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COMPARATIVE KINETIC STUDY OF THE NON-ISOTHERMAL THERMAL CURING OF *bis*-GMA/TEGDMA SYSTEMS

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The thermal polymerization kinetics of dimethacrylate monomers was studied by differential calorimetry using non-isothermal experiments. The kinetic analysis compared the following procedures: isoconversional method (model-free method), reduced master curves, the isokinetic relationship (IKR), the invariant kinetic parameters (IKP) method, the Coats–Redfern method and composite integral method I. Although the study focused on the integral methods, we compared them to differential methods. We saw that even relatively complex processes (in which the variations in the kinetic parameters were only slight) can be described reasonably well using a single kinetic model, so long as the mean value of the activation energy is known (E). It is also shown the usefulness of isoconversional kinetic methods, which provide with reliable kinetic information suitable for adequately choosing the kinetic model which best describes the curing process. For the system studied, we obtained the following kinetic triplet: $f(\alpha)=\alpha^{0.6}(1-\alpha)^{2.4}$, E=120.9 kJ mol^{-1} and ln$A$=38.28 min^{-1}.

Keywords: *dimethacrylate monomers, non-isothermal kinetics*

Introduction

This paper studies thermally initiated radical copolymerization of mixtures of dimethacrylate monomers containing triethylene glycol dimethacrylate (TEGDMA) and 2,2-*bis*[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]propane (*bis*-GMA) in a 25/75 (*bis*-GMA/TEGDMA) mass ratio. These systems may reasonably be considered to be simplified models of the resins used at present in commercial filling composites [1, 2]. Theoretically, the reactivity of the C=C double bonds of the methacrylate groups in different dimethacrylate monomers is similar. This means that the curing mechanism should not change when we change the mixture of dimethacrylates or during curing. In reality, however, different factors may have significant effects on the curing kinetics. These factors include the high rigidity and viscosity of the resins (which can reduce the mobility of the monomers), the concentration of radical species, autocatalysis, the formation and the connection of microgels, etc. This leads us to expect that the systems will exhibit relatively complex curing and that the kinetic parameters may change slightly during the reactive process. In most of the research carried out to date, the curing kinetics of these systems has been considered kinetically, from a mechanistic point of view (both in photo-initiated and in thermally initiated processes) [3–5]. Although in certain cases these studies allow us to determine the kinetic constants of initiation, propagation and termination, the working method is complex and if the reactivity is high it is not always possible to determine the constants correctly. Furthermore, they necessarily presuppose that the reaction rate is directly proportional to the monomer concentration (mechanism of order n with n=1). This paper analyses the kinetic methods usually used in the study of heterogeneous solid-state reactions and attempts to adapt them to non-isothermal curing of these systems, and thereby determine the complete kinetic triplet. A paper to be published at a later date compares the results obtained with those obtained in isothermal curing, both thermally initiated and initiated by UV radiation. The kinetics of the latter systems is of great interest in the development of materials for carrying out dental repairs.

A second objective of the present paper is to compare the different methodologies used to determine kinetic parameters. In general, linear integral methods were used and compared to their differential equivalents, and also to several non-linear methods.

The kinetic study may begin with the use of an isoconversional method; in this case we need to know the relationship between the degree of conversion and the temperature, α–T for different heating rates. This method allows us to establish whether the activation energy depends on the conversion. If E does not vary with α, the study is straightforward and one single kinetic triplet describes the curing. If E changes with α,

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the process is more complex and the shape of the E-α curve may provide information on the reaction mechanism [6–8]. In certain cases the variations observed in E can be artificial and lead to false conclusions regarding the mechanism [9]. Due to the compensatory effect, it is also necessary to study the evolution of the second kinetic parameter, which includes the pre-exponential factor and the kinetic model. Not using this second parameter could lead to errors.

It is widely accepted that the use of differential methods, although they demonstrate significant numerical instability and noise interference [10], leads to more consistent values of the activation energy than does the use of integral methods. Integral methods, on the other hand, are easy amenable and show a lesser degree of dependence of E on α, which can make it easier to determine the kinetic model even for relatively complex processes [11, 12]. Although the Vyazovkin non-linear integral method [13, 14] gives more consistent activation energies than do conventional integral methods, we do not use it here since it leads to kinetic parameters similar to those produced by the differential methods, which are easier to apply [11, 12].

We used the following methods to establish the kinetic model:

- Methods which use a single curve α–T for only one linear heating rate (the Coats–Redfern method [15–17] and differential D method [12, 16, 18]).
- Composite integral method I [19, 20] and its corresponding differential version [7, 21]. We select the kinetic model that allows us to superimpose the results obtained at different heating rates in one single master curve.
- Methods based on the existence of a compensation effect between E and $\ln A$ when the degree of conversion or the kinetic model changes [22]. In the first case, we chose the model that exhibits a good isokinetic relationship (IKR) with a given isokinetic temperature within the experimental working range [17, 22–24]. In the second case we used the invariant kinetic parameter (IPK) method introduced by Lesnikovich and Levchik [25, 26] and since widely used by different authors [6, 7, 27–29].
- Methods that use the integral and differential master curves based on the generalized kinetic equations [21, 30, 31].

Due to the differences observed between the integral E value and the differential E value, we did not use methods that use master curves that mix integral and differential functions [32, 33].

It may seem contradictory that in the comparison of methods, isoconversional procedures, in which the kinetic parameters can change during the process, were mixed with others whose objective was to describe the system's transformations through a single kinetic triplet. In our opinion, the comparison is justified since, according to the system and the process analysed, the best and most useful kinetic description is sometimes provided by the isoconversional procedure and sometimes by the single kinetic triplet procedure, or even by a combination of the two. Moreover, this contrast serves to justify our research.

From the kinetic study we were able to conclude that, for the system considered, all the methods provided valid information for describing the curing. As a general rule, the integral methods allowed us to solve the kinetic triplet more easily, even for relatively complex processes, although the differential methods provide values for the activation energy which are usually accepted as being more consistent. Despite the variations observed in the kinetic parameters, we were able to establish the complete kinetic triplet that is valid in the region in which the variations are relatively small.

Experimental

Materials

Bis-GMA (M_w=512) and TEGDMA (M_w=286) monomers supplied by Aldrich were used as received. As an initiator a dispersion of benzoyl peroxide in dibutyl phthalate with a content of 40 mass% (Luperox AFR40, Aldrich) was used.

Samples were prepared by dissolving the initiator in TEGDMA monomer by means of magnetic stirring for 2 h at 30°C. Then, *bis*-GMA was added to obtain a formulation with a *bis*-GMA concentration of 25 mass%. This was stirred for 2 h at 30°C and kept at –20°C before use to prevent polymerization. A mixture containing 2 parts of initiator per 100 parts of mixture, by mass, was used.

DSC calorimetry

Calorimetric analyses were carried out on a Mettler DSC-821^e calorimeter with a TSO801RO robotic arm. Samples weighing approximately 5 mg were cured in aluminium pans in a nitrogen atmosphere. In order to determine the reaction heat, non-isothermal experiments were performed between 0 and 250°C at heating rates of 5, 7.5, 10 and 15°C min^{-1}. At a given temperature T, the degree of conversion was calculated as the quotient of the heat released up to T and the total reaction heat associated with the complete conversion of all the reactive groups. As the total reaction heat, we used a value of 345 J g^{-1}, which was the average value of the reaction heat obtained non-isothermally at the different heating rates, since the FTIR analysis of the crosslinked material did not show any residual double bonds. The reaction rate, $d\alpha/dt$, was expressed as the ratio of the instant heat released (calorimetric signal) to the total reaction heat.

Methods used to evaluate the kinetic parameters

In non-isothermal kinetics of heterogeneous condensed phase reactions, it is usually accepted that the reaction rate is given by [34]:

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

where α is the degree of conversion, T temperature, t time, $f(\alpha)$ the differential conversion function, R the gas constant, β the linear constant heating rate $\beta=dT/dt$ and A and E the pre-exponential factor and the activation energy given by the Arrhenius equation.

By integrating Eq. (1), the integral rate equation, so-called temperature integral, may be expressed as:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^T e^{-(E/RT)}dT \tag{2}$$

where $g(\alpha)$ is the integral conversion function.

If E/RT is replaced by x and integration limits transformed, Eq. (2) becomes:

$$g(\alpha) = \frac{AE}{\beta R}\int_x^\infty \frac{e^{-x}}{x^2}dx = \frac{AE}{\beta R}p(x) \tag{3}$$

where $p(x)$ is the exponential integral, which has no analytic solution [35]. However, there are many approximations that make it possible to obtain the kinetic parameters through the linearization of the experimental data [15, 36–41]. There are more complex variations of $p(x)$, such as those put forward by Senum and Yang [42, 43] and Agrawal [44] whose approximations of the temperature integral at an interval of x offer far higher accuracy and lower error.

Isoconversional methods

Isoconversional methodology in non-isothermal experiments assumes that for a given degree of conversion, the reaction mechanism does not depend on the heating rate.

By applying logarithms to Eq. (1), the differential isoconversional method suggested by Friedman [35] is obtained:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln[Af(\alpha)] - \frac{E}{RT} \tag{4}$$

The linear plot of $\ln(d\alpha/dt)$ *vs.* T^{-1}, obtained from DSC curves recorded for several heating rates makes it possible to determine E and the kinetic parameter $\ln[Af(\alpha)]$ for every value of α.

By using the Coats–Redfern [15] approximation to solve Eq. (3) and considering that $2RT/E$ is much lower than 1, the Kissinger–Akahira–Sunose (KAS) equation may be written [39, 40]:

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

For each conversion degree, the linear plot of $\ln(\beta/T^2)$ *vs.* T^{-1} enables E and $\ln[AR/g(\alpha)E]$ to be determined from the slope and the intercept. If the reaction model, $g(\alpha)$, is known, the corresponding pre-exponential factor can be calculated for each conversion. The Flynn–Wall–Ozawa integral [37, 38] method based on Doyle's approach [36] was not used because it gives similar results to the KAS method.

Methods which use a single $\alpha=\alpha(T)$ curve for only one linear heating rate

From these methods we use the integral Coats–Redfern (CR) method based on Eq. (5):

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

and a differential (D) method [12, 16] based on Eq. (4):

$$\ln\left(\frac{d\alpha/dt}{f(\alpha)}\right) = \ln A - \frac{E}{RT} \tag{7}$$

For a given model and heating rate, the linear plot of the left-hand sides of Eqs (6) and (7) *vs.* T^{-1} allowed us to obtain the average activation energy and average pre-exponential factor from the slope and the intercept. We then chose the model with an activation energy similar to that obtained isoconversionally and with a good correlation coefficient [17, 18].

Composite methods

The composite methods presuppose one single set of activation parameters for all conversions and heating rates. In this way all the experimental data can be superimposed in one single master curve.

Composite integral method I [19, 20, 45] is based on the Coats–Redfern equation, which is rewritten as follows:

$$\ln\left(\beta\frac{g(\alpha)}{T^2}\right) = \ln\left[\frac{AR}{E}\right] - \frac{E}{RT} \tag{8}$$

For each form of $g(\alpha)$, the curve $\ln(\beta g(\alpha)/T^2)$ *vs.* T^{-1} was plotted for the experimental data obtained at different heating rates. We then chose the kinetic model for which the data falls in a single master straight line and which gives the best correlation coefficient. A single set of activation parameters, *E* and *A*, can be obtained from the slope and the intercept of the straight line. Logically, these must be similar to those obtained for each heating rate using the Coats–Redfern method.

The differential version of this method is based directly on Eq. (7) [21]. The data for different heating rates must be grouped together in a single relation, from which a single set of parameters, *E* and *A*, is obtained.

In order to compare integral and differential data, the straight line defined by Eq. (8) can be adjusted by subtracting $\ln(R/E)$ from both sides, thus leaving all the data grouped together in a single linear relation represented by Eq. (7). This straight line will be unique and will have a good correlation if the differential and integral parameters are similar.

Compensation effect (isokinetic relationship)

The activation energy and the pre-exponential factor may be linked due to a compensation effect or the isokinetic relationship (IKR) through the following equation [22, 46, 47]:

$$\ln A_x = a + bE_x \qquad (9)$$

where a and b are constants and the subscript x refers to a factor producing a change in the Arrhenius parameters (conversion, heating rate, model). The slope $b=1/RT_{\text{iso}}$ is related to the isokinetic temperature and the intercept $a=\ln k_{\text{iso}}$ is related to the isokinetic constant.

The appearance of the IKR shows that only one mechanism is present, whereas the existence of parameters that do not agree with the IKR implies that there are multiple reaction mechanisms [46]. According to certain authors [22], we selected the model whose IKR in relation to the conversion had the best linear correlation and in which the associated T_{iso} value was near the experimental temperature range.

Vyazovkin and Linert [22] claims that the real pre-exponential factor can be predicted by using the isoconversional activation energy and the compensation effect in relation to the kinetic model, at an average heating rate, without needing to know the kinetic model. As we explained elsewhere [12] the most suitable model is that which presents the lowest error or deviation rate in the following equation:

$$\Omega(\%) = 100\frac{1}{n}\sum_{\alpha}\frac{\left|\ln A_{\alpha,\text{pred}} - \ln A_{\alpha,\text{iso}}\right|}{\ln A_{\alpha,\text{pred}}} \qquad (10)$$

where n represents the number of elements for which the deviation is calculated, $\ln A_{\alpha,\text{pred}}$ is the predicted pre-exponential factor based on the IKR in relation to the model and $\ln A_{\alpha,\text{iso}}$ is the pre-exponential factor calculated by applying the model to the isoconversional data.

Invariant kinetic parameters method (IKP)

To determine the invariant activation parameters, we used the IPK method as set out by Budrugeac *et al.* [6, 7, 16] in different papers. The method is based on the experimental observation that the same calorimetric curve can be described relatively correctly by several different conversion functions.

Using an integral (CR) or differential (D) method, for each heating rate and for each conversion function a pair of activation parameters (E, A) is established. Using the apparent compensatory effect that exists when the model changes, for each heating rate the compensation parameters, a_{v} and b_{v}, are determined according to Eq. (9) (Budrugeac *et al.* [7] denote these parameters α_{v}^{*} and β_{v}^{*}). The point of intersection of the straight lines of compensation for several heating rates corresponds to the real values of E and A, called invariant activation parameters (E_{inv} and A_{inv}), as they are independent of the conversion, the model and the heating rate [25, 26]. Since determining the point of intersection by graphic means is uncertain, the invariant kinetic parameters can be defined by the following supercorrelation:

$$a_{\text{v}} = \ln A_{\text{inv}} - b_{\text{v}}E_{\text{inv}} \qquad (11)$$

The straight line a_{v} *vs.* b_{v} allows us to determine the invariant kinetic parameters (E_{inv} and A_{inv}) from its slope and intercept.

Although the IKP method aims to determine the invariant parameters independently of the kinetic model, comparing them to those obtained using other methods (the Coats–Redfern method, isoconversional methods, etc.) also allows us to decide which kinetic model best describes the process.

Integral and differential master plots

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

$$\frac{f(\alpha)}{f(0.5)} = \frac{\mathrm{d}\alpha/\mathrm{d}t}{(\mathrm{d}\alpha/\mathrm{d}t)_{0.5}}\frac{\exp(E/RT)}{\exp(E/RT_{0.5})} \qquad (12)$$

where $(\mathrm{d}\alpha/\mathrm{d}t)_{0.5}$, $T_{0.5}$ and $f(0.5)$ are respectively the reaction rate, the temperature reaction and the differential conversion function at $\alpha=0.5$.

The left side of Eq. (12), is a reduced theoretical curve which is characteristic of each kinetic function. The right side of the equation is associated with the reduced rate and can be obtained from experimental data if the activation energy is known and remains constant throughout the reaction. Comparison of both sides of Eq. (12) tells us which kinetic model describes an experimental reaction process.

Using as reference point at $\alpha=0.5$, the following integral master equation is easily derived from Eq. (3):

$$\frac{g(\alpha)}{g(0.5)}=\frac{p(x)}{p(x_{0.5})} \tag{13}$$

where $p(x_{0.5})$ is the temperature integral at α=0.5.

The function $p(x)$ can be expressed using the fourth rational approximation by Senum and Yang [42]:

$$p(x)=\frac{\mathrm{e}^{-x}}{x}\frac{x^3+18x^2+86x+96}{x^4+20x^3+120x^2+240x+120} \tag{14}$$

Using the Coats–Redfern approximation (Eq. (5) or (6)) the Eq. (13) becomes:

$$\frac{g(\alpha)}{g(0.5)}=\frac{\exp(-E/RT)T^2}{\exp(-E/RT_{0.5})T_{0.5}^2} \tag{15}$$

Following the same method as for the differential master curves and using Eq. (13) or (15) the kinetic model can be established.

Recently, some authors [21, 31] have given a universal expression to the master plots using the concept of generalized time introduced by Ozawa [37]. The particularization of the generalized kinetic equations for non-isothermal experiments leads to Eqs (12) and (13).

In order to determine the kinetic model, it is necessary that the conversion function, $f(\alpha)$, characteristic of the process studied, to be included in the set of functions analysed. Different kinetic models were studied: diffusion (D_1, D_2, D_3 and D_4), Avrami-Erofeev ($A_{3/2}$, A_2, A_3 and A_4), power law (P_2), phase-boundary-controlled reaction (R_2 and R_3), reaction-order *n* (n=3, 2, 1.5 and 1 denominated F_1) and autocatalytic ($n+m$=1, 2 and 3 with different values of *n* and *m*) [17, 23]. Although there is no reason for some of these models to have any physicochemical meaning in the curing processes, they can still be used to aid description of the calorimetric curve.

Results and discussion

Figure 1 shows the calorimetric curves that correspond to curing the *bis*-GMA/TEGMA system at different heating rates. There is a main peak at a low temperature with a shoulder at a high temperature. This behaviour has been observed by other authors, who have related it to physical changes during curing [1]. Specifically, radical curing with multifunctional monomers can occur in two autocatalytic-type stages. In the first stage (at low temperatures) microgellation occurs, and in the second (at higher temperatures) the connection between microgels occurs. The first stage would mainly be controlled by the formation of the primary peroxide radicals, while in the second stage, diffusion effects would also have a slight effect [48].

Table 1 gives the kinetic data obtained isoconversionally through differential and integral methods. Figures 2 and 3 demonstrate that these parameters reproduce the experimental data correctly. In general, similar behaviour is observed using both methods, although the data are somewhat different. This can be

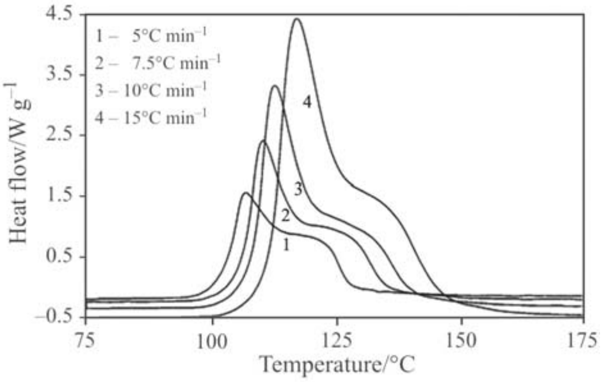

Fig. 1 Non-isothermal DSC curves at different heating rates (5, 7.5, 10 and 15°C min^{-1})

Table 1 Isoconversional kinetic parameters of nonisothermal curing

α	Integral data (Eq. 5)				Differential data (Eq. 4)			
	E/kJ mol^{-1}	ln[$AR/g(\alpha)E$]/K^{-1} min^{-1}	lnA^a/min^{-1}	r^2	E/kJ mol^{-1}	ln$f(\alpha)A$/min^{-1}	lnA^b/min^{-1}	r^2
0.1	121.5	28.40	38.06	0.9979	121.4	37.00	38.63	0.9958
0.2	117.0	26.75	36.73	0.9970	123.3	37.92	39.42	0.9945
0.3	116.7	26.50	36.74	0.9943	131.1	40.18	41.76	0.9979
0.4	120.6	27.54	38.05	0.9902	137.8	41.90	43.68	0.9967
0.5	126.0	29.00	39.80	0.9885	130.4	39.10	41.18	0.9949
0.6	127.4	29.16	40.23	0.9917	102.7	30.15	32.66	0.9973
0.7	119.7	26.48	37.82	0.9954	90.8	26.12	29.23	0.9950
0.8	109.3	23.04	34.76	0.9973	83.4	23.54	27.54	0.9961
0.9	98.8	19.59	32.04	0.9962	77.0	21.11	26.70	0.9976
average^c	121.3	27.69	38.21	0.9936	119.6	36.05	38.08	0.9960

^{a}ln$A$ has been calculated using kinetic model n=2.4, m=0.6 and ln[$AR/g(\alpha)E$], ^{b}ln$A$ has been calculated using kinetic model n=2.4, m=0.6 and ln[f(α)A], ^{c}Average values determined in the interval where kinetic parameters are relatively constants

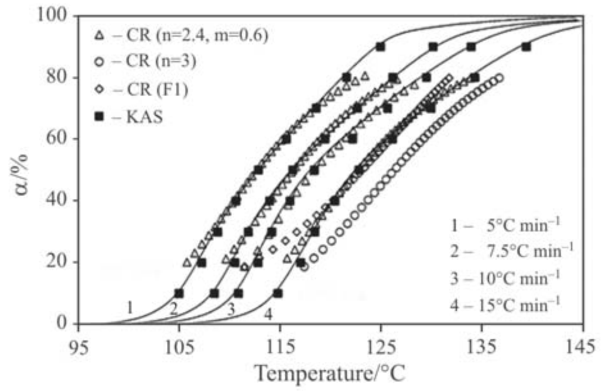

Fig. 2 Experimental and simulated conversion *vs.* T at different heating rates (5, 7.5, 10 and 15°C min^{-1}). The continuous line represents the experimental data. The symbols represent the simulated conversions using isoconversional integral method (Eq. (5), KAS) and CR method with different kinetic model

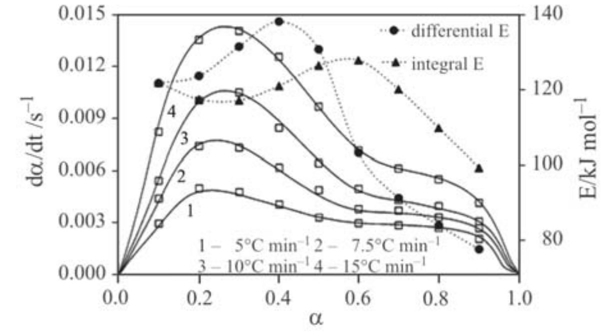

Fig. 3 Experimental and simulated reaction rate *vs.* conversion at different heating rates (5, 7.5, 10 and 15°C min^{-1}). The continuous line represents the experimental data. The empty symbols represent the simulated dates using isoconversional differential method (Eq. (4)). Integral and differential activation energy *vs.* conversion curves (Table 1) are also shown

due to the different conception of differential and integral isoconversional methods. Differential method uses the point value of the overall reaction rate, while the integral method uses integrals which describe the history of the system. Figure 3 shows how E increases to a maximum value and then decreases again. These variations can be related to the different stages of curing. The integral E appears to have more physical meaning as its maximum value coincides with the decrease in the first stage and the increase of the second. However the differential E has a maximum at some poorly defined point during the first stage, where the second stage is negligible. Although the parameters vary a certain amount during curing (a conversion factor between 0.1 and 0.7), they are relatively constant (especially those obtained from the integrals). Therefore, we have attempted to find the model that best reproduces the curing process as a whole. Furthermore, the values for E in this region of curing, which are similar to the values given in the literature for the decomposition of benzoyl peroxide [49, 50], suggest that this process is the determining factor during this stage of curing. On the other hand, the variations in E are compensated by variations in A once the model is fixed, and the integral and differential parameters (Table 1) become grouped together in one single IKR with a=0.9149 min^{-1}, b=0.3092 mol kJ^{-1}, r^2=0.9966 and T_{iso}=116°C. This would mean that close to T_{iso}, if the variations in E are not very large, one single mechanism could describe the whole process. It is also possible to imagine that the kinetic model is constant throughout curing while E and A can vary slightly. This behaviour has already been described for curing dimethacrylate monomers [3].

We used the integral CR method and differential D method to determine the kinetic model and several overall kinetic parameters, within the range in which the kinetic parameters are relatively constant (α between 0.2 and 0.8). Table 2 gives the results obtained for rates of 7.5 and 15°C min^{-1}. Other rates tested (5 and 10°C min^{-1}) produced equivalent, though slightly different, results. The CR method shows that many models result in a clear regression and that it is therefore not possible to decide which is best. If we compare the E resulting from the CR method with the isoconversional average E=121.3 kJ mol^{-1}, we can see how it is now possible to choose the model. Of the models tested, only the F_1 and the n=2.4 m=0.6 models produce an E similar to the isoconversional value. From these two models, we have chosen the latter as correct because it exhibits a better regression. Figure 2 simulates curves showing conversion *vs*. temperature for the model n=2.4 m=0.6 using the kinetic parameters obtained using the CR method (Table 2). It can be seen that one single activation energy describes the curing reasonably well in the central area of curing in which E was fairly constant. In the same figure, for a rate of 15°C min^{-1} we simulated the curing with the F_1 and n=3 models with the parameters obtained using the CR method. It can now be seen how the F_1 model which had an E similar to the isoconversional value fits the curing quite well, but not as well as the n=2.4 m=0.6 model. The n=3 model, which had a very good correlation coefficient, fits the curing badly as the E is very different from the isoconversional value. This shows that, in general, using the model with the best regression as the correct one in the CR method does not guarantee a correct choice in the case of E being different from the real value, since the linearization of the curves can induce calculation errors. However, choosing models with poor regression but with E similar to the isoconversional value does guarantee a certain quality of results.

Table 2 Integral and differential kinetic parameters determined using CR method and D method

Models	Integral data (CR method, Eq. (6))						Differential data (D method, Eq. (7))					
	β=15°C min^{-1}			β=7.5°C min^{-1}			β=15°C min^{-1}			β=7.5°C min^{-1}		
	E/kJ mol^{-1}	ln$A$/min^{-1}	r^2	E/kJ mol^{-1}	ln$A$/min^{-1}	r^2	E/kJ mol^{-1}	ln$A$/min^{-1}	r^2	E/kJ mol^{-1}	ln$A$/min^{-1}	r^2
$A_{3/2}$	79.3	23.72	0.9443	83.9	24.94	0.9557	–13.7	–4.29	0.1416	–10.2	–3.89	0.0580
A_2	57.8	16.95	0.9443	61.3	17.72	0.9534	–32.5	–10.23	0.4460	–32.8	–11.09	0.3487
A_3	36.4	10.03	0.9342	38.7	10.35	0.9482	–51.3	–16.28	0.6367	–55.4	–18.40	0.5641
A_4	25.6	6.45	0.9733	27.4	6.55	0.9421	–60.7	–19.39	0.6969	–66.7	–22.15	0.6340
D_1	164.2	48.97	0.9443	174.4	52.40	0.9557	–10.0	–3.62	0.1416	19.4	4.71	0.0580
D_2	194.7	58.70	0.9181	205.8	62.51	0.9309	33.2	9.16	0.8763	64.5	18.30	0.9213
D_3	218.8	64.09	0.9339	231.1	68.44	0.9458	85.9	24.03	0.9691	118.4	33.83	0.9692
D_4	198.4	57.66	0.9206	210.0	61.68	0.9339	51.4	13.31	0.9355	83.1	22.66	0.9476
R_2	98.6	28.79	0.9198	104.6	30.54	0.9337	–27.8	–9.36	0.5305	–18.0	–7.11	0.2640
R_3	106.1	30.78	0.9299	112.3	32.65	0.9427	–10.6	–4.40	0.1324	–0.3	–1.93	0.0001
P_2	36.1	9.70	0.8640	38.7	10.12	0.8853	–114.3	–35.65	0.9296	–116.2	–37.45	0.9026
F_1	122.3	37.07	0.9472	129.1	39.20	0.9579	23.9	7.41	0.4052	35.0	10.34	0.5126
n=1.5	149.9	45.85	0.9666	157.6	48.40	0.9744	75.6	23.94	0.8495	88.0	27.09	0.8405
n=2	181.3	55.80	0.9794	190.0	58.81	0.9847	127.3	39.57	0.9306	141.0	43.85	0.9162
n=3	254.3	78.76	0.9923	265.1	82.81	0.9927	230.7	71.72	0.9697	247.0	77.35	0.9583
n=0.25, m=0.75	19.4	5.59	0.8926	20.9	5.58	0.9150	–105.8	–32.02	0.8923	–112.4	–35.18	0.8546
n=0.75, m=0.25	75.6	22.85	0.9259	80.1	24.05	0.9390	–19.3	–5.73	0.2757	–14.1	–4.83	0.1230
n=1.5, m=0.5	87.4	27.22	0.9778	91.7	28.43	0.9836	40.8	13.28	0.5181	42.8	13.50	0.4259
n=1.6, m=0.4	106.2	32.94	0.9784	111.4	34.51	0.9840	58.1	18.54	0.6962	62.4	19.57	0.6274
n=1.9, m=0.1	162.5	50.08	0.9793	170.3	52.73	0.9846	110.0	34.31	0.9051	121.4	37.78	0.8844
n=2.1, m=0.9	33.1	11.57	0.9911	34.8	11.57	0.9833	75.1	24.40	0.7013	70.2	22.73	0.5440
n=2.3, m=0.7	94.1	30.11	0.9958	97.9	31.15	0.9930	109.7	34.92	0.8449	109.5	34.87	0.7630
n=2.4, m=0.6	120.1	37.99	0.9957	123.1	38.92	0.9939	126.9	40.18	0.8839	129.2	40.94	0.8250
n=2.9, m=0.1	233.3	73.28	0.9928	243.2	76.03	0.9939	213.4	66.47	0.9634	227.4	71.28	0.9491

Table 2 shows the equivalent results for D method. In general, it is possible to extract the same conclusion as with the CR method, although the adjustments are much less precise. This can be attributed to the fact that in the differential method *E* varies more than in the integral method (Table 1).

To check the results from the CR method, we used the composite integral method I. Figure 4 shows our results for the F_1, *n*=3 and *n*=2.4 *m*=0.6 models. Once again it can be seen that the *n*=2.4 *m*=0.6 model best fits the curing, since all the different heating rate data is in just one master curve. Furthermore, this is the model with the best regression and unique parameters that are similar to those obtained isoconversionally and using the CR method at each heating rate. The data from the *n*=3 model which produced very good regression using the CR method for each heating rate are grouped together in four different curves, one for each rate. Meanwhile the F_1 model, which did not result in a good regression using the CR method but did have an *E* similar to the isoconversional value, produced data which fitted into one single master curve reasonably well and has kinetic parameters of the same order as the isoconversional parameters (although once again the regression is not as good as for the *n*=2.4 *m*=0.6 model). We can therefore conclude that selection of the model using the criterion of the CR method that shows good regression and parameters similar to the isoconversional ones is the same as choosing the model according to the composite integral method I with the criterion that all the data must be grouped together in one single master curve and that the kinetic parameters be similar to the isoconversional ones.

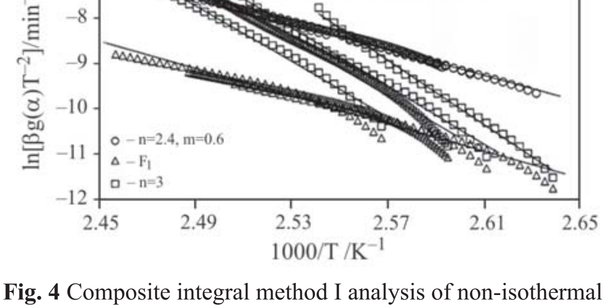

Fig. 4 Composite integral method I analysis of non-isothermal DSC data (5, 7.5, 10 and 15°C min^{-1}) based on Eq. (8)

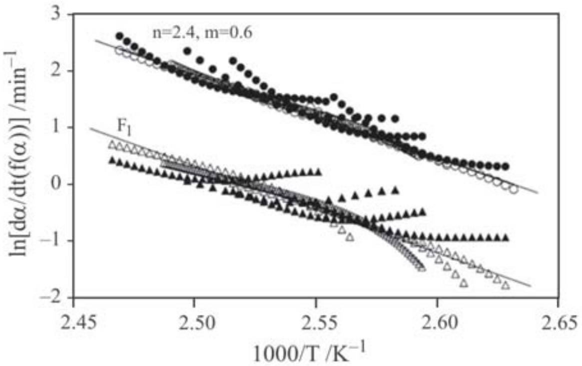

Fig. 5 Composite differential method analysis of non-isothermal DSC data (5, 7.5, 10 and 15°C min^{-1}) based on Eq. (7). The filled symbols correspond to the differential data and the empty symbols correspond to the integral data

Use of the differential version of the composite method (Eq. (7)) produces similar results to those produced using the integral method, but with less accuracy. Figure 5 shows how all the data for the *n*=2.4 *m*=0.6 model fits onto just one curve but with a significant deviation at high and low temperatures. Furthermore, the overall differential kinetic parameters for this model (E=122.3 kJ mol^{-1}, ln$A$=38.81 min^{-1}, r^2=0.9258) are similar to the isoconversional parameters and those we obtained from one single curve (Tables 1 and 2). With the F_1 model the overall kinetic parameters are not consistent (E=68.5 kJ mol^{-1}, ln$A$=20.72 min^{-1}, r^2=0.7483) and there is not such a good match with one single curve. The other models we tested produced experimental data that do not sit on one single curve (we include no figure for this) and deviate far from linearity. The deviations from the single master curve which are observed at high and low temperatures, even using the *n*=2.4 *m*=0.6 model, are consistent with the poor regression observed for the data using D method (Table 2). Figure 5 also contains the overlapping integral data obtained using composite integral method I adjusted by subtracting from both sides of Eq. (8) ln(*R*/*E*). It can be observed how the differential and integral data are approximately grouped together in a single curve. The data does not totally overlap, which suggests that the methods that mix integral and differential data will lead to results that are not very precise. Using integral and differential data separately, however, allows us to establish the model reasonably well, and for the system studied the best results are obtained from the integral data. Criado *et al.* [21] demonstrated that for the thermal decomposition of a solid, composite methods allow us to differentiate between models that can correctly reproduce the thermal process despite having different kinetic parameters. According to these authors, the model in which the data are grouped together in just one straight line (Eq. (7)) is the correct one and the kinetic parameters obtained from this straight line are the real ones. Accepting this hypothesis as correct, we have taken as the kinetic model that describes the curing the *n*=2.4 *m*=0.6 and as the real *E* and ln*A* those obtained from overlapping in one single master integral curve (E=120.9 kJ mol^{-1}, ln$A$=38.28 min^{-1}).

As a criterion for establishing the kinetic model, some authors have obtained good results using the existence of an IKR with good regression when the conversion changes, together with the fact that the T_{iso} is within the experimental range of temperatures [12, 17, 22–24]. Table 3 shows the results obtained using the different models. Although the n=2.4 m=0.6 model exhibits the best regression, many other models also show a good regression and have T_{iso} close to the experimental value. The data in Table 3 only rules out certain models. This means that, for the system studied, the IKR relationships are not sufficiently discriminatory to determine the kinetic model and cannot be used as the only criterion.

For the integral data we have established the error Ω (%) that occurs when comparing the pre-exponential factors estimated from the IKRs when conversion changes to the factors predicted from the IKRs when the model changes, according to Eq. (10). Table 3 shows how the models D_n, A_n, R_n and P_2 have a large error and can be ruled out, and only a few autocatalytic models, including the n=2.4 m=0.6 model, have a low error and are suitable to be used. Although this procedure does not allow us to establish the model unambiguously, it does provide information about which family of functions best describes the process.

In order to establish the invariant parameters and decide on the kinetic model, we also used the IKP method. Due to the poor regressions obtained using D method, we only used integral data established using the CR method (Table 2). The compensation parameters calculated from the integral data in Table 2 together with the data corresponding to rates of 10 and 5°C min^{-1} (not shown in Table 2) are given in Table 4. It is accepted that the selection of the set of functions for the degree of conversion can affect the compensation parameters [7]. In our case, significant variations in the parameters only depend on whether or not we include the models of type D_n and P_2 in the set of functions. As these models exhibited poor regressions and values of E very different from the isoconversional values in the CR method, they were not included in the set of functions. The remaining functions in Table 2 were used to determine the compensation parameters in Table 4. It is interesting to see that the values of T_{iso} associated with these IKRs are similar to those obtained in the IKRs established when changing the conversion for

Table 3 Compensation effect in relation to conversion (Eq. (9)

Model	Integral data					Differential data			
	a/min^{-1}	b/mol kJ^{-1}	T_{iso}/°C	r^2	Ω/%	a/min^{-1}	b/mol kJ^{-1}	T_{iso}/°C	r^2
$A_{3/2}$	–3.073	0.329	93.0	0.9984	2.9	–2.895	0.329	92.8	0.9977
A_2	–3.177	0.330	91.4	0.9946	2.7	–5.997	0.353	67.5	0.9938
A_3	–3.282	0.332	89.7	0.9845	2.5	–4.403	0.337	83.7	0.9957
A_4	–3.334	0.332	88.9	0.9773	2.4	–4.894	0.339	81.5	0.9952
D_1	–4.549	0.330	92.0	0.9928	5.6	–3.807	0.327	94.7	0.9986
D_2	–4.403	0.331	90.1	0.9948	6.5	1.454	0.331	90.9	0.9983
D_3	–5.234	0.336	85.0	0.9378	6.3	–2.977	0.324	98.2	0.9998
D_4	–5.165	0.331	90.0	0.9101	7.6	–2.331	0.315	108.2	0.9998
R_2	–5.607	0.325	97.6	0.8689	11.0	–2.262	0.305	121.1	0.9993
R_3	–6.322	0.329	92.4	0.8973	11.4	–3.295	0.312	112.6	0.9997
P_2	–3.927	0.335	86.2	0.9860	3.2	–6.020	0.349	71.7	0.9946
F_1	–2.864	0.326	96.3	0.9865	3.2	–3.807	0.327	94.7	0.9986
n=1.5	–1.815	0.319	104.5	0.9689	2.7	–0.126	0.310	114.6	0.9994
n=2	–0.572	0.310	114.9	0.9386	2.1	1.424	0.300	127.7	0.9991
n=3	2.397	0.289	142.6	0.8287	1.8	4.523	0.280	156.7	0.9965
n=0.25, m=0.75	–2.160	0.333	87.8	0.9730	1.3	–4.829	0.348	72.6	0.9939
n=0.75, m=0.25	–3.073	0.331	90.5	0.9980	2.0	–2.727	0.330	91.9	0.9979
n=1.5, m=0.5	–1.338	0.322	100.2	0.9991	0.3	–0.678	0.319	104.6	0.9982
n=1.6, m=0.4	–1.229	0.320	103.0	0.9965	0.7	–0.258	0.315	109.0	0.9986
n=1.9, m=0.1	–0.758	0.313	111.8	0.9600	1.8	1.003	0.304	122.9	0.9992
n=2.1, m=0.9	0.120	0.325	97.6	0.9786	4.4	0.739	0.313	111.2	0.9976
n=2.3, m=0.7	0.568	0.313	111.4	0.9995	1.9	1.580	0.306	120.5	0.9993
n=2.4, m=0.6	0.839	0.309	116.7	0.9997	1.2	2.000	0.302	125.3	0.9998
n=2.9, m=0.1	2.142	0.292	138.6	0.8674	1.6	4.103	0.284	151.1	0.9973

Table 4 The values of the integral compensation parameters for the data from Table 2 and data at heating rates of 10 and 5°C min^{-1}

β/°C min^{-1}	a_v /min^{-1}	b_v /mol kJ^{-1}	T_{iso} /°C	r^2
15	0.334	0.309	116.8	0.9990
10	–0.035	0.311	112.8	0.9991
7.5	–0.258	0.313	110.8	0.9991
5	–0.564	0.316	107.5	0.9994

the model n=2.4 m=0.6 and other similar autocatalytic models (Tables 2 and 4). The invariant parameters established from the data in Table 4 using the supercorrelation of Eq. (11) are E_{inv}=119.7 kJ mol^{-1}, lnA_{inv}=37.27 min^{-1}, r^2=0.9991. These parameters are similar to those obtained using an integral isoconversional method and through the CR method as well as the composite integral method I. This once again allows us to establish unique kinetic parameters for the region of conversions where E does not show any great variation and chose the model n=2.4 m=0.6 to describe this region of the curing.

We have attempted to establish the model using the master curves. Figure 6 shows the theoretical and experimental integral master curves using a constant value of E=120.9 kJ mol^{-1}, established using composite integral method I, and similar to the determined by other procedures. The best fitting between 0.2 and 0.8 conversion is once again performed by the n=2.4 m=0.6 model. The same figure compares the experimental master curve established according to Eq. (15) (Coats–Redfern approximation of the temperature integral) with that established using Eqs (13) and (14) (Senum–Yang approximation of the temperature integral). You can see that visually both approximations give the same result; therefore, the Coats–Redfern approximation is sufficient for determining the kinetic model. Furthermore, it would appear consistent to use this latter approximation since it was used previously to determine the kinetic parameters using other methods (KAS method, CR method and composite integral method I). The use of a more precise approximation of the temperature integral does not provide more information.

Finally, we selected the model using the differential master curves. The increased variation in E established differentially leads us to expect greater difficulties in this determination. Figure 7 shows the theoretical and experimental differential curves established using Eq. (12). The experimental curves are shown for three different E. It can be seen that by using a medium value for E of 120 kJ mol^{-1} the model that works best is still the n=2.4, m=0.6 model, although not over the entire experimental range. Using higher or lower values of E, but within the range of isoconversional data, results in the experimental curve deviating from the theoretical curve for the n=2.4 m=0.6 model, although it retains the same profile. Therefore, this model can be considered to be the best even if E is altered. We would expect that in general this differential method allows us to establish the model easily if E is known, since it makes direct use of the normalized calorimetric signal without the other experimental factors affecting it.

Once the model has been established by one of the processes described, if it is necessary to be more precise regarding the kinetic changes that take place during curing, the pre-exponential factors can be established using the isoconversional data (Table 1). As has been mentioned before all the isoconversional kinetic data (integral and differential) fit onto one single IKR with a T_{iso} within the experimental range of tem-

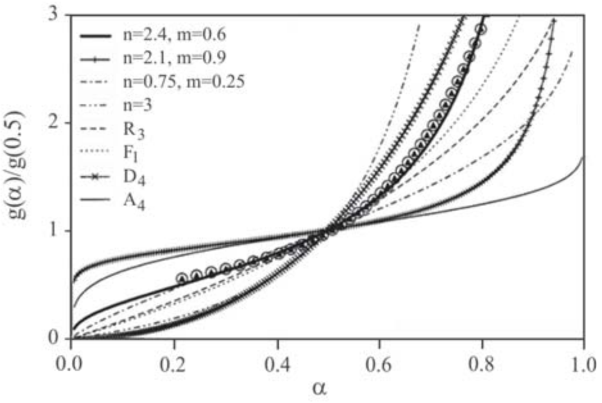

Fig. 6 A comparison of the theoretical integral master plots of $g(\alpha)/g(0.5)$ *vs.* α with the experimental master curve. The empty symbols correspond to experimental data determined using Coats–Redfern approximation (Eq. (15)). The filled symbols correspond to experimental data determined using Senum–Yang approximation (Eqs (13) and (14))

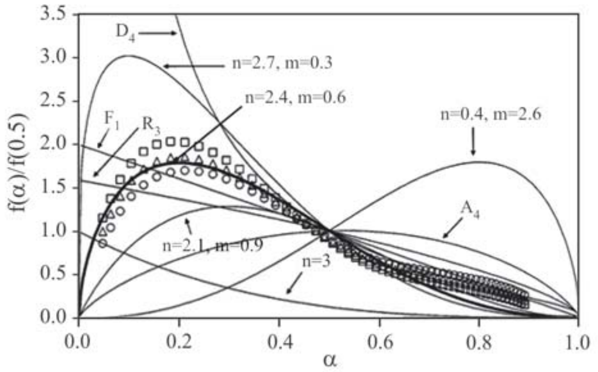

Fig. 7 A comparison of the theoretical differential master plots of $f(\alpha)/f(0.5)$ *vs.* α with the experimental master curve. The symbols correspond to experimental data determined using Eq. (12) with different activation energy values: ○ – 100, △ – 120 and □ – 140 kJ mol^{-1}

peratures. If one does not wish to decide on the kinetic model, however, the isoconversional data can be used to describe the curing, so long as two kinetic parameters, *E* and a second parameter that groups together the conversion function and the pre-exponential factor, are used.

Conclusions

The methodology usually used in the study of heterogeneous solid-state reactions can be used to good effect in order to study the non-isothermal curing of dimethacrylate monomers. Whatever the kinetic procedure used, it is not possible to obtain the complete kinetic triplet from just one calorimetric curve. It is also necessary to know the value of the activation energy so as to be able to determine the kinetic function.

Although differential and integral methods produce equivalent results for the system studied, the latter are more manageable and produce better results. The differences observed are due to the different values of the activation energy in the two procedures, and to the variations of *E* with conversion. It is not clear whether these variations and differences express any real kinetic change or are simply the result of mathematical artefacts. Even if the changes in *E* and *A* are due to kinetic effects, if they are not very large and remain grouped together in just one single IKR it is possible to find a single kinetic model that describes the entire process reasonably well, so long as integral and differential data are not mixed.

Although each of the methods used has its advantages and disadvantages, the results obtained lead us to conclude that using only the composite integral method I allows the complete kinetic triplet to be established and that it can be considered to be the real triplet since it groups together the experimental data for all the conversions and heating rates. For our system, the triplet has the following values: E=120.9 kJ mol^{-1}; ln$A$=38.28 min^{-1} and $f(\alpha)=\alpha^{0.6}$ $(1-\alpha)^{2.4}$. If the kinetic model is not required or the value of *E* varies greatly during the process, the use of an isoconversional method may be sufficient to describe the curing.

In general, non-linear methods based on the master curves produce good results, and their only drawback is that they are heavily dependent on *E*, which has to be established by some other procedure (normally isoconversional).

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