

Determination of Activation Energy and Preexponential Factor of Thermoset Reaction Kinetics Using Differential Scanning Calorimetry in Scanning Mode: Influence of Baseline Shape on Different Calculation Methods

JEROME DUPUY, ERIC LEROY, A. MAAZOUZ

Laboratoire des Matériaux Macromoléculaires, UMR CNRS 5627, Institut National des Sciences Appliquées, 20 Avenue A. Einstein, 69621 Villeurbanne Cedex, France

Received 7 July 1999; accepted 25 February 2000

ABSTRACT: Differential scanning calorimetry (DSC) is one of the most used methods for kinetic studies of thermoset cure reactions. The basic assumption made in this technique is the proportionality between the heat generation rate and cure reaction rate. To have access to the heat generation rate that provides information about reaction kinetics, one must know the baseline under the measured curve. Various methods of baseline construction are described and recommended, but most thermoset cure kinetic studies only use a straight line between the exothermal peak start and the end. The influence of changes in the sample's heat capacity is rarely taken into consideration. The use of data obtained with this type of baseline to determine kinetic parameters can lead to significant errors. DSC thermograms in the scanning mode are simulated for two epoxy-amine type systems of known cure kinetic and thermophysical characteristics. Simulated thermograms are analyzed using a straight baseline, and different parameter estimation techniques are applied to the resulting data to characterize the cure reaction. The results are compared with real values. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 2262–2271, 2000

Key words: thermoset; differential scanning calorimetry; kinetics; simulation; parameter estimation

INTRODUCTION

The optimization of thermoset molding processes (reaction transfer molding, reaction injection molding, prepreg cure, etc.) requires reliable simulation methods to predict and control the evolution of temperature and conversion fields in the material during the process and the final values when the part is unmolded.¹ Such methods are generally based on numerical resolution of the

heat equation with a source term that corresponds to the heat produced by the cure reaction^{1–3} and is assumed to be proportional to the rate of reaction:

$$\text{heat source} = \Delta_r H \frac{d\alpha}{dt} \quad \text{with} \quad \frac{d\alpha}{dt} = f(\alpha, T) \quad (1)$$

where f is a kinetic function of temperature T and conversion α , and a certain number of adjustable parameters have to be determined previously. An important problem arises: kinetic studies are generally made on small samples and, although the set of kinetic parameters found seems to describe

Correspondence to: J. Dupuy (jdupuy@insa.insa-lyon.fr).

Journal of Applied Polymer Science, Vol. 78, 2262–2271 (2000)
© 2000 John Wiley & Sons, Inc.

the reaction kinetics well in that case, one can still have problems when trying to simulate the reaction in thick pieces. It has been shown that a small error in the values of kinetic parameters, especially the activation energy,³ can have a huge effect on the accuracy of temperature field prediction.³⁻⁵ Consequently, the previous kinetic parameter determination must be carried out with the best precision possible.

One of the most used techniques for cure kinetic studies of thermoset materials (such as epoxy-amine, cyanate-ester systems, etc.) is differential scanning calorimetry (DSC).⁶ In this particular case it has the advantage of being based on the same assumption as the heat equation, which is the proportionality between the rate of heat generation and the rate of reaction. Different errors may affect the accuracy of the cure kinetic parameter determination based on DSC measurements: use of an inappropriate kinetic model function (an incorrect empirical function⁷ or a simplified mechanistic kinetic model neglecting the presence of secondary reactions, vitrification effects,^{8,9} etc.), intrinsic defaults of the apparatus (time lags,¹⁰ heat leaks, reproducibility of measurements, etc.), and errors in the interpretation of the DSC thermograms (baseline error). It is known that the baseline of a DSC scan experiment for a thermoset is not a straight line,¹¹ but it is a complicated process to obtain its real shape: it can be obtained by heat capacity measurements (as explained below) or direct measurement by temperature modulated DSC.¹² Nevertheless, this recent method is still not commonly used and most of the kinetic studies are made with conventional DSC. Moreover, the type of baseline used is generally a simple straight line drawn from the beginning to the end of the exothermic signal.¹³⁻¹⁵

The present article attempts to evaluate the effect of such an approximation on the accuracy of the kinetic parameters further calculated. In order to focus only on the baseline shape effect, it is necessary to eliminate all other error sources (inaccuracy of the kinetic model, apparatus defaults, etc.).

Even when using a thermoset system of a known simple kinetic model and a very good DSC apparatus, it is impossible to totally eliminate this type of error. The only way to avoid experimental errors is to simulate DSC thermograms for a virtual chemical system of an imposed kinetic model and parameters (suppression of "chemical" error): it would be tested with a "per-

fect" DSC apparatus for which the monitored signal is only a function of the sample characteristics as detailed below.

The resulting thermograms (which can be considered perfect) are analyzed with different methods of kinetic parameter determination, and the values of the parameters found are compared to the true values of the virtual chemical system (used for the thermogram construction). In this way the possible differences between the calculated and true values of these parameters may be exclusively assigned to the DSC thermogram interpretation.

EXPERIMENTAL

When considering DSC experiments, it is important to specify some terms. The *zero line* is the curve measured by the instrument without any sample; it reflects the asymmetry of the instrument. The *baseline* is the curve measured for a sample that does not evolve any heat during the experiment. Thus, the measured signal is only due to the difference in heat capacities between the sample and reference. In a reactive sample, the baseline lies under an exothermal peak and must be interpolated.

In this study two important assumptions are made that correspond to optimal conditions: the zero line remains horizontal over the entire time-temperature range considered, and the temperature response of the apparatus is immediate ("pseudo-steady-state conditions"). In such conditions the signal monitored by the apparatus is only due to the thermoset sample characteristics.

Thermodynamic Aspects

Under constant pressure conditions, the enthalpy H of a thermoset material can be described by the first law of thermodynamics as a function of only two variables of state: temperature T and degree of conversion α . This latter variable describes the system transformation from the unreacted state ($\alpha = 0$) to a complete reaction ($\alpha = 1$):

$$H = f(T, \alpha) \quad (2)$$

The total differential is

$$dH = \left(\frac{\partial H}{\partial T} \right)_{P,\alpha} dT + \left(\frac{\partial H}{\partial \alpha} \right)_{P,T} d\alpha \quad (3)$$

where $(\partial H/\partial T)_{P,\alpha} = C_p(\alpha, T)$ is the molar heat capacity of the thermoset at constant pressure and $(\partial H/\partial \alpha)_{P,T} = -\Delta_r H(T)$ is the isobaric and isothermal enthalpy of the reaction (assuming an exothermic reaction).

Building DSC Thermograms

When performing a DSC experiment in the optimal conditions previously described, the measured signal is due to thermoset sample characteristics only and is given by the following formula:

$$\frac{dH}{dt} = C_p q - \Delta_r H \frac{d\alpha}{dt} \quad (4)$$

in which q is the heating rate. The heat capacity contribution $\{C_p q\}$ in eq. (4) is the underlying baseline. It is referred to as the “true baseline” in the rest of this article, which is in opposition to the straight line that is used later on. The $\{-\Delta_r H(d\alpha/dt)\}$ is the heat source term due to the chemical reaction (assumed exothermic). Therefore, in order to simulate thermograms obtained by DSC, one needs to know the variations of C_p , $\Delta_r H$, and $d\alpha/dt$ during the experiment considered.

For defined time–temperature conditions, discrete values of $(d\alpha/dt)(t, T)$ and $\alpha(t, T)$ can be calculated by a numerical integration of a kinetic model of the thermoset cure reaction. The heat capacity of a thermoset system under cure varies continuously, depending on both the conversion and temperature. As explained before, it cannot be measured by a conventional DSC because of the superposition of the reaction contribution [see eq. (3)]. But the evolution C_p during the cure can be interpolated using the following equation demonstrated by Bailleul et al.¹:

$$C_p(\alpha, T) = C_{p0}(T)(1 - \alpha) + C_{p\infty}(T)\alpha \quad (5)$$

where C_{p0} and $C_{p\infty}$ are the respective heat capacities of the unreacted and totally reacted thermosets. This equation is similar to a simple mixing law but is based on thermodynamic equations.

The variations of C_{p0} and $C_{p\infty}$ as a function of temperature are determined experimentally. The C_{p0} can only be measured at low temperature where no reaction occurs; behavior at higher temperatures must be extrapolated (linear dependence¹). In opposition, the $C_{p\infty}$ can be measured

over the entire temperature range under consideration, the only problem being possible degradation of the material at high temperature. Nevertheless, while Bailleul et al.¹ chose to consider the value of $C_{p\infty}$ measured in the glassy state, we chose here to consider its value in the rubbery state because the simulated reaction takes place exclusively in the rubbery state. So, $C_{p\infty}$ can only be measured at high temperature and has to be extrapolated for low temperatures (linear dependence, too, according to our measurements on different systems).

The variation of the reaction enthalpy, assuming a total reaction during the DSC scan, is only a function of temperature, following Kirchoff's law:

$$\Delta_r H(T_1) = \Delta_r H(T_0) + \int_{T_0}^{T_1} (C_{p\infty}(T) - C_{p0}(T)) dT \quad (6)$$

Finally, to build a thermogram, one only needs a kinetic model and the values of $C_{p0}(T)$, $C_{p\infty}(T)$, and $\Delta_r H(T_0)$ (T_0 is a reference temperature).

Models

For the present study, the cure kinetic models and thermophysical and thermochemical parameters used are representative of those measured in our laboratory or found in the literature for different thermoset systems such as various epoxy-amine systems¹⁶ (heat capacities varying between 1 and 2 J/g/K, heat of reaction between 300 and 500 J/g, activation energy between 60 and 80 kJ/mol, gel times of a few minutes between 100 and 200°C, and no vitrification effect during DSC experiments). The cure reactions are described by a simplified Kamal–Sourour model containing only two adjustable parameters in order to simplify the calculations and interpretations. Although many epoxy-amine systems do not follow such a simple kinetic law (difference of reactivity between primary and secondary amines) exactly, such a model is available for certain ones¹⁷ and is an acceptable approximation for many others, so its choice is sufficiently representative.

In order to illustrate the influence of the catalytic model, two different simple kinetic models were investigated: an autocatalytic one, corresponding to an epoxy-amine system, whose physical and kinetic parameters were identified with an inverse method³; and a noncatalytic one whose

physical and kinetic parameters do not correspond to a specific chemical system but are representative of the usual ones.

The numerical values used for building thermograms are listed below. The kinetic parameter values given here are referred to as true data for the rest of the article in opposition to experimental values that are later determined from simulated thermograms analysis by different methods.

Also, in the following sections the kinetic model is assumed to be n th order (as already explained) and no discussion about the way to determine this order is made ($n = 2$ for the noncatalytic model and $2 + 0.65$ for the autocatalytic one). This study only focuses on the determination of its adjustable parameters k and E in "DSC anisothermal curing": the unreacted sample is placed directly in a DSC oven and submitted to a scan from low to high temperature in order to obtain a complete reaction.^{17,18} This can be carried out at different heating rates.

In the present study all thermograms were simulated with temperatures ranging from 27 to 327°C (300–600 K) at different heating rates. The kinetic model was integrated by a fourth-order Runge–Kutta method with a time step of 5 s and an initial degree of conversion equal to zero at the beginning of the experiment. The temperature of the sample was

$$T = qt + 300 \text{ (K)} \quad (7)$$

where q is the scanning rate and t is the time. The heat capacities (J/g/K) were

$$C_{p0}(T) = 0.9 + 0.0026T$$

$$C_{pz}(T) = 1.8 + 0.0003T$$

$$C_p(x, T) = (1 - x)C_{p0}(T) + xC_{pz}(T) \quad (8)$$

Autocatalytic Systems

The first kinetic model was

$$\frac{d\alpha}{dt} = k \exp\left(\frac{-E}{RT}\right) (\alpha + 0.07)^{0.65} (1 - \alpha)^2 \quad (9)$$

where $k_{\text{true}} = 9.3 \times 10^6 \text{ s}^{-1}$, $E_{\text{true}} = 67.6 \text{ kJ/mol}$, and $R = 8.314 \text{ J/mol/K}$. The reaction heat was

$$\Delta_r H_{\text{true}}(T_0) = 440 \text{ J/g}$$

with $T_0 = 300 \text{ K}$.

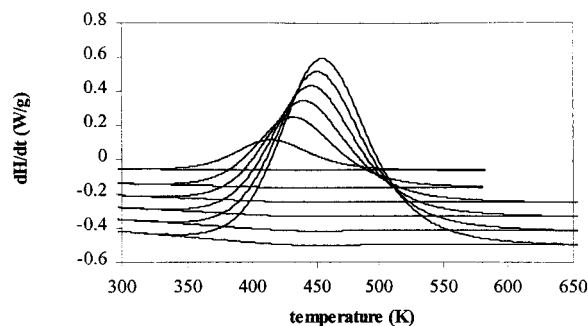


Figure 1 DSC thermograms of the noncatalytic system at scanning rates of 2, 5, 7.5, 10, 12.5, and 15°C/min for the peaks from left to right, respectively, and their true sigmoidal baseline ($C_p(x, T)dT/dt$) as a function of temperature.

The second kinetic model was

$$\frac{d\alpha}{dt} = k \exp\left(\frac{-E}{RT}\right) (1 - \alpha)^2 \quad (10)$$

where $k_{\text{true}} = 10^6 \text{ s}^{-1}$, $E_{\text{true}} = 70 \text{ kJ/mol}$, and $R = 8.314 \text{ J/mol/K}$. The reaction heat was

$$\Delta_r H_{\text{true}}(T_0) = 400 \text{ J/g}$$

with $T_0 = 300 \text{ K}$.

Thus, the DSC thermogram can be calculated in three steps:

1. For a given scan rate q , the time–temperature profile is calculated between 300 and 600 K [eq. (7)].
2. The reaction rates and conversions are calculated (as a function of the time–temperature profile previously calculated) using eq. (9 and 10) and a Runge–Kutta integration method.
3. The DSC signal is then calculated using eqs. (4)–(6) and the previous values of α and $d\alpha/dt$.

RESULTS AND DISCUSSION

Figure 1 shows simulated thermograms (obtained with the non catalytic model) as a function of temperature for six heating rates ranging from 2 to 15°/min, which correspond to the usual values found in the literature. (The curves corresponding to the autocatalytic model are not represented because they are very similar.) Figure 2 repre-

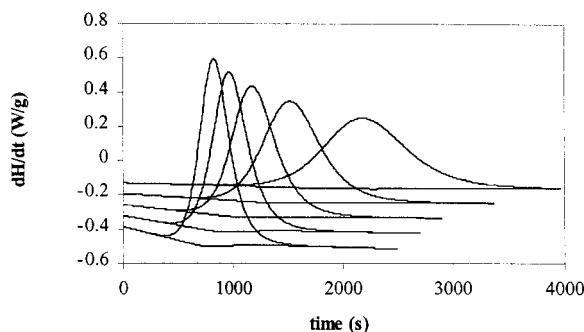


Figure 2 DSC thermograms of the noncatalytic system at scanning rates of 15, 12.5, 10, 7.5, and 5°C/min for the peaks from left to right, respectively, and their true sigmoidal baseline ($C_p(x, T)dT/dt$) as a function of time.

sents the same thermograms as a function of time, except for the thermogram at 2°C/min that is out of scale. In the rest of the article the scanning DSC experiments are represented as a function of time; the previous figures allow the reader to calculate the corresponding temperatures if necessary. Even if the experiment at 2°C/min is not always represented in the figures because of a problem of scale, it was always taken into account in all calculations.

The “real baselines” are also plotted in Figures 1 and 2. As already explained, although it is known that such a baseline is a sigmoid,¹¹ most of the reaction kinetic studies in the literature use a simple straight line between the beginning and

end of the reaction points. It can be chosen arbitrarily or by defining the beginning of the reaction as the moment where the signal derivative begins to rise and the end as the moment when it approaches zero for the second time (the first time being the maximum of the thermogram).

Although the enthalpy of the reaction varies with the temperature, in most studies found in the literature^{17,18} this value is considered as a constant equal to the integral of the DSC exothermal peak. In the present case, for a temperature ranging from 300 to 600 K, the $\Delta_r H(T)$ varies from 360 to 410 J/g for the noncatalytic system and from 420 to 460 J/g for the autocatalytic one, which is not negligible.

To measure the effect of the variation of C_p (on the baseline and enthalpy of reaction values), exothermal peaks of simulated thermograms were integrated with a straight baseline: the corresponding area was noted as $\Delta H_{\text{DSCscan}}$. The resulting values listed in Table I show that the $\Delta H_{\text{DSCscan}}$ is roughly constant ($\Delta H_{\text{DSCscan}} \approx 364 \pm 5$ and 419 ± 8 J/g for the autocatalytic and noncatalytic systems, respectively): it can be considered as independent of the heating rate in agreement with the assumption made on $\Delta_r H$ being constant in the entire temperature range. But it is obvious that the heat of reaction slightly decreases when increasing the scanning rate, which is consistent with reported observations made on different chemical systems.^{19,20} In fact, because of the shape of the thermogram, it is

Table I Heat Evolved during DSC Scans Calculated with Straight Baseline ($\Delta H_{\text{DSCscan}}$) and True Baseline (Q) and Comparison with Isothermal Heat of Reaction [$\Delta_r H(T_{\text{max}})$] Calculated at Maximum Temperature (T_{max}) of DSC Peak

	Scan Rate (°C/min)					
	2	5	7.5	10	12.5	15
Autocatalytic system						
$\Delta H_{\text{DSCscan}}$ (J/g)	427	425	422	417	414	411
T_{max} (K)	360	380	396	409	411	415
$\Delta_r H(T_{\text{max}})$ (J/g)	451	453	454	454	454	454
Q (J/g)	450	448	446	444	441	439
Noncatalytic system						
$\Delta H_{\text{DSCscan}}$ (J/g)	368	368	368	366	362	359
T_{max} (K)	414	432	440	446	451	455
$\Delta_r H(T_{\text{max}})$ (J/g)	409	408	407	406	405	405
Q (J/g)	405	401	399	396	394	392

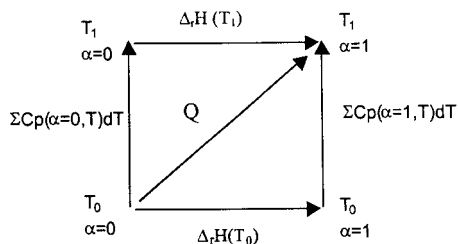


Figure 3 The physical meaning of the heat Q evolved during a DSC scan.

obvious that most of the heat is evolved around the maximum T_{\max} , which does not vary too much for scanning rates between 2 and 15°C/min (see Table I); this explains the fact that the heat evolved during the reaction $Q \approx \Delta_r H(T_{\max})$ is a constant with $Q = \int_0^1 \Delta_r H(\alpha, T) d\alpha$. However, it may be pointed out that the value of $\Delta H_{\text{DSCscan}}$ is not equal to Q . (The physical meaning of Q is illustrated in Fig. 3.). In this case, the choice of a correct baseline affects the value of the calculated heat of reaction by about 10%. It is also clear that the so-called “enthalpy of reaction” measured during a DSC scan $\Delta H_{\text{DSCscan}}$ corresponds neither to the real (isothermal) enthalpy of reaction nor to the heat evolved during the DSC scan.

Moreover, the choice of a straight baseline can also affect the values of the reaction rate and the degree of conversion that is generally calculated by partial integration¹⁸ as follows:

$$\frac{d\alpha}{dt}(t, T)_{\text{exp}} = \frac{1}{\Delta H_{\text{DSCscan}}} \left(\frac{dH}{dt}(t, T) - BL(t, T) \right) \quad (11)$$

$$\alpha_{\text{exp}}(t, T) = \frac{\int_0^t dH(t, T)}{\Delta H_{\text{DSCscan}}}$$

where $BL(t, T)$ is the baseline value, $(dH/dt)(t, T)$ is the DSC signal at time t and temperature T , and $dH(t, T)$ is the partial area between $t - dt$ and t that is calculated by the trapezoidal method.

As can be seen in Figures 4 and 5 for the noncatalytic system, the discrepancy between the calculated values and true ones (obtained with the kinetic model) is not negligible, but it is always less than 10%. The effect is equivalent for the autocatalytic system (not represented). Could these relatively small mismatches have a significant influence on kinetic parameter determina-

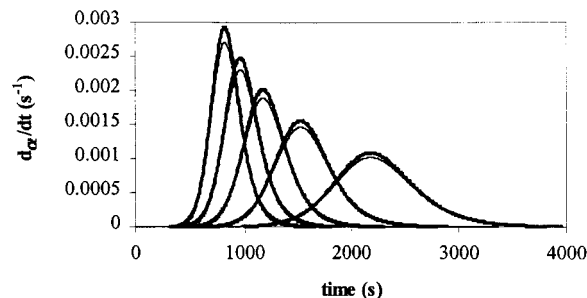


Figure 4 The reaction rate of the noncatalytic system as a function of time at scanning rates of 15, 12.5, 10, 7.5, and 5°C/min from left to right, respectively. The thin lines represent the true values (from the kinetic model), and the thick lines represent the calculated values with a straight baseline.

tion? In order to answer to this question, four different methods of kinetic parameter identification were tested on both systems.

For such a simple kinetic model (with only one activation energy), the easiest way to determine E is Kissinger’s method²¹ that consists of measuring the maximum temperature T_{\max} and then drawing $\ln[\text{DSCscanning rate}/T_{\max}^2]$ against $1/T$. The results are illustrated in Figure 6 for the noncatalytic system and lead to an activation energy value of 70.5 kJ/mol, which is very close to the true value of 70 kJ/mol. For the autocatalytic system, the calculated activation energy value is 68 kJ/mol, in spite of 67.6 kJ/mol for the true value. These results are not surprising because in this method the determination of E only depends on the measurement of T_m , which is not very sensitive to the baseline shape.

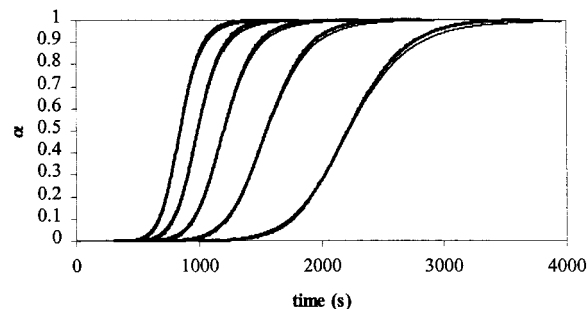


Figure 5 The conversion of the noncatalytic system as a function of time at scanning rates of 15, 12.5, 10, 7.5, and 5°C/min from left to right, respectively. The thin lines represent the true values (from the kinetic model), and the thick lines represent the calculated values with a straight baseline.

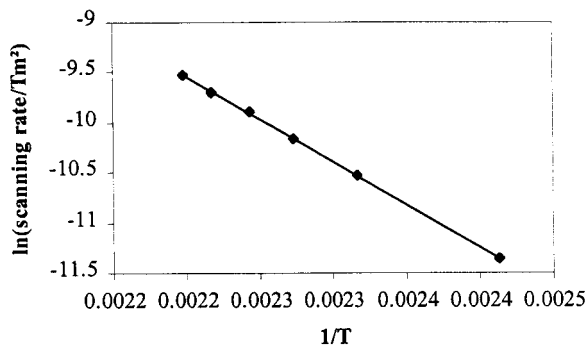


Figure 6 The determination of the activation energy by the Kissinger method for the noncatalytic system.

Another way to determine k and E is the classic Barrett method,¹⁷ which consists of the following plot:

$$\ln\left(\frac{\frac{d\alpha}{dt}}{(1-\alpha)^2}\right) \text{ vs } \frac{1}{T} \quad (12)$$

One must have a unique straight line whatever the heating rate is. Figure 7 shows that this assumption is roughly verified for the noncatalytic system for a temperature range between 110 and 200°C ($0.0021 < 1/T < 0.0026$), that is to say in the usual range of temperature reaction. Divergence of all the curves at the beginning and end of reaction can be explained by the fact that $d\alpha/dt$ tends to zero at these points, so that the logarithm function diverges. Consequently, these extremities of the curves are neglected for linear regression and only the points measured between 110 and 200°C are taken into account.

The plot of

$$\ln\left(\frac{\frac{d\alpha}{dt}}{(\alpha + 0.07)^{0.65}(1-\alpha)^2}\right) = f\left(\frac{1}{T}\right)$$

for the autocatalytic system (not represented) gave similar curves.

Table II gives the results of the linear regression for both systems. Although activation energies found by this method are fairly constant within the experimental error whatever the scanning rate is ($E_{\text{exp}} = 76 \pm 1$ or 75.5 ± 2 kJ/mol for the autocatalytic and noncatalytic systems, respectively), these mean values are different from the true ones ($E_{\text{true}} = 67.6$ and 70 kJ/mol, respectively).

We found evidence that using a straight baseline has an important effect on the activation energy values one determines. This effect is even more important on k values showing a larger dispersion and total inaccuracy (k_{exp} ranging between 1 and $2.5 \times 10^8 \text{ s}^{-1}$ instead of $9.3 \times 10^6 \text{ s}^{-1}$ or between 3 and $10 \times 10^6 \text{ s}^{-1}$ instead of 10^6 s^{-1} for the autocatalytic and noncatalytic systems, respectively). In fact, as k is calculated as the exponential of the intercept, which is an extrapolation to zero of values measured between 0.0021 and 0.0026, a very small variation of the E_{exp} value has an irremediable effect on the k calculation.

This points to one limitation of this type of Arrhenius plot: the activation energy is determined with a reasonably weak dispersion (± 2 kJ/mol), which can be interpreted as a validation of the kinetic parameter, while the result is wrong.

A more sophisticated way to determine activation energy parameters is the isoconversional method²² introduced by Montserrat and Malek. Like the two preceding methods, it can be used for a kinetic model in the following form:

$$\frac{d\alpha}{dt} = f(\alpha)g(T)$$

where f is a function of α only and g is a function of T only. Our models agree with this assumption.

For a given conversion α_i , the corresponding values of $(d\alpha/dt)_{ij}$ and T_{ij} can be measured for each scanning rate $(dT/dt)_j$. So, for each conver-

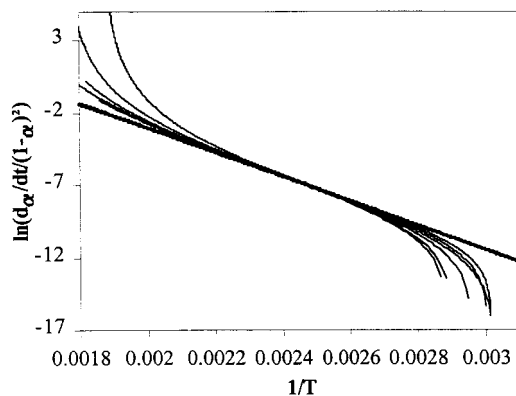


Figure 7 The $\ln[(d\alpha/dt)/(1-\alpha)^2]$ for the noncatalytic system as a function of the inverse of the absolute temperature calculated for scanning rates of 2, 5, 7.5, 10, 12.5, and 15°C/min. The thick line represents the true values calculated with the kinetic model.

Table II Values of E and k Calculated by Linear Regression for Different Scanning Rates Using Baret's Method

	Scan Rate (°C/min)						True Value
	2	5	7.5	10	12.5	15	
Autocatalytic system							
E (kJ/mol)	76.7	77.7	75.7	75.7	75.4	75.7	67.6
$k \times 10^{-6}$ (s $^{-1}$)	206	251	126	126	108	115	9.3
Noncatalytic system							
E (kJ/mol)	77.5	75.6	74.0	73.7	74.0	74.2	70
$k \times 10^{-6}$ (s $^{-1}$)	9.8	5.8	3.3	3.0	3.2	3.4	1

sion degree α_i , the values of $\ln(d\alpha/dt)_{ij}$ can be plotted against $1/T_{ij}$. For the two kinetic models this gives

$$\ln\left(\frac{d\alpha}{dt}\right)_{ij} = \ln k + \ln(f(\alpha_i)) - \frac{E_{\alpha_i}}{RT_{ij}} \quad (13)$$

The interest of such a method is twofold: one does not have to make any assumptions on function $f(\alpha)$ and afterward the variations of the apparent activation energy E_{α} with conversion can provide information on the reaction mechanism.²³

In our case the activation energy is supposed to be constant, so the resulting plots must be straight lines with a constant slope over all the conversion range.

The results obtained [calculated with eq. (11) and a straight baseline] for different α_i values are illustrated in Figure 8 for the noncatalytic system (nonrepresented equivalent plot for the autocatalytic system). It can be seen that the dispersion of

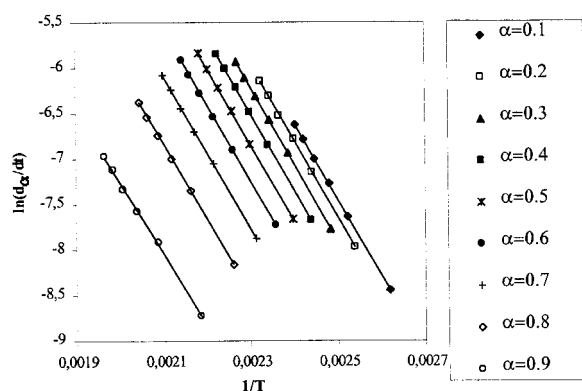


Figure 8 The determination of the activation energy by the isoconversional method for scanning rates of 2, 5, 7.5, 10, 12.5, and 15°C/min for different α values in the noncatalytic system.

experimental points around the regression straight lines is relatively small. So we suppose we can determine the activation energy with good accuracy. Figures 9 and 10 show that the measured E values are relatively close to the true ones. However, whatever the system E regularly varies with conversion: the conclusion of such a study would be that the activation energy is not unique, showing that the proposed kinetic model is not true.

In fact, this shows that when using this isoconversional method, the choice of the baseline is crucial and may drastically change the conclusions of the study.

The last method tested here for anisothermal DSC is a numerical method consisting of finding k and E by minimizing the least squares (LS) criterion between measured values (obtained by DSC) and calculated ones (obtained by integrating the kinetic model for the same time–temperature profile).¹⁸ This method can be applied to the conversion values or to the rate of conversion values for the autocatalytic (see Figs. 11, 12) and noncatalytic (not represented) systems. The LS criterion was minimized on the rate of conversion

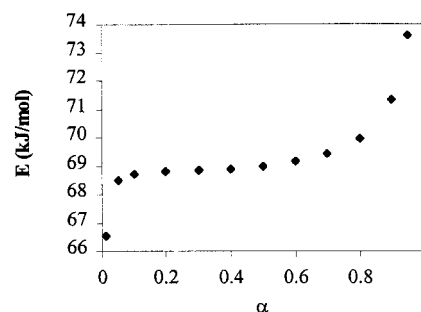


Figure 9 The activation energy of the autocatalytic system determined by the isoconversional method as a function of α .

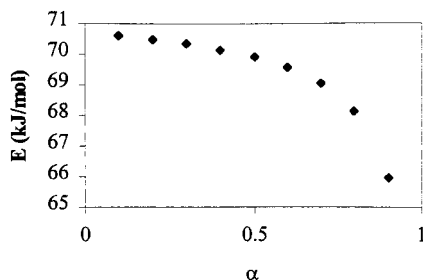


Figure 10 The activation energy of the noncatalytic system determined by the isoconversional method as a function of α .

using Microsoft Excel Solver. The choice of *a priori* values for k and E (in the range of values found in literature: $50 < E < 100$ kJ/mol and $10^5 < k < 10^9$ s⁻¹) did not seem to have a significant influence on the final optimized values that are shown below:

- $k = 1.0 \times 10^8$ s⁻¹ and $E = 75.0$ kJ/mol is totally different from the true ones for the autocatalytic system.
- $k = 1.0 \times 10^6$ s⁻¹ and $E = 70.0$ kJ/mol is exactly equal to the true ones for the noncatalytic system.

The last results illustrate the strong correlation between parameters²⁴ k and E , which makes their simultaneous identification by the LS method very hazardous.

CONCLUSION

This article attempted to show the influence of common assumptions made when using DSC to

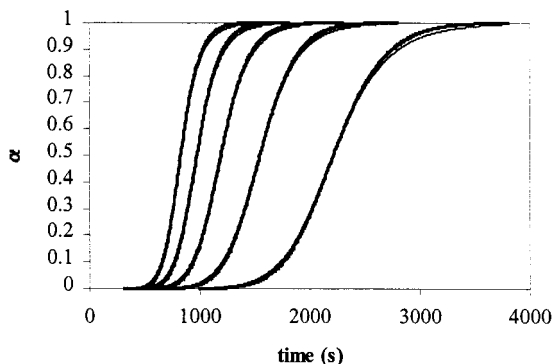


Figure 11 A comparison of the conversion values of the noncatalytic system obtained from DSC measurements (thin lines) and calculated values (thick lines) at scanning rates of 5, 7.5, 10, 12.5, and 15°C/min from right to left, respectively.

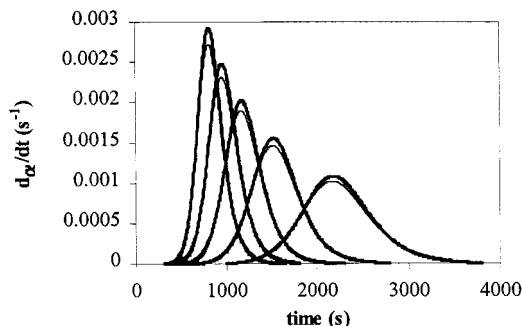


Figure 12 A comparison of the rate of conversion values of the noncatalytic system obtained from DSC measurements (thin lines) and calculated values (thick lines) at scanning rates of 5, 7.5, 10, 12.5, and 15°C/min from right to left, respectively.

calculate kinetic parameter values of thermoset systems. The baseline is supposed to be a straight line and the heat of reaction can be measured by DSC scanning (commonly at 10°C/min).

The process of anisothermal DSC data using these assumptions leads to more or less accurate values of the activation energy, depending on the parameter estimation technique used. Kissinger's method enables values to be obtained with a remarkable accuracy, but the classical Barrett's method and the LS fit can lead to clearly inaccurate values of activation energy E and preexponential factor k . The isoconversional method was also tested; it gives a relatively good estimation of the activation energy but leads to the conclusion that E varies with conversion, which is unacceptable.

These results can explain the fact that many authors⁶ observed that, for a given chemical system, the kinetic parameters obtained with anisothermal DSC are different from those obtained with isothermal DSC (or mixed mode).

It was also pointed out that anisothermal DSC does not enable an enthalpy of reaction, which is a function of the temperature to be measured, but leads to values inferior by about 10% in this case to the mean value of $\Delta_r H$ in the temperature range considered. This last observation may explain the differences in the values of the heat of reaction observed in the literature²⁵ for the same reactive system, depending on the method used: DSC in scanning mode, isothermal mode, or mixed mode (consisting of an isothermal cure followed by an anisothermal measurement of residual heat).

One has to keep in mind, however, that these results may depend on the kinetic function and

parameters used and even more on the variation law of C_p with temperature and conversion. For some other thermoset systems, the differences between experimental and true values would be smaller (e.g., in a small variation of C_p), while for another material it would be exacerbated.

NOMENCLATURE

H	enthalpy (J/g)
T	temperature (K)
α	degree of conversion
$d\alpha/dt$	rate of conversion (s^{-1})
C_p	heat capacity (J/g/K)
C_{p0}	C_p of the unreacted thermoset resin (J/g/K)
$C_{p\infty}$	C_p of totally reacted thermoset material in rubbery state (J/g/K)
$\Delta_r H$	enthalpy of reaction (absolute value, J/g)
$\Delta_r H(T_0)$	value of $\Delta_r H$ at reference temperature T_0 (J/g)
$\Delta_r H_R$	residual enthalpy of the reaction (after an isothermal cure, J/g)
$\Delta H_{DSCscan}$	heat measured during DSC in scanning mode with a straight baseline (J/g)
E	activation energy of the second-order reaction kinetic model (J/mol)
k	preexponential factor of the second-order reaction kinetic model (s^{-1})
$q = dT/dt$	heating rate ($^{\circ}C/s = K/s$)
$\Delta_r H_{true}, \Delta_r H_{Rtrue}, k_{true}, E_{true}$	true values of $\Delta_r H, \Delta_r H_R, k, E$, respectively
$\Delta_r H_{exp}, \Delta_r H_{Rexp}, k_{exp}, E_{exp}$	experimental values of $\Delta_r H, \Delta_r H_R, k, E$, respectively

REFERENCES

- Bailleul, J.-L.; Delaunay, D.; Jarny, Y. *J Reinforced Plast Compos* 1996, 15, 479.
- Reboredo, H. M.; Vazquez, A. *Polym Eng Sci* 1995, 35, 1521.
- Bournez, E.; Raynaud, M.; Dupuy, J.; Nicolle, P. *Therm Conduct* 1998, 24, 695.
- El Brouzi, A.; Bouzon, J.; Vergnaud, J. M. *Plast Rubber Process Applic* 1989, 12, 71.
- Yousefi, A.; Lafleur, P. G.; Gauvin, R. *Polym Eng Sci* 1997, 35, 757.
- Yousefi, A.; Lafleur, P. G.; Gauvin, R. *Polym Compos* 1997, 18, 157.
- Koga, N.; Sestak, J.; Malek, J. *Thermochim Acta* 1991, 188, 333.
- Simon, S. L.; Gilham, J. K. *J Appl Polym Sci* 1993, 47, 461.
- Riccardi, C. C.; Williams, R. J. J. *J Appl Polym Sci* 1986, 32, 3445.
- Isayev, A. I.; Wan, M. *Rubber Chem Technol* 1996, 69, 277.
- Hemminger, W. F.; Sarge, S. M. *J Therm Anal* 1991, 37, 1455.
- Van Assche, G.; Van Hemelrijck, A.; Rahier, H.; Van Mele, B. *Thermochim Acta* 1996, 286, 209.
- Opalicki, M.; Kenny, J. M.; Nicolais, L. *J Appl Polym Sci* 1996, 61, 1025.
- Gonzales-Romero, V. M.; Casillas, N. *Polym Eng Sci* 1989, 29, 295.
- Spoelstra, A. B.; Peters, G. W. M.; Meijer, H. E. H. *Polym Eng Sci* 1996, 36, 2153.
- Grillet, A. C.; Galy, J.; Pascault, J. P.; Bardin, I. *Polymer* 1989, 30, 2094.
- Riccardi, C. C.; Adabbo, H. E.; Williams, R. J. J. *J Appl Polym Sci* 1984, 29, 2481.
- Hédreul, C.; Galy, J.; Dupuy, J.; Delmotte, M.; More, C. *J Appl Polym Sci* 1998, 68, 543.
- Ng, H.; Manas-Zloczower, I. *Polym Eng Sci* 1989, 29, 302.
- Galy, J.; Sabra, A.; Pascault, J. P. *Polym Eng Sci* 1986, 26, 1514.
- Kissinger, H. E. *Anal Chem* 1957, 29, 1702.
- Monserrat, S.; Malek, J. *Thermochim Acta* 1993, 228, 47.
- Vyazovkin, S.; Sbirrazzuoli, N. *Macromolecules* 1996, 29, 1867.
- Militky, J.; Malek, J.; Sestak, J. *J Therm Anal* 1989, 35, 1837.
- Snow, A. W. In *Chemistry and Technology of Cyanate Ester Resins*; Hamerton, I., Ed.; Blackie Academic and Professional: London, 1994; p 7.