope of the

Table 2
The most representative kinetic equations for the differential and integral methods [1]

Differential method	Equation	Integral method	Equation
$\frac{1}{Q_{tot}}\frac{dQ}{dt} = \frac{d\alpha}{dt} = k(T)f(\alpha)$	1	$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)}$	7
$k(T) = A\exp\left(\frac{-E}{RT}\right)$	2	$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = A\exp(-\frac{E}{RT})t$	8
$\frac{d\alpha}{dt} = A\exp\left(-\frac{E}{RT}\right)f(\alpha)$	3	$\ln t_\alpha = -\ln\left[\frac{A_\alpha}{g(\alpha)}\right] + \frac{E_\alpha}{RT}$	9
$\beta\frac{d\alpha}{dT} = A\exp\left(-\frac{E}{RT}\right)f(\alpha)$	4	$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^T e^{-E_\alpha/RT}\,dT$	10
$\ln\left(\frac{d\alpha}{dt}\right)_\alpha = \ln[A_\alpha f(\alpha)] - \frac{E_\alpha}{RT}$	5	$\log\beta = \log\left[\frac{A_\alpha E_\alpha}{g(\alpha)R}\right] - 2.315 - 0.4567\frac{E_\alpha}{RT}$	11
$\ln\left(\beta\frac{d\alpha}{dT}\right)_\alpha = \ln[A_a f(\alpha)] - \frac{E_\alpha}{RT}$	6	$A_{\alpha,int,T} = -\ln\left[\frac{A_\alpha}{g(\alpha)}\right]$	12
$A_{\alpha,dif} = \ln[A_\alpha f(\alpha)]$	13	$A_{\alpha,int} = \log\left[\frac{A_\alpha E_\alpha}{g(\alpha)R}\right] - 2.315$	14

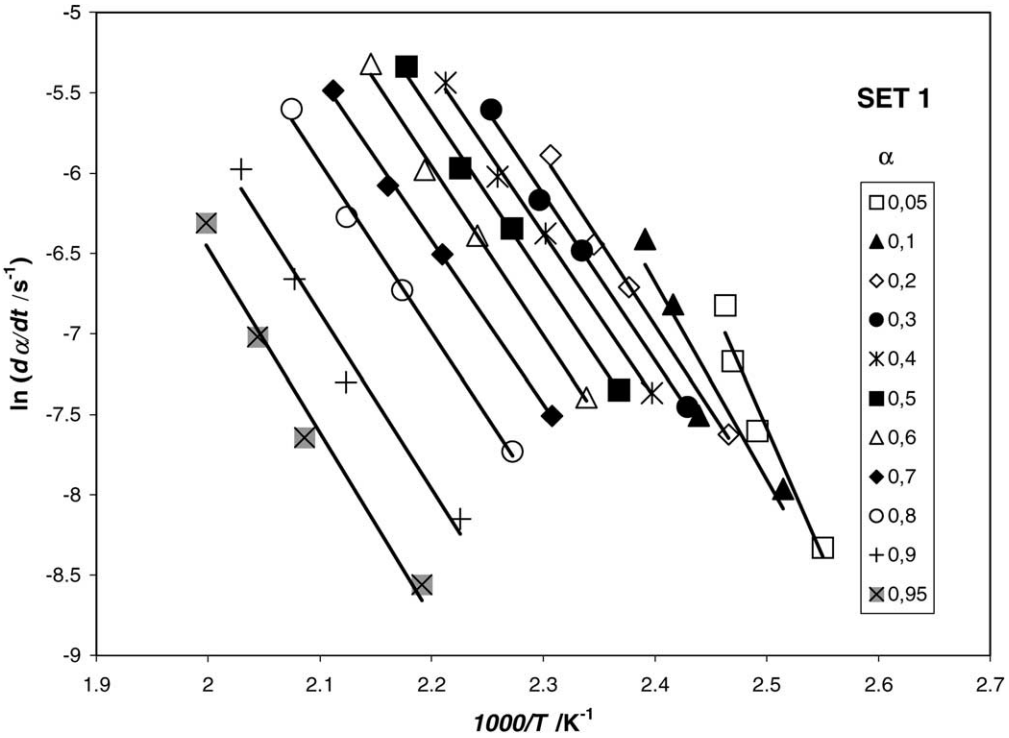


Fig. 2. Linear relationship between ln dα/dt and T^{-1} obtained from the set of rates in Fig. 1.

plot ln t_α against 1/T. For non-isothermal data, the analytical integration of Eq. (4) can be expressed as in Eq. (10). Flynn [10], Ozawa [11], Coats [12], Vyazovkin [13] and Sbirrazzuoli [14], among others, proposed different approximate integration procedures for Eq. (10). The integral isoconversional method of Ozawa, which we have used in previous works, uses the solution of Eq. (11). For constant α, the plot log β versus 1/T, obtained from experiments recorded at several heating rates, should be a straight line whose slope is E_α. Fig. 3 shows the linear relationships $log\,\beta - 1/\mathrm{T}$ obtained from the set of rates in Fig. 1.

The subscript α in Eqs. (9) and (11) shows that the functional relationship between $\log\beta - 1/T$ and $\ln t - 1/T$ is for each degree of constant conversion α. In dynamic tests the slope of the linear correlation between $\log\beta - 1/\mathrm{T}$ for each α allows us to know the value and variation of E with α. In the same way, in isothermal tests, the slope of the linear correlation $\ln t - 1/T$ for each α yields the same information. Furthermore, if the hypotheses that lead to Eqs. (9) and (11) are true, their independent terms are related so that it is possible to derive the kinetic equation (Eq. (9)) from dynamic tests using Eq. (11) and to simulate isothermal processes without any other experimental information.

4. Results and discussion

We feel that the interest in the use of model-free isoconversional methods versus the use of model-fitting methods lies in the fact that the isoconversional procedure makes for relatively easy analysis of isothermal and non-isothermal data and consistent kinetic parameters. In particular, the variation of E_α with the extent of the reaction makes it possible to reveal the complexity of the reactive process and the multi-stage effects that are typical of reactions in condensed phases [15,16]. However, as recently pointed out by authors such as Wilburn [17] and Budrugeac [18], the activation parameters may vary for reasons that have nothing to do with the extent of

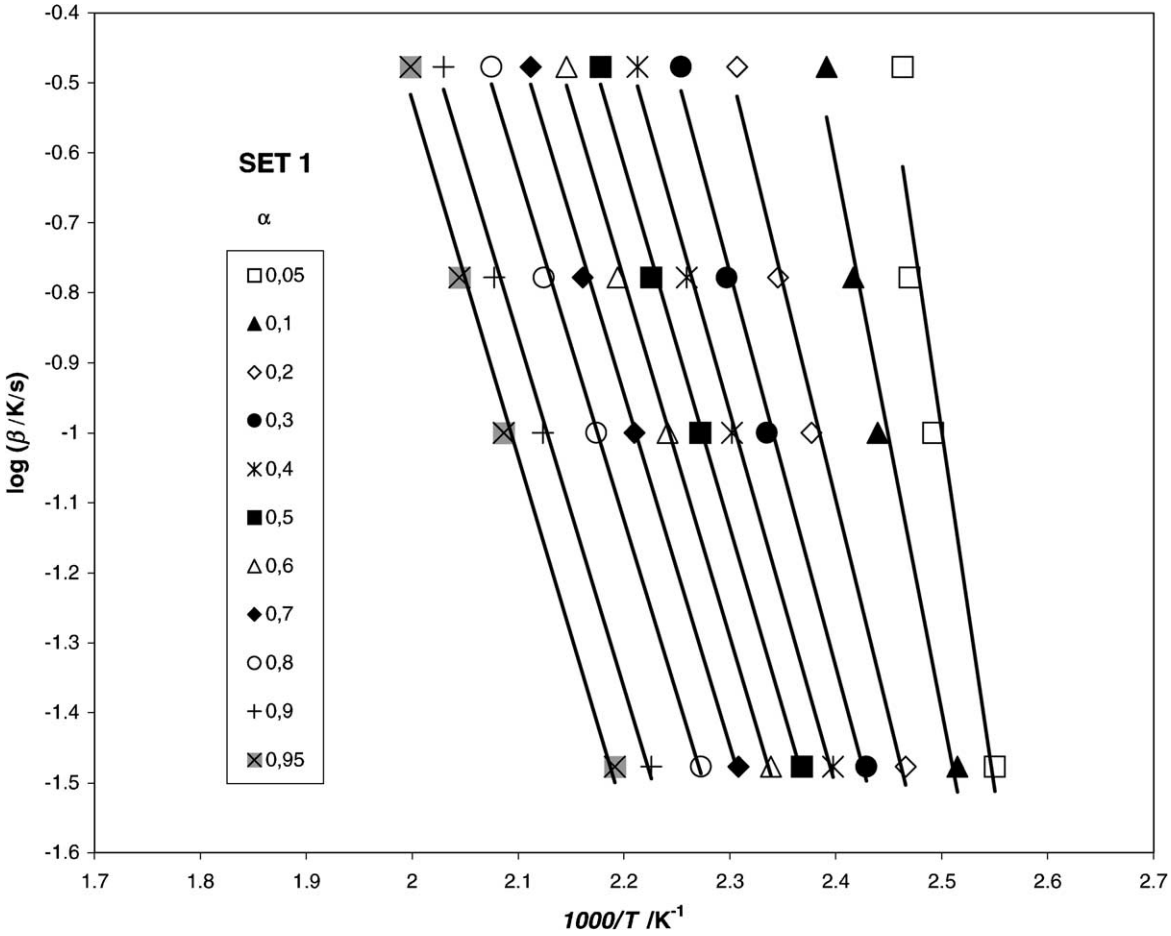


Fig. 3. Linear relationship between log β and T^{-1} obtained from the set of rates in Fig. 1.

the reaction. In this study, we have reached the conclusion that the set of rates chosen, the shape of the DSC curves, the lack of definition of the limits of integration and the lack of correct heat detection at the beginning and end of the reaction, have an influence on the kinetic parameters obtained and their evolution with the degree of conversion. Other authors have pointed out these facts, but generally they are underestimated when obtaining kinetic parameters. Authors such as Criado [19] and Málek [20] indicate in their studies the relationship between the values that form the kinetic triplet [A, E, $f(\alpha)$] and that it would be a mistake to obtain them separately. These authors also pay special attention, using characteristic functions or master curves, to the choice of reaction model, and the shape of the function $f(\alpha)$. For example, Málek [20] determined a representative E for the process from experimental information. Then, using an elaborate procedure, he chose the most suitable model of $f(\alpha)$ and finally obtained the frequency factor A from E and $f(\alpha)$. This procedure is only valid if E is constant.

Using the isoconversional procedure, it is not necessary to specify the function $f(\alpha)$ or $g(\alpha)$, and therefore, the reactive process may be followed through the evolution of the activation energy as a function of the extent of the reaction [9].

Fig. 4 shows the variation of E_α with the degree of conversion for each set of rates used (Table 1), obtained by Ozawa's method (Eq. (11)). As can be seen, E_α varies with α, but also with the set of heating rates. The fact that the evolution of E_α with α is not independent of the set of rates used and that the pattern

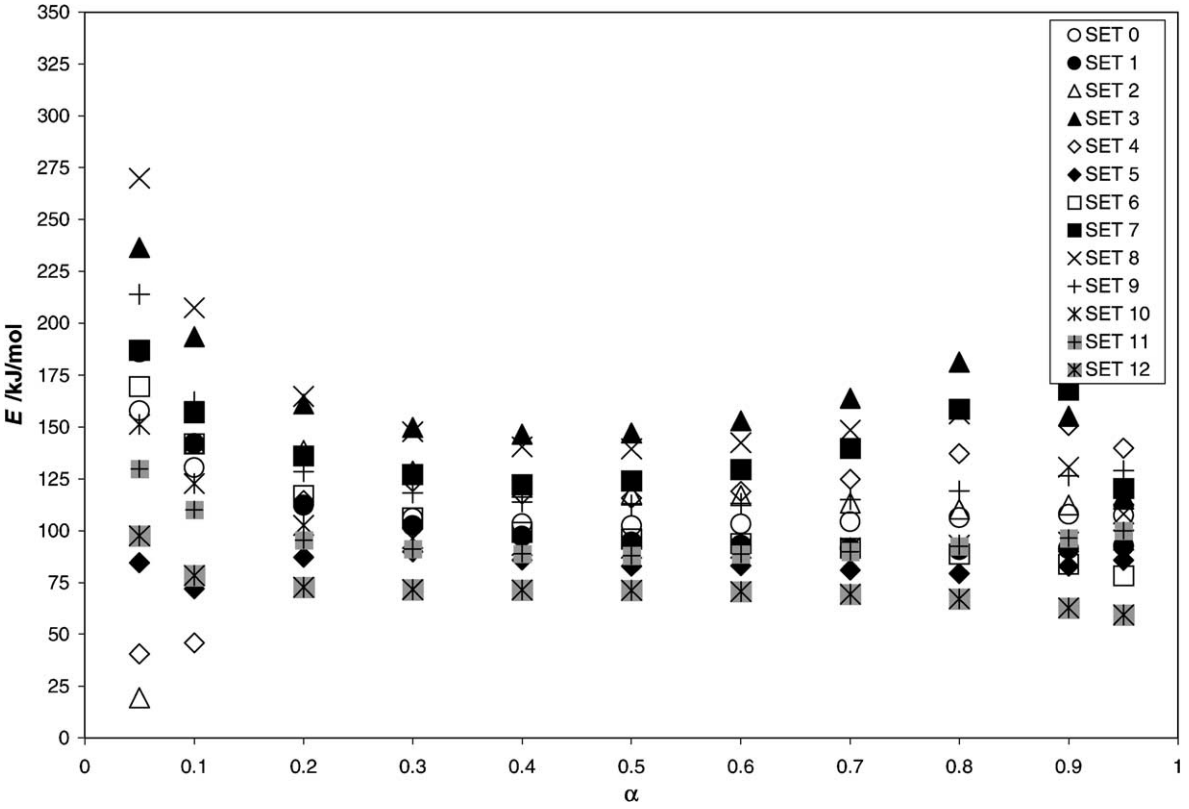


Fig. 4. Variation of E_α with α for each set of rates studied from the slopes of the straight lines (Eq. (11)).

of variation of E_α is not the same in the various sets, makes it difficult to kinetically interpret this variation. It also shows that E_α can vary due to causes other than the reactive multi-stage effect that would be expected of the system under study.

This variation is also observed if the differential method is used Eq. (5). Furthermore, in most cases the activation energy does not coincide in the two procedures for a given alpha. Fig. 5 shows the $E_{\alpha,\mathrm{dif}}$ obtained with Eq. (5) and the $E_{\alpha,\mathrm{int}}$ obtained with Eq. (11). Points that should be in theory lie on the 45° line are in fact widely dispersed. In our opinion, these results are a reflection of the influence of the set of rates used and the manipulation done to obtain the variation of the extent of the reaction with temperature. The sets that include a wide rate interval, for example, sets 1 and 11, produce results that are more similar to set 0 (obtained with all of the experimental rates) than to those sets that uses closer rates, such as sets 4 and 8. This result agrees with what Prime [1] proposed: to use a set of heating rates that is as wide as possible.

The assumption that there exists a triplet [A_α, E_α, $f(\alpha)$ or $g(\alpha)$], for a given system and for each conversion, together with the assumption that the rate constant $k(T)$ is related to the activation energy E through the Arrhenius relationship, implies the existence of a linear relationship between A_α and E_α, called the compensation effect.

Using Eqs. (1) and (2) and re-ordering terms, we get

$$\ln\left[\frac{(\mathrm{d}\alpha/\mathrm{d}t)_\alpha}{f(\alpha)}\right] + \frac{E_\alpha}{RT} = \ln A_\alpha \equiv aE_\alpha + b \tag{15}$$

The linear Eq. (15) between $\ln A_\alpha$ and E_α defines the so-called compensation effect [9,21,22]. It also enables a possible interpretation of the slope a and the intercept b of the linear relationship. Whereas $a = 1/RT$ is related to an isokinetic temperature that

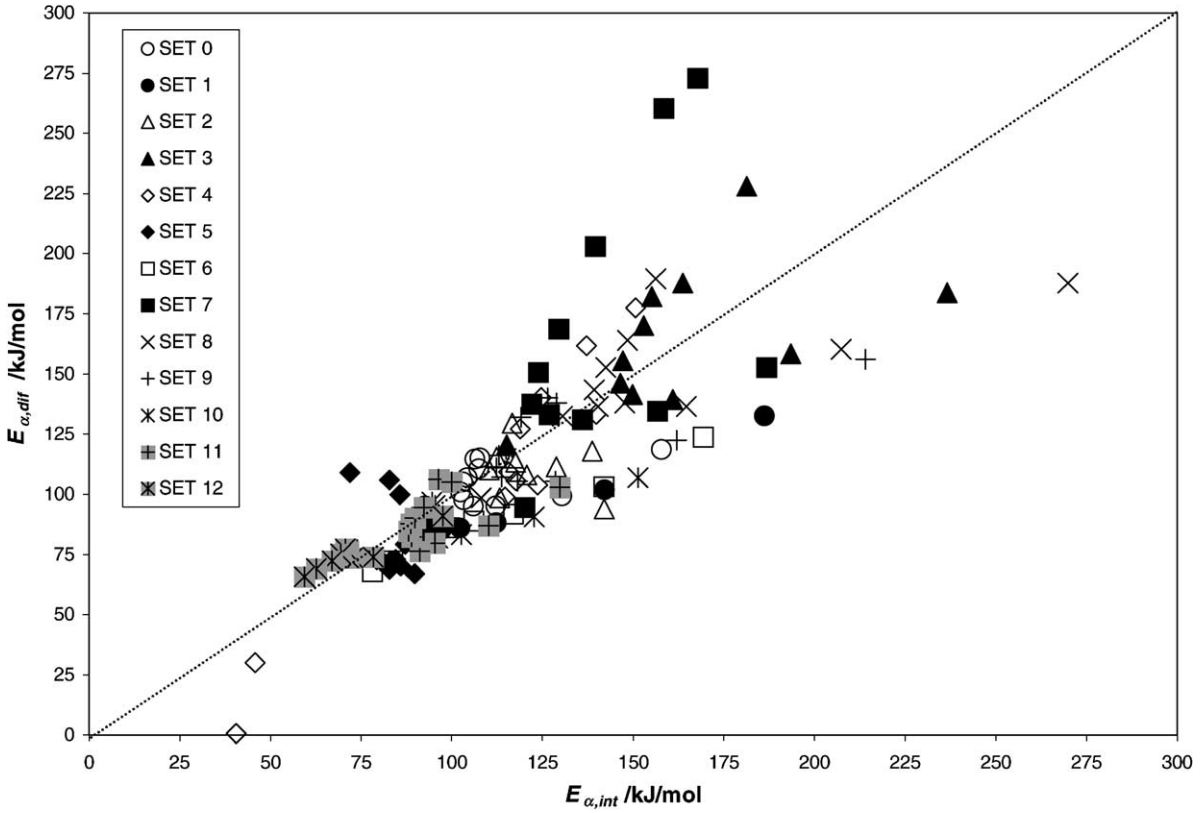


Fig. 5. Representation of $E_{\alpha,\mathrm{dif}}$, $E_{\alpha,\mathrm{int}}$ obtained from the slopes of the straight lines in Figs. 2 and 3 with Eqs. (5) and (11), respectively.

is characteristic of the kinetics at a degree of conversion α, b is independent of temperature and is related to the reaction model $f(\alpha)$. The compensation effect is mentioned in various studies by Linert [21], Budrugeac [23] and Vyazovkin [9]. This compensation effect has been found in previous studies in the curing of epoxy [9] and unsaturated polyester resins [24].

According to Vyazovkin [22] the linear relationship in Eq. (15) can be generalised as

$$\ln A_\xi \equiv aE_\xi + b \tag{16}$$

where ξ represents any factor that produces a change in the Arrhenius parameters.

In Fig. 6 the pairs $[A_{\alpha,\mathrm{dif}}, E_{\alpha,\mathrm{dif}}]$ and $[A_{\alpha,\mathrm{int}}, E_{\alpha,\mathrm{int}}]$ are shown for each conversion and for each set of rates under study. They are values that are found from experimental values using Eqs. (6) and (11). It can be seen that in spite of the variability of $E_{\alpha,\mathrm{dif}}$ and $E_{\alpha,\mathrm{int}}$, there is a certain ordering of pairs of values due to the compensation effect. Clearly, this ordering cannot be unique due to the fact that the constant $A_{\alpha,\mathrm{dif}}$ not only depends on A_α, but also depends on $f(\alpha)$ (Eq. (13)) and $A_{\alpha,\mathrm{int}}$ depends on $g(\alpha)$ and E_α as well as A_α (Eq. (14)). However, if $f(\alpha)$ (and $g(\alpha)$) were known, it would be possible to find a relationship $\ln A_\alpha = aE_\alpha + b$ for each set of rates that did not depend on whether the set of values $[A_\alpha, E_\alpha]$ originated from the differential or the integral procedure. This condition can be established through the equation

$$\ln\left(\frac{A_\alpha^{\mathrm{int}}}{A_\alpha^{\mathrm{dif}}}\right) = a(E_\alpha^{\mathrm{int}} - E_\alpha^{\mathrm{dif}}) \tag{17}$$

The exponents int and dif in Eq. (17) refer to the origin of the pairs of values $[E_\alpha, A_\alpha]$, where $E_\alpha^{\mathrm{int}} = E_{\alpha,\mathrm{int}}$ and $E_\alpha^{\mathrm{dif}} = E_{\alpha,\mathrm{dif}}$. The values of A_α^{int} and A_α^{dif} can be deduced from the experimental values $A_{\alpha,\mathrm{int}}$ and $A_{\alpha,\mathrm{dif}}$ from Eqs. (13) and (14), respectively. Each set of rates should produce a straight line with slope a that would go through the origin of the axes with coordinates $\ln(A_\alpha^{\mathrm{int}}/A_\alpha^{\mathrm{dif}})$ versus $(E_\alpha^{\mathrm{int}} - E_\alpha^{\mathrm{dif}})$. As

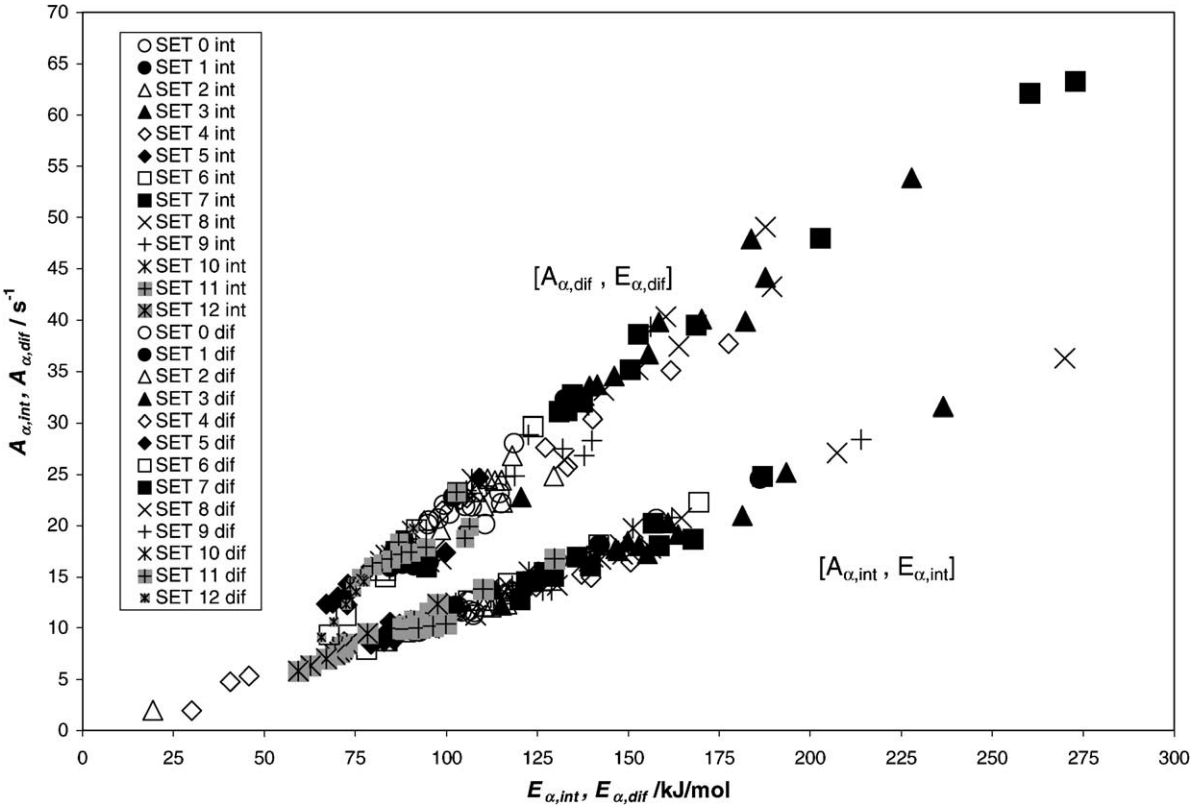


Fig. 6. Representation of pairs of values [$A_{\alpha,\mathrm{dif}}$, $E_{\alpha,\mathrm{dif}}$] and [$A_{\alpha,\mathrm{int}}$, $E_{\alpha,\mathrm{int}}$] for each set of rates and for each α obtained from Eqs. (6) and (11), respectively.

the values of a get very close or if they have the same value, it may be said that the set of rates does not influence the reaction kinetics.

To confirm the above hypotheses, it is necessary to use a reaction model of the type $f(\alpha)$. As has been previously mentioned, authors such as Criado [19], Málek [20] and Wilburn [17] provide well-established procedures to find $f(\alpha)$ from experimental curves. In this study, using previous results as a basis, we have assumed an autocatalytic model $f(\alpha) = a^m(1-\alpha)^n$ in which $n+m=2$ or $n+m=3$ has been imposed. In both cases, the value of n was found from the best correlation of the values of the set 0 of rates, by using Eq. (17) and checking to see if it was the same for the other sets. As can be seen in Table 3 for $n=1.9$ using $(n+m=2)$ and $n=2.8$ for $(n+m)=3$, the correlations found are very good. Table 3 also shows the expression for $g(\alpha)$, the integrated form of $f(\alpha)$ according to whether $n+m=2$ or $n+m=3$.

Note that the constant a in Eq. (17) must be the same as the a of the straight line that defines the compensation effect for each set of rates (Eq. (15)). The choice of $f(\alpha)$, needed for the determination of $\ln A_\alpha$, should not affect the value of a (of the slope). In the linear fit using Eq. (17), b has been set to zero. As can be seen in Table 3, the values found for a for each set of rates using $f(\alpha)$ with $n+m=2$ or $n+m=3$ are very similar, as the theory would lead us to expect.

The variation of values of a for each set of rates, cannot be attributed to shape effects of the experimental curves. It should be accepted that it is a consequence of how the reactive process (the heating rates in our case) was carried out, which has different influences on how the reaction develops. The representation of the pairs of values of each set of rates on the axes $\ln(A_\alpha^{\mathrm{int}}/A_\alpha^{\mathrm{dif}})$ versus $(E_\alpha^{\mathrm{int}} - E_\alpha^{\mathrm{dif}})$ in Fig. 7a may produce the effect that all of the points fall on the same line. To highlight the fact that the value of the

Table 3
Values of the slope and correlation coefficients of the linear fits using Eq. (17)

	$f(\alpha)=\alpha^m(1-\alpha)^n$ $n+m=2$ $g(\alpha)=\frac{z^{1-n}}{n-1}$; $z=\frac{1-\alpha}{\alpha}$ $n=1.9$		$f(\alpha)=\alpha^m(1-\alpha)^n$ $n+m=3$ $g(\alpha)=\frac{z^{1-n}}{n-1}+\frac{z^{2-n}}{n-2}$; $z=\frac{1-\alpha}{\alpha}$ $n=2.8$	
	a	R^2	a	R^2
Set 0	0.3032	0.9991	0.3082	0.9982
Set 1	0.3057	0.9991	0.3055	0.9954
Set 2	0.3005	0.9988	0.3013	0.9966
Set 3	0.2909	0.9958	0.2983	0.9958
Set 4	0.2767	0.9873	0.2840	0.9967
Set 5	0.2801	0.9992	0.2814	0.9976
Set 6	0.3002	0.9954	0.2962	0.9863
Set 7	0.2653	0.9983	0.2699	0.998
Set 8	0.3107	0.9964	0.3132	0.9971
Set 9	0.3078	0.9983	0.3123	0.9994
Set 10	0.301	0.9993	0.3018	0.9947
Set 11	0.2983	0.9994	0.3042	0.9962
Set 12	0.2855	0.9938	0.3398	0.9789

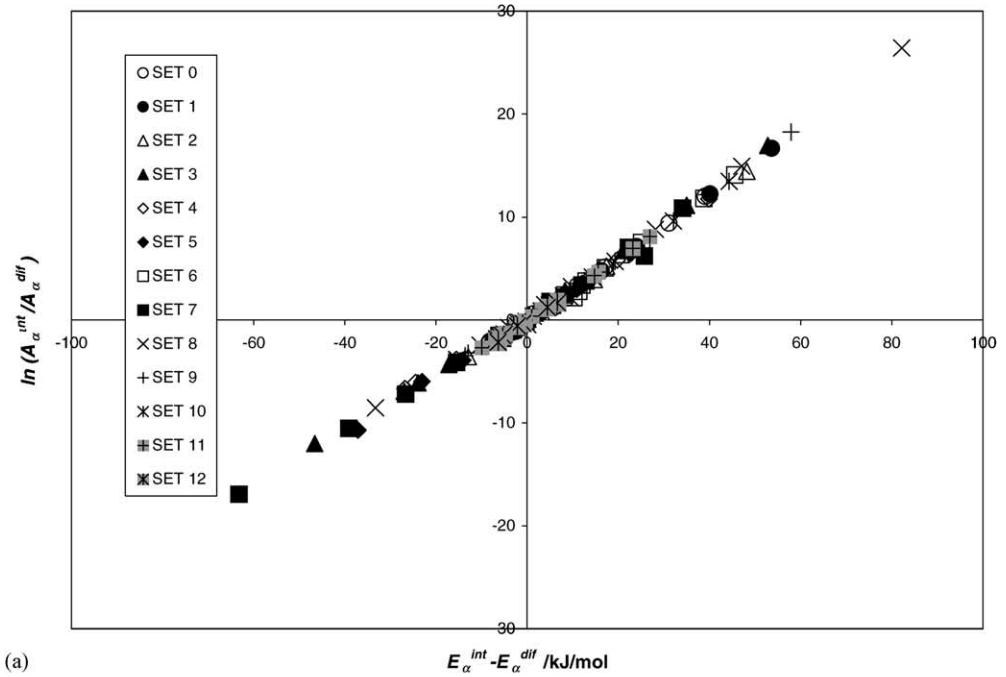
slope varies for each set of rates, Fig. 7b shows straight lines of the type $\ln A_\alpha = aE_\alpha$. Each set of rates is clearly differentiated in this representation. It can be seen that the slopes of sets 0–2 and 10 are very similar. On the other hand, sets 6 and 7 should have the same slope as they have equal heating rates, and this is not the case. Set 7 differs from all of the others in that it is the set of experiments that was done using temperature modulation. It can be deduced that the alternating heating-cooling effect associated with temperature modulation means that the kinetic response that it produces in the material is different to that produced by a constant heating rate.

An equation that is equivalent to Eq. (17) is Eq. (18), which can be used to see the compensation effect for the extent of the reaction, α.

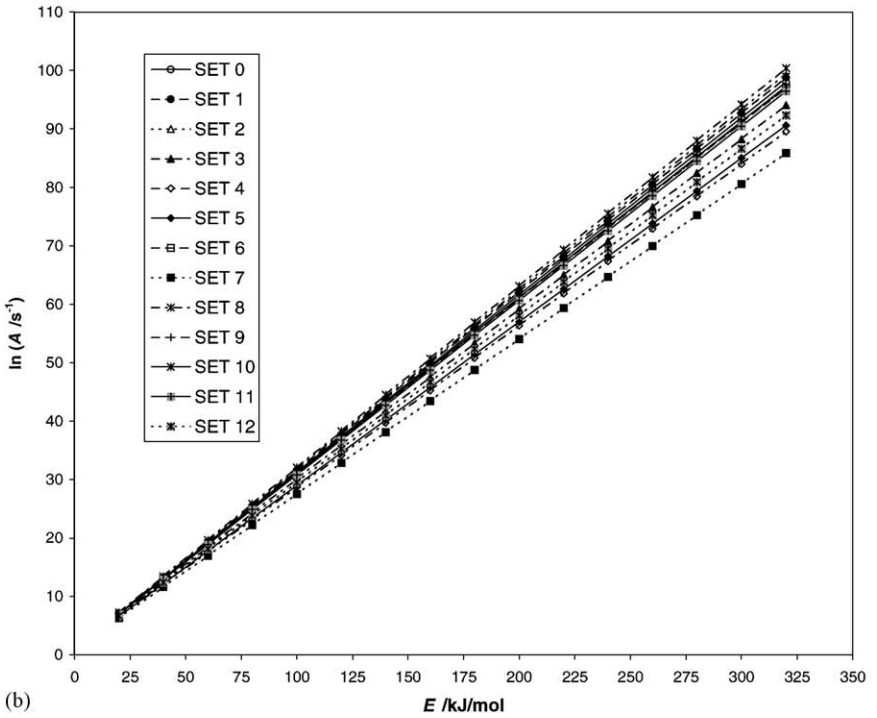
$$\ln\left(\frac{A_\beta^{\text{int}}}{A_\beta^{\text{dif}}}\right) = a_\alpha(E_\beta^{\text{int}} - E_\beta^{\text{dif}}) \tag{18}$$

Table 4
Values of the slope and correlation coefficients of the linear fits using Eq. (18)

α	$f(\alpha)=\alpha^m(1-\alpha)^n$ $n+m=2$ $g(\alpha)=\frac{z^{1-n}}{n-1}$; $z=\frac{1-\alpha}{\alpha}$ $n=1.9$		$f(\alpha)=\alpha^m(1-\alpha)^n$ $n+m=3$ $g(\alpha)=\frac{z^{1-n}}{n-1}+\frac{z^{2-n}}{n-2}$; $z=\frac{1-\alpha}{\alpha}$ $n=2.8$	
	a_α	R^2	a_α	R^2
0.05	0.3141	0.9984	0.3159	0.9987
0.1	0.3053	0.9990	0.3067	0.9989
0.2	0.3041	0.9986	0.3040	0.9986
0.3	0.2959	0.9960	0.2919	0.9969
0.4	0.2884	0.9959	0.2809	0.9983
0.5	0.2729	0.9972	0.2720	0.9991
0.6	0.2669	0.9990	0.2717	0.9986
0.7	0.265	0.9997	0.2695	0.9982
0.8	0.2619	0.9999	0.2679	0.9984
0.9	0.2585	0.9998	0.2660	0.9982
0.95	0.2527	0.9905	0.2527	0.9904

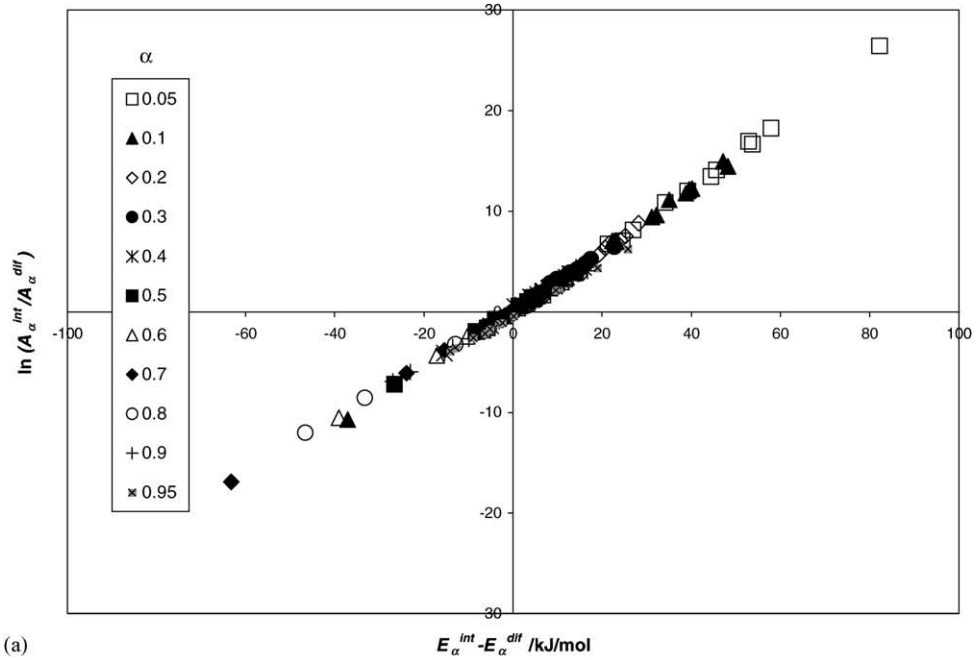


(a)

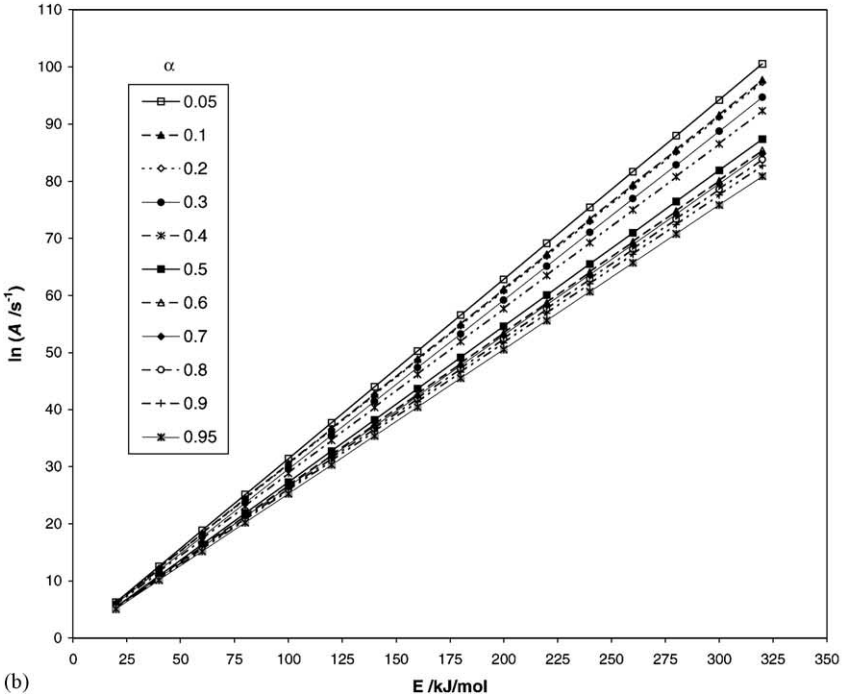


(b)

Fig. 7. (a) Representation of pairs of values $\ln(A_{\mathrm{int},\alpha}/A_{\mathrm{dif},\alpha})$, $E_{\mathrm{int},\alpha} - E_{\mathrm{dif},\alpha}$ for each set of rates obtained with Eq. (17); (b) representation of straight lines of the type $\ln A_\alpha = aE_\alpha$ to highlight the difference in value of the slope associated with each set of rates.



(a)



(b)

Fig. 8. (a) Representation of pairs of values $\ln(A_{\mathrm{int},\alpha}/A_{\mathrm{dif},\alpha})$, $E_{\mathrm{int},\alpha} - E_{\mathrm{dif},\alpha}$ for each conversion obtained with Eq. (18); (b) representation of straight lines of the type $\ln A_\alpha = a_\alpha E_\alpha$ to highlight the different values of the slope associated with each set of conversion.

The values found for a_α are shown in Table 4 and Fig. 8a and b. They are similar representations to Fig. 7a and b in relation to the degree of conversion. A gradual, non-uniform variation of the slope can be seen, that is associated with each conversion (Fig. 7b). As the reaction takes place, the slope becomes shallower. In the system under study for $0.2 < \alpha < 0.8$, the values of a_α are very close, with a uniform increase, while the initial and final stages are somewhat different. For this system, this behaviour is also seen in the variation of E_α with the extent of the reaction (Fig. 4). In other studies this variation is attributed to both physical and chemical features and to the inadequacy of the standard peak area calibration [4,25–27].

Once the values E_α, $f(\alpha)$ and $g(\alpha)$ are known for each set of rates, Eqs. (13) and (14) can be used to find the values of $\ln A_\alpha$, which should be independent of their source. We see this in Fig. 9, where for set 0 of the rates all of the possible pairs of $[A_\alpha, E_\alpha]$, have been represented in the case of using $f(\alpha)$ with $n = 1.9$ and $n + m = 2$. Similar results are obtained with the other sets of rates. An equally good agreement has been observed with the other $f(\alpha)$ studied.

Linear representations like those in Fig. 9 for each set of rates have been used to find the values of the intercept of the compensation equations (the independent term b). The result of all of this is that, for each set of rates and for each alpha, the kinetic process (the kinetic triplet) is established for a set of values of $[E_i, A_i, f(\alpha)_i]$, that is not unique. Knowing $f(\alpha)$, there are a large number of pairs of values $[A, E]$ that describe the kinetic process, with the only restriction that they

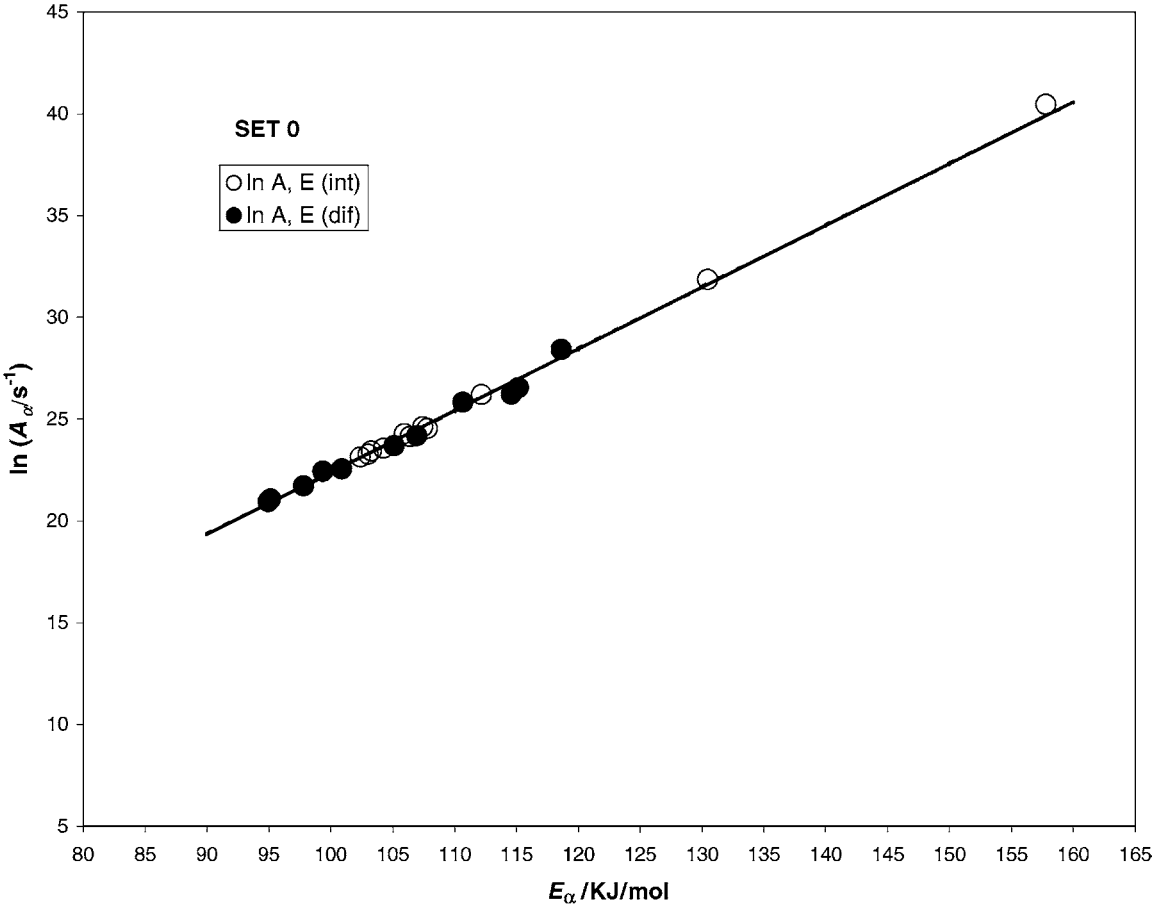


Fig. 9. Linear regression of pairs of values $[A_\alpha, E_\alpha]$ which come from both the analysis of the integral procedure and the integral procedure for the set 0.

satisfy the compensation equation $\ln A = aE + b$. This result would explain why there are a great variety of values of E in the literature for the same reactive system, as is seen in [9], in the case of the curing of epoxy resins. This result also shows the difficulty encountered in obtaining a unique activation energy that responds to the classical concept of energy associated with the transformation of inactive molecules into active molecules. The above state that there are many pairs of [A, E] to describe the kinetic process under study, should be conditioned by saying that only a few of these pairs can be interpreted physically. It should also be pointed out that the most interest parameter of the kinetic triplet is the activation energy. Once this is known, it is not difficult to find values of A and $f(\alpha)$ that are coherent with this value. This is also what is proposed by the isoconversional procedure [20,22,24].

The compensation curves have been represented for each set of rates used and for each alpha in Figs. 10 and 11. Fig. 10 shows the influence that each set of rates has on the compensation effect. It is very clear that the kinetic information will be very similar when sets 0, 1, 2 and 10 are chosen, while that associated with set 7 will be different to the remaining ones. Fig. 11 shows what is accepted by the isoconversional principle: each extent of the reaction modifies the Arrhenius parameters so that there is a compensation relationship for each of them.

Both Figs. 10 and 11 show a single cutoff point for the various compensation curves. This fact is not exclusive to the system under study; it has been

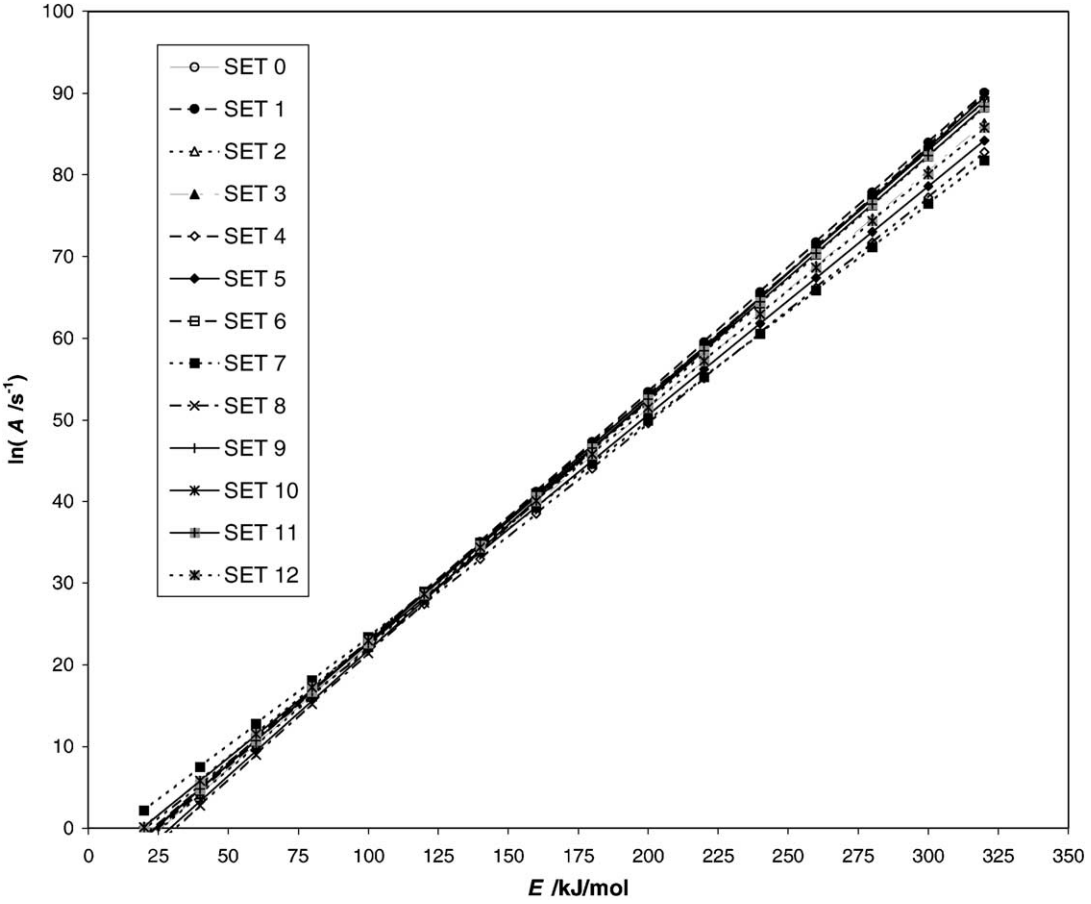


Fig. 10. Compensation curves associated with each of the sets of rates under study.

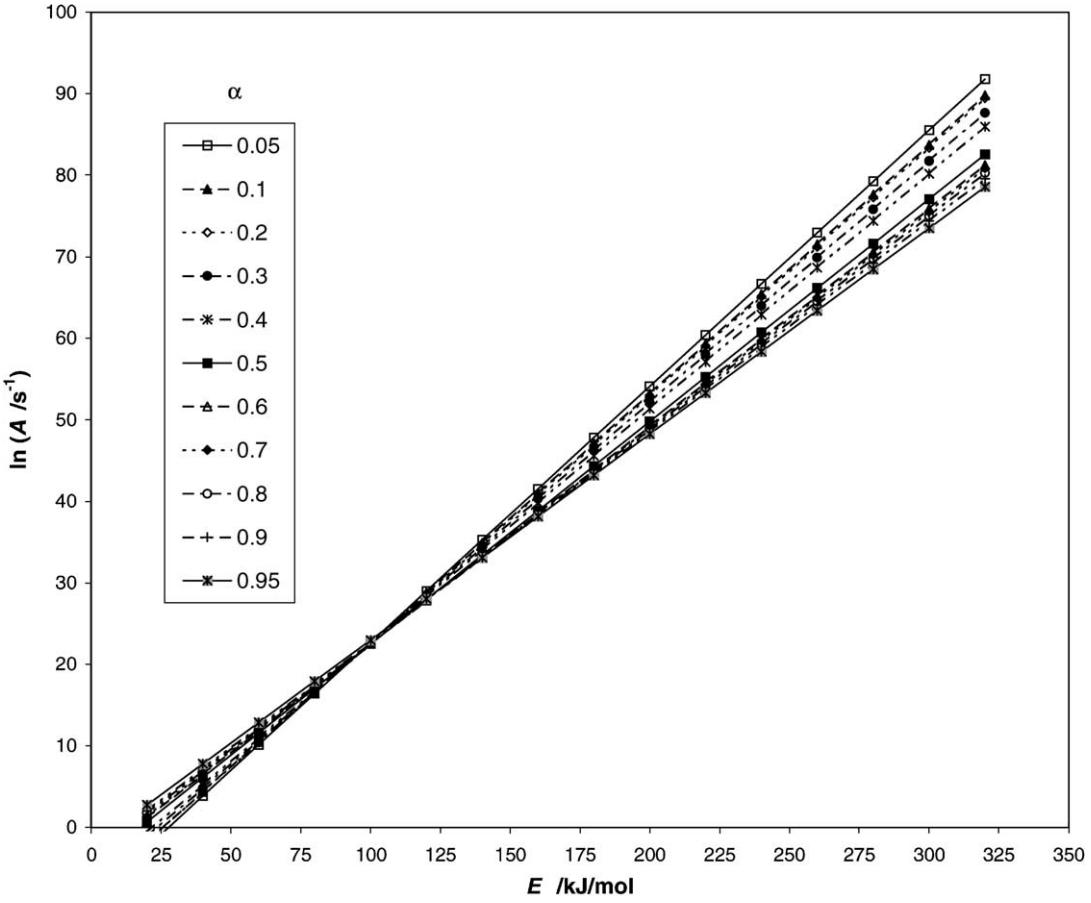


Fig. 11. Compensation curves associated with each degree of conversion α.

referred to by other authors [16] and we have found it previously in the kinetics of unsaturated polyester resin [24]. This cutoff point may be taken as an invariant point, that is independent of the set of rates and of the extent of the reaction, and that describes in the most compact way possible the kinetic process under study. This point depends on the choice of $f(\alpha)$, so that for the system under study, the kinetic information is summarised by saying that for a $f(\alpha) = \alpha^m(1-\alpha)^n$ in which $n = 1.9$ and $n + m = 2$, $E = 110$ kJ/mol and $\ln A = 24\ \mathrm{s}^{-1}$. However, the kinetic description using the other $f(\alpha)$ analysed is equally valid. In this case, it has been found that the kinetic process is described by $f(\alpha) = \alpha^m(1-\alpha)^n$ in which $n = 2.8$ and $n + m = 3$, $E = 125$ kJ/mol and $\ln A = 40\ \mathrm{s}^{-1}$.

As explained in the introduction, one of the aims of an experimental kinetic study with non-isothermal tests is to obtain adequate kinetic information to be able to predict or simulate isothermal processes and to answer the question that is of great interest from the point of view of the application of thermoset powder systems, namely: for a given oven curing temperature, how much curing time is needed to reach the right conversion? In other studies [26], the link between non-isothermal kinetics and isothermal simulation has been established using Eq. (9) and the relationships described by Eqs. (12) and (14). Once the experimental evolution of E_α is known for each conversion together with the experimental values of $A_{\alpha,\mathrm{int}}$, we can calculate the values of $A_{\alpha,T}$ that together with E_α through Eq. (9), reproduce the isothermal kinetics for each conversion and each temperature without the need to know either $f(\alpha)$ or $g(\alpha)$. With the procedure described in this study, the isothermal kinetics can be

obtained by direct application of Eq. (9), as the kinetic triplet [$\ln A_\alpha$, E_α, $g(\alpha)$] is known. Evaluation of these procedures by comparing results with experimental data will be published in another work.

5. Conclusions

The kinetic parameters obtained by a non-isothermal procedure from the set of heating rates are not unique and depend on the set of rates chosen.

For the system studied, using the isoconversional procedure and accepting that E_α and A_α vary with the degree of conversion, the kinetics of the reactive process are established by the so-called kinetic triplet [E_α, A_α, $f(\alpha)$]. When $f(\alpha)$, E_α and A_α are fixed, they are not independent, as there is the so-called compensation effect between them, which takes the form of a linear relationship of the type $\ln A_\alpha = aE_\alpha + b$.

The experimental results that were processed using the differential and integral isoconversional procedure enable a kinetic triplet [E_α, A_α, $f(\alpha)$] to be obtained for a certain set of rates. This triplet is not unique, but it is coherent with experimental results and with the compensation effect. The compensation curve allows the pairs of values [E_α, A_α,] obtained by the differential and integral procedures to be grouped in the same set, thus, showing that the same kinetic description is obtained by both methods.

The use of different sets of rates in the system under study and the characterisation by means of a compensation curve has shown the extent to which the heating rate can influence the determination of kinetic parameters, and what selection of rates may yield similar results. In the same way, the determination of the compensation effect for each degree of conversion, α, makes it possible to see the variation in the kinetics of the reactive process in each extent of the reaction.

The compensation curves for each set of rates and each alpha are found to cut at one point, thus, enabling the following values to be chosen for the system under study: $E = 110$ kJ/mol, $A = 24\ \mathrm{s}^{-1}$ with $f(\alpha) = \alpha^m(1-\alpha)^n$ in which $n = 1.9$ and $m = 0.1$ as a kinetic triplet that is independent of both the set of rates chosen and the degree of conversion α. This kinetic triplet is the most compact and general way of describing the kinetics of the system under study.

Acknowledgements

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