SIMULATION OF ISOTHERMAL CURE OF A POWDER COATING
Non-isothermal DSC experiments

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Abstract

The curing of a thermosetting powder coating was studied by means of differential scanning calorimetry (DSC). The isothermal cure was simulated by non-isothermal experiments. The results of the simulation were compared with experimental isothermal data. From non-isothermal isoconversional procedures (free model), it was concluded that these permit simulation of the isothermal cure but do not enable us to determine the complete kinetic triplet (A preexponential factor, E activation energy, $f(\alpha)$ and/or $g(\alpha)$ function of conversion). Non-isothermal procedures based on a single heating rate or on master curves present difficulties for determination of all the kinetic parameters, due to the compensation effect between preexponential factor and activation energy. The kinetic triplet can be determined by a combination of various non-isothermal methods or by using experimental isothermal data in addition to non-isothermal data.

Keywords: activation energy, compensation effect, isothermal kinetics, non-isothermal kinetics, thermosetting powder coating

Introduction

Maximum properties are obtained for thermosetting coatings through a curing process by temperature or ultraviolet light. Cure temperature is strongly influenced by glass transition temperatures and by fusion of non-reticulate material, and also by viscosity before and during the curing process. Normally, thermosetting powder coatings are cured at temperatures oscillating between 130 and 220°C [1, 2]. These temperatures are an obstacle to monitoring the process by means of isothermal calorimetry. At high temperatures, heat is lost during stabilisation of the apparatus. At low temperatures heat is released slowly but it falls below the apparatus's sensitivity range. Furthermore, in these materials the exothermal heat released during curing is relatively low (around 40 J g^{-1}) [3]. Due to these difficulties, it may prove more useful to study the cure dynamically and then simulate isothermal curing. Another possibility is to monitor the cure indirectly, by dynamic scanning of partially isothermally cured samples. This procedure is effective but costly [4, 5].

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In general, the final objective of non-isothermal studies of reactive processes (curing, degradation, etc.) is to obtain kinetic parameters, which reproduce the isothermal processes. So-called isoconversional procedures are based on the fact that a reaction mechanism, at a given degree of conversion, does not vary with temperature. These methods, both in their integral and differential forms, permit us to obtain two kinetic parameters for each degree of conversion, one being activation energy and the other related to preexponential factor and to the function $f(\alpha)$ or $g(\alpha)$ [6–11]. Isoconversional methods usually reproduce both non-isothermal and isothermal kinetic data correctly but do not permit separation of preexponential factor from function $f(\alpha)$ or $g(\alpha)$. Furthermore, activation energy, may vary with the procedure employed [5, 12–14] and the set of dynamic rates used, and usually depends on the degree of conversion [3, 14–17]. All this is usually attributed to changes taking place during the reactive process and to the so-called compensation effect. This compensation effect may either be real, i.e., the reflection of some kinetic change, or imaginary [18–20]. The difficulty of determining these considerations limits the acceptance of isoconversional methods [21].

Use of a single dynamic experiment to obtain kinetic parameters, usually leads to serious errors because there are many mathematical solutions which reproduce the experimental data [4].

Other methods are based on use of the function $z(\alpha)=f(\alpha)g(\alpha)$ which combines integral and differential data. Through these methods it is possible to predict the function describing the reactive process, but the kinetic triplet can only be determined if the true value of the activation energy is previously known and if it remains constant throughout the reactive process [22, 23].

Finally, there are methods, both non-isothermal and isothermal, which are based on the time-temperature superposition principle. Through these methods it is possible to determine activation energy and generate a master curve for the data obtained by any thermal analysis technique. The time-temperature superposition principle is applicable in systems in which the entire reactive process can be described with a single activation energy and $f(\alpha)$ is only a function of the conversion degree and is independent of the temperature. In this procedure, activation energy is proportional to the shift factor [4, 24, 25].

For this work, non-isothermal cures were carried out, the isothermal cures were simulated by various procedures and the results were compared with those obtained isothermally from partially cured samples.

Experimental

The powder coating studied is a physical blend of a lightly branched carboxyl-terminated polyester and triglycidylisocyanurate (TGIC), with a polyester/TGIC mass proportion of 93/7 (Cray Valley, 4704). The polyester has a functionality of $f=2.3$, an acid number of 33 and an $M_n=3910$, while the TGIC has $f=3$ and $M_n=297$. In general, these coatings were cured at temperatures approaching those of industrial curing, higher than $T_{g\infty}$.

Calorimetric analysis was carried out using a Mettler-Toledo DSC30 calorimeter. The mass of the samples was approximately 10 mg. All of the samples were cured in a nitrogen atmosphere. Dynamic curing was carried out at rates of 2, 3, 4, 6, 7.5, 10, 15 and 20°C min^{-1} from –50 to 250°C. In the dynamic curing processes the degree of conversion, α and the reaction rate, $d\alpha/dt$, were calculated as:

$$\alpha = \frac{\Delta H_T}{\Delta H_{dyn}} \qquad \frac{d\alpha}{dt} = \frac{(dH/dt)_T}{\Delta H_{dyn}} \tag{1}$$

where ΔH_T is the heat released up to a temperature T, obtained by integration of the calorimetric signal up to that temperature, $(dH/dt)_T$ is the rate of heat generation and is the direct calorimetric signal at a temperature T and ΔH_{dyn} is the total reaction heat associated with complete conversion of all reactive groups. A value of 37.5 J g^{-1} was taken for ΔH_{dyn}, calculated as the average value for heat reaction obtained dynamically at the different rates of heating. Isothermal curing was carried out for different times at temperatures of 120, 135, 150, 165 and 180°C. After curing, the sample was cooled and by means of a dynamic scan at 10°C min^{-1} the residual heat was determined.

The isothermal degree of conversion was calculated on the basis of residual heat as:

$$\alpha = 1 - \frac{\Delta H_{t,res}}{\Delta H_{dyn}} \tag{2}$$

where $\Delta H_{t, res}$ is the residual heat obtained after isothermal curing up to a time t.

Theoretical analysis

Accepting that rate of conversion, $d\alpha/dt$, depends on the temperature and the advance of the reaction and that the Arrhenius equation is met, non-isothermal kinetic analysis may start with the kinetic equation:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \tag{3}$$

where A is preexponential factor, E activation energy, R universal gas constant, T temperature and $f(\alpha)$ is a function of degree of conversion which depends on the mechanism governing the reactive process.

By reordering, we can write the so-called temperature integral:

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

where β is the heating rate and $g(\alpha)$ an integral function of the degree of conversion.

Equation (4) may be integrated employing Doyle's approach [26] and rewritten in logarithm form as:

$$\log\beta = \log\left[\frac{AE}{g(\alpha)R}\right] - 2.315 - \frac{0.4567E}{RT} = A_{\alpha,int} - \frac{0.4567E}{RT} \tag{5}$$

This equation applied to constant conversion, enables us to determine E and the kinetic parameter $A_{\alpha,\text{int}}$ (Ozawa method [7]) for each degree of conversion.

By using the Coats–Redfern [9] approximation for resolution of Eq. (4) and considering that $2RT/E \ll 1$ may be written:

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

for a given kinetic model, linear representation of $\ln[g(\alpha)/T^2]$ *vs.* $1/T$ permits us to determine E and A from the slope and the ordinate in the origin.

Reordering Eq. (6) we can write:

$$\ln \frac{\beta}{T^2} = \ln\left[\frac{AR}{g(\alpha)E} \right] - \frac{E}{RT} = A'_{\alpha,\text{int}} - \frac{E}{RT} \qquad (7)$$

Linear representation of $\ln[\beta/T^2]$ *vs.* $1/T$ permits determination of E and the kinetic parameter $A'_{\alpha,\text{int}}$, for each conversion degree. This isoconversional procedure is equivalent to Kissinger's method [27] and comparable to Ozawa's method.

Integration of Eq. (4) in isothermal experiments gives the expression:

$$\ln t = \ln\left[\frac{g(\alpha)}{A} \right] + \frac{E}{RT} = A_{\alpha,\text{iso,int}} + \frac{E}{RT} \qquad (8)$$

where t is cure time. It can be observed how the non-isothermal parameters $A'_{\alpha,\text{int}}$ and $A_{\alpha,\text{int}}$ are directly related to the isothermal parameter $A_{\alpha,\text{iso,int}}$. By using the non-isothermal kinetic data from Eqs (5) and (7) it is possible to determine the isothermal parameters of Eq. (8) and then simulate the isothermal cure.

By combining Eqs (3) and (6) without logarithms and as described by Criado [22], we can obtain reduced master curves of the type:

$$\frac{z(\alpha)}{z(0.5)} = \frac{f(\alpha)g(\alpha)}{f(0.5)g(0.5)} = \left(\frac{T}{T_{0.5}} \right)^2 \frac{(d\alpha/dt)}{(d\alpha/dt)_{0.5}} \qquad (9)$$

where 0.5 refers to the conversion of 0.5.

The left side of Eq. (9), $f(\alpha)g(\alpha)/f(0.5)g(0.5)$, is a reduced theoretical curve which is characteristic of each reaction mechanism, whereas the right side of the equation associated to reduced rate can be obtained from experimental data. Comparison of both sides of Eq. (9) tells us which kinetic model describes an experimental reactive process.

If the true value of the activation energy is known, then the kinetic model can be determined by means of the procedure employed by Criado *et al.* [23], based on the function:

$$z(\alpha) = f(\alpha)g(\alpha) = \frac{d\alpha/dt}{\beta} \pi(x)T \qquad (10)$$

where $x=E/RT$ and $\pi(x)$ is an approximation of the temperature integral which can be expressed in its analytical form. In this we shall use the fourth rational expression of Senum and Yang [28]. Equation $z(\alpha)=f(\alpha)g(\alpha)$ can be used to obtain the master curves as a function of the degree of conversion for different models. By plotting the graph of the right side of Eq. (10) on the basis of the experimental data and comparing the graph with the master curves, it is possible to determine the mechanism governing the process.

We have recently presented a new isoconversional methodology combining the differential and integral methods. From the isoconversional lines obtained from Eq. (5) and Eq. (3) in logarithms, it is possible to obtain the kinetic model which best describes a process, by making all the E and A values, both integral and differential, lie on a single compensation line. Variation of the degree of conversion or the set of heating rates selected, enables us to see that a compensation effect exists. Details of this methodology can be found in [3].

Results and discussion

Figure 1 shows the degree of conversion *vs.* the temperature for coating cure at various heating rates. The degrees of conversion have been obtained by integration of the exothermal calorimetric peak by means of Eq. (1). Some dynamic DSC curves for the coating used can be found in one of our earlier paper [3]. By application of Eqs (5) and (7) to the curves in Fig. 1, the kinetic parameters have been obtained at different degrees of conversion. Table 1 sets out the results obtained for each method and the isothermal parameters which can be derived for these through Eq. (8). Figure 1 also shows the α-T curves simulated by using parameters obtained with Eq. (5) (Table 1). By the quality of the regressions and simulations obtained, it can be concluded that the two isoconversional methods correctly describe the non-isothermal cure. Table 1 shows how the kinetic parameters vary at the start of curing, and then, in conversions above 20%, re-
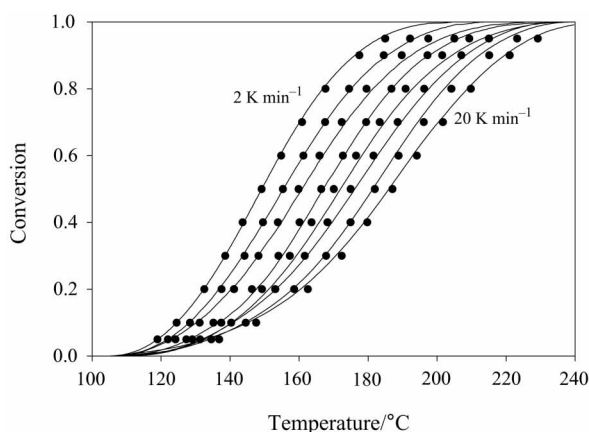

Fig. 1 Experimental and simulated degrees of conversion *vs.* temperature for non-isothermal curing. Heating rates of 2, 3, 4, 6, 7.5, 10, 15 and 20 K min^{-1} are shown. The solid lines represent the experimental data and the symbols correspond to the data calculated by using the parameters obtained with Eq. (5)

main practically constant. Figure 2 compares the experimental isothermal curves, degree of conversion *vs*. time of curing, α-*t*, with the simulated by means of various methodologies. In general, it can be observed how isoconversional simulation, on the basis of the data obtained through Eqs (5) and (7) correctly describes the isothermal cure. However, this procedure does not permit us to determine the mechanism governing the curing process. The small differences observed between both isoconversional methods (Table 1 and Fig. 2) must be attributed to the different solution of the temperature integral.

Table 1 Non-isothermal and isothermal kinetic parameters at different degrees of conversion, obtained using Eqs (5) and (7) at various heating rates

α	Eq. (5)				Eq. (7)			
	$A_{\alpha,\text{int}}/$ K min^{-1}	r	$E/$ kJ mol^{-1}	$A_{\alpha,\text{iso,int}}/$ min	$A'_{\alpha,\text{int}}/$ K^{-1}min^{-1}	r	$E/$ kJ mol^{-1}	$A_{\alpha,\text{iso,int}}/$ min
0.05	23.21	0.958	163.5	−48.88	39.47	0.965	165.3	−49.36
0.10	18.54	0.989	132.0	−38.35	28.66	0.987	132.1	−38.33
0.20	14.80	0.992	107.0	−29.95	20.00	0.991	105.6	−29.45
0.30	13.50	0.995	98.9	−27.03	16.96	0.994	96.9	−26.33
0.40	12.83	0.996	95.0	−25.53	15.38	0.996	92.8	−24.71
0.50	12.43	0.997	93.2	−24.63	14.44	0.997	90.8	−23.74
0.60	12.18	0.997	92.5	−24.06	13.84	0.996	89.9	−23.13
0.70	11.94	0.996	91.9	−23.51	13.25	0.996	89.1	−22.53
0.80	11.75	0.995	91.8	−23.08	12.79	0.995	88.9	−22.07
0.90	11.64	0.992	93.0	−22.81	12.50	0.991	90.0	−21.79
0.95	11.65	0.988	94.6	−22.81	12.48	0.987	91.5	−21.79

$A_{\alpha,\text{iso,int}}$ was calculated by means of Eq. (8) using the kinetic parameters obtained from Eqs (5) and (7)

In order to establish the kinetic model, the Coats–Redfern method (Eq. (6)) was employed. Table 2 summarises the results obtained at a curing rate of 10 K min^{-1} for the different models tested. In general, it can be observed how all the functions present good regressions, with the exception of models F_2, F_3 and power, which are slightly inferior. This would seem to indicate, first of all, that any model serves to describe the curing process if it is combined correctly with *E* and *A*. Figure 3 shows ln*A vs. E* according to the model used. The compensation effect between both parameters can be seen and how all the kinetic data are grouped on a compensation line of the type:

$$\ln A_\xi = aE_\xi + b \tag{11}$$

where ξ represents any factor which produces changes in the Arrhenius parameters. Here, the factor would be the kinetic model. It is clear that the detected compensation effect is imaginary since the models proposed have different forms ($f(\alpha)$ or $g(\alpha)$) and cannot therefore adequately describe the cure even if activation energy and pre-exponential factor are changed. Specifically, $f(\alpha)$ is proportional to the isothermal
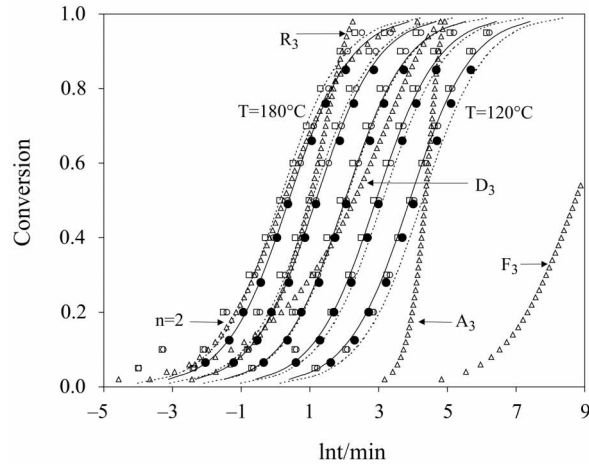
Fig. 2 Experimental and simulated degrees of conversion *vs.* curing times for samples cured at different temperatures. Curing temperatures of 180, 165, 150, 135 and 120°C are shown. — – curves obtained by using function $f(\alpha)=\alpha^m(1-\alpha)^n$ with $n+m=2$ and $n=1.9$ and kinetic parameters contained in Table 2. – – – –curves obtained by using function $f(\alpha)=\alpha^m(1-\alpha)^n$ with $n+m=2$ and $n=1.9$ and compensation equation (Eq. (11)) with $a=0.2972$ and $b=3.2707$. ● – experimental isothermal curves, □ – curves calculated by Eq. (8) with kinetic parameters obtained by Eq. (5), o – curves calculated by Eq. (8) with kinetic parameters obtained by Eq. (7). Triangles represent the simulation at 180°C using different kinetic models (Table 2)
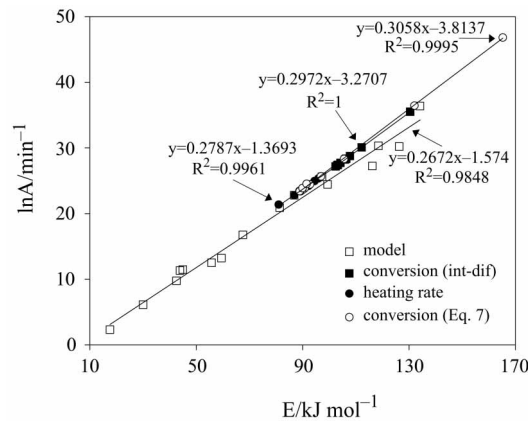

Fig. 3 Compensation curves $\ln A=aE+b$ associated with each factor, indicated in the figure, producing a change in the Arrhenius parameters. □ – kinetic parameters determined at a rate of 10 K min^{-1}, for the different models, using the Coats–Redfern method (Eq. 6), ■ – kinetic parameters determined, for different degrees of conversion, using the integral-differential isoconversional method, ● – kinetic parameters determined, for different heating rates, using the Coats–Redfern method (Eq. 6), o – kinetic parameters determined, for different degrees of conversion, using the isoconversional method of Eq. (7). For (■), (●) and (o), $f(\alpha)=\alpha^m(1-\alpha)^n$ was used with $n+m=2$ and $n=1.9$

rate and $g(\alpha)$ to the isothermal time. In addition, some values of E are very far from those which could be associated with the true value of E for the curing process. Figure 2 plots the graph for the α-t curve obtained from the Table 2 data at a temperature of 180°C for some of the models used. For the system used, it can be seen clearly that only some of the autocatalytic ($f(\alpha)=\alpha^m(1-\alpha)^n$) or n order models ($f(\alpha)=(1-\alpha)^n$) correctly reproduce the isothermal cure. This indicates that in the absence of further experimental data, the Coats–Redfern procedure (Table 2) does not enable us to discern which mechanism governs the reactive process.

Table 2 Algebraic expressions for $f(\alpha)$ and $g(\alpha)$ for the kinetic models used and Arrhenius parameters determinated by Coats–Redfern's method (Eq. (6))

Models	$f(\alpha)$	$g(\alpha)$	E/kJ mol^{-1}	ln$A$/min^{-1}	r
A_2	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$	30.1	6.12	0.999
A_3	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$	17.6	2.31	0.998
R_2	$2(1-\alpha)^{1/2}$	$[1-(1-\alpha)]^{1/2}$	55.7	12.50	0.996
R_3	$3(1-\alpha)^{2/3}$	$[1-(1-\alpha)]^{1/3}$	59.4	13.22	0.997
D_1	$1/2(1-\alpha)^{-1}$	α^2	99.4	24.44	0.991
D_2	$-\ln(1-\alpha)$	$(1-\alpha)\ln(1-\alpha)+\alpha$	118.5	30.31	0.995
D_3	$3/2(1-\alpha)^{2/3}[1-(1-\alpha)]^{-1/3}$	$[1-(1-\alpha)^{1/3}]^2$	126.3	30.22	0.998
D_4	$3/2(1-\alpha)^{1/3}[1-(1-\alpha)]^{-1/3}$	$(1-2/3\alpha)(1-\alpha)^{2/3}$	116.2	27.25	0.996
F_1	$(1-\alpha)$	$-\ln(1-\alpha)$	67.5	16.76	0.999
F_2	$(1-\alpha)^2$	$(1-\alpha)^{-1}$	43.9	11.33	0.971
F_3	$1/2(1-\alpha)^3$	$(1-\alpha)^{-2}$	95.3	26.76	0.975
power	$2\alpha^{1/2}$	$\alpha^{1/2}$	19.3	2.59	0.983
$n+m=2$; $n=1.9$	$\alpha^{0.1}(1-\alpha)^{1.9}$	$[(1-\alpha)\alpha^{-1}]^{-0.9}(0.9)^{-1}$	86.8	22.78	0.999
$n+m=2$; $n=1.5$	$\alpha^{0.5}(1-\alpha)^{1.5}$	$[(1-\alpha)\alpha^{-1}]^{-0.5}(0.5)^{-1}$	44.9	11.46	0.997
$n=1.5$	$(1-\alpha)^{1.5}$	$2[-1+(1-\alpha)^{-1/2}]$	81.4	20.90	1.000
$n=2$	$(1-\alpha)^2$	$-1+(1-\alpha)^{-1}$	97.3	25.60	0.999
$n=3$	$(1-\alpha)^3$	$2^{-1}[-1+(1-\alpha)^{-2}]$	134.1	36.38	0.994

To attempt to determine the exact kinetic model underlying the cure, we used the methods based on master curves proposed by Criado. Figure 4 presents the graph of the reduced master curves according to Eq. (9) for different models and they were compared with those obtained experimentally at different heating rates. It can be observed how the method enables us to discern some mechanisms. In the case of the system studied, the functions in best agreement are types $n+m=2$, $n=1.5$ and $n=2$. Some of these models remain grouped within the same master curve and therefore it would not be possible to differentiate them. Models such as D_3 and R_3 or F_1 and A_2,

which are completely different, are also grouped within a single curve and cannot therefore be discriminated either. This indicates that the methodology employed gives a general indication as to the model but additional kinetic information is required in order to be able to always specify it. If the true value of the activation energy is known, it is always possible to specify the kinetic model. We take the true value of the activation energy as 90 kJ mol^{-1} estimated from the isoconversional data (Eq. (7)) in the range of conversions in which they remain almost constant. Of the models presenting a master curve (Fig. 4) similar to the experimental one, those which have an E, determined by the Coats–Redfern method, which is similar to the true value, are those that describe the reactive process. For the system studied, the function of conversion with $n+m=2$ where $n=1.9$ is the one which best meets these requirements and will be considered as the model describing the cure. Figure 2 shows how this model, using the data obtained through Eq. (6), correctly define the experimental isothermal data. Other models such as $n=2$ which presents a master curve which is equal to that of model $n+m=2$ (where $n=1.9$) and a similar E also provide an acceptable description of the isothermal cure.
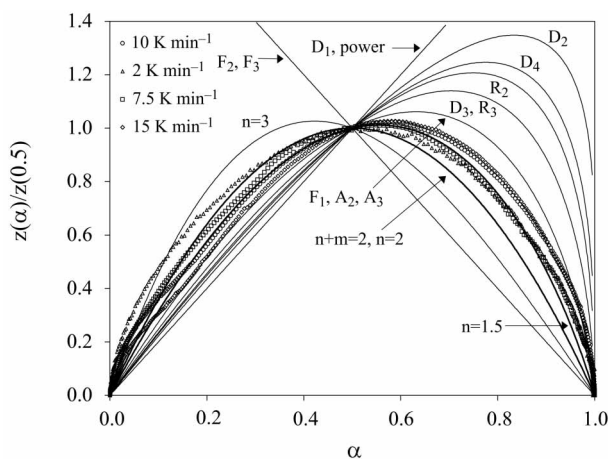

Fig. 4 Reduced master curves of different kinetic models and experimental data at different heating rates calculated by Eq. (9)

With this same approach, if the true value of the activation energy is known, Eq. (10) can be used to establish the kinetic model. Figure 5 shows the graph of the master curves $z(\alpha)$–α for different models and the experimental master curve for a rate of 10 K min^{-1} taking true value of E as 90 kJ mol^{-1}. Again, it is the function $n+m=2$ (where $n=1.9$) that is in best agreement with the experimental data, although similar models such as $n=1.5$ and $n=2$ are also correct. Figure 5 also shows the experimental curve using the activation energy (Table 2) obtained for model A_2 ($E=30.1$ kJ mol^{-1}). This model, as we have seen, is part of a family that does not reproduce the cure (Fig. 2). It can be seen that the experimental data are in fairly good agreement with the master curve for the model whose activation energy is being used (A_2). This occurs when the form of $z(\alpha)$–α does not differ greatly from that of the real
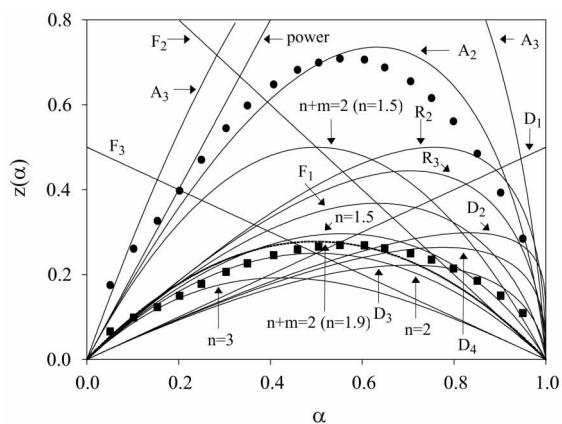
Fig. 5 Master curves $z(\alpha)$–α of different kinetic models and experimental data at
10 K min^{-1} calculated by Eq. (10). ■ – experimental data using E=90 kJ mol^{-1},
● – experimental data using E=30.1 kJ mol^{-1} (model A$_2$)

model. It can therefore be concluded that if the activation energy is not known, it is not possible to define the kinetic model with this methodology.

By means of the integral-differential isoconversional method described in the authors' previous paper [3] it was found that the model which best described the cure was $n+m$=2 (where n=1.9) and E and A were grouped, when α was varied, in a straight compensation line (Eq. (11)) with a=0.2972 and b=3.2707. Using these kinetic data, the isothermal cure was simulated (Fig. 2) and the straight compensation line was represented (Fig. 3). It can be seen how the methodology provides a reasonable description of the isothermal cure but does not define the true value of activation energy but rather a relation between E and A.

For a function of the type $n+m$=2 (where n=1.9) E and A were calculated, at different heating rates, through Eq. (6). Also, E and A were calculated for this same function but based on the isoconversional data obtained from Eq. (7) (Table 1). The results obtained in both cases are set out in Fig. 3. It can be observed how there is a compensation effect between E and A when heating rate and degree of conversion are varied. Figure 4 shows that there are slight variations in the model describing the process with changes in heating rate and degree of conversion. In Fig. 5 it can also be observed how the model which best describes the cure does not do so for its entire length. All these considerations may incline one to think that the reaction mechanism varies slightly with degree of conversion and heating rate and that, therefore, isoconversional methods and methods employing master curves are not entirely accurate. Despite this, since the variations are very slight, the procedures may be considered to be acceptable as a first step. If a more accurate description of activation energy and the kinetic model is required, isothermal data should be employed to eliminate the effect of heating rate and it must be determined whether activation energy and the mechanism depend on the degree of conversion or not.

We know that the separation between isothermal curves is related to the true value of E. Therefore, the necessary shift factor $\ln a_T$ in order to shift an isothermal curve towards a reference temperature T_r, can be obtained from Eq. (8) as:

$$\ln a_T = \ln t_r - \ln t = \frac{E}{R}\left(\frac{1}{T_r} - \frac{1}{T}\right) \tag{12}$$

where t_r is the time necessary to reach the conversion degree at T_r. For our experimental data and taking reference temperature as 150°C, the isothermal curves (Fig. 2) displace almost completely with a single shift factor. The activation energy associated with this shift factor (Eq. (12)) takes a value close to 90 kJ mol^{-1}. This result permits us to conclude that choice of a single model such as $n+m=2$ (where $n=1.9$) for the entire curing process, along with the use of the kinetic data associated with this process (Table 2) is a good procedure for characterisation of the isothermal cure. In addition, choosing the true value of activation energy on the basis of non-isothermal isoconversional data would also seem to be correct.

Conclusions

Use of a single non-isothermal method for simulation of the isothermal cure may lead to errors due to the existence of a compensation effect between the activation energy and the preexponential factor. This effect was detected when varying the curing rate, kinetic model or degree of conversion. The results lead us to believe that these effects are fictitious and do not reflect kinetic changes.

For correct determination of the kinetic triplet, a combination of various non-isothermal methods is required or else combined use of non-isothermal and isothermal data. For example, the true value of activation energy may be obtained on the basis of two isothermal experiments or by means of non-isothermal isoconversional methods.

Once the true value of the activation energy is known, the remainder of the kinetic triplet can be determined unambiguously by means of the Coats–Redfern method or the kinetic model by the procedures based on master curves.

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