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The Málek method in the kinetic study of polymerization by differential scanning calorimetry

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Abstract

A comparative kinetic study of polymerization by differential scanning calorimetry (DSC) has been carried out by use of calculations based on the Freeman–Carroll, Ellerstein, Achar–Brindley–Sharp, multiple linear regression and Málek methods. With the Šesták–Berggren model of a modified Málek method, we have extracted kinetic information from curves showing a presence of more than one component using criteria based on the minimization of the difference between experimental and calculated thermograms.

Keywords: DSC; Kinetics; Málek; Model; Polymerization

1. Introduction

In a previous paper, the influence of a thermal gradient on the apparent values of kinetic parameters of exothermic cure using differential scanning calorimetry (DSC) was discussed [1]. For this, measurements of the sample temperature were made and the kinetic parameters were obtained by the Achar–Brindley–Sharp method [2] using the homogeneous kinetic law and the peak maximum evolution methods (Kissinger, Ozawa and Lam). From the methods considered, it has been

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established [1] that the best fit of the experimental data was obtained using the homogeneous kinetic law for the kinetic interval studied (10–90%). The fair agreement of the general Šesták–Berggren [3] method with that of Achar–Brindley–Sharp led us to retain the homogeneous kinetic law. Meanwhile, the iterations on m and n (p was set to zero) were performed with a precision of 10^{-2} only, as this method had the disadvantage of quickly becoming very time consuming.

With the aim of extracting meaningful kinetic information from DSC profiles, we present in this paper a more extensive treatment of the polymerization in order to check other kinetic methods. The surprising application of the Málek method [4] and its modification [5] is investigated by means of criteria based on the minimization of the difference between experimental and calculated thermograms.

2. Experimental

2.1. Materials and preparation of samples

The polymerization process used in this study was described in previous work [1]. The epoxy resin and curing agent were supplied by Ciba-Geigy. The mixture was obtained by adding 27.5 wt% of the hardener HY 5052 (a mixture of isophoronediamine and diaminodimethyldicyclohexylmethane) to 72.5 wt% of Araldite LY 5052 (a mixture of butane-1,4-diol diglycidyl ether and an epoxidized novolac resin). To slow down the reaction in the early stage of mixing, we mixed the two components after having stored them at a subambient temperature of $\approx 3°C$. In preparing a set, each sample was obtained from the same mixture and cooled for the same time before analysis. Samples (≈ 160 mg) were hermetically sealed in aluminium cells.

2.2. Modelling mode

To allow comparisons between numerous mathematical treatments, the computations were performed with the kinetic software described previously [5]. This software enables kinetic analysis under non-isothermal or isothermal conditions from DSC or thermogravimetric data. The program offers thirteen methods of kinetic analysis for DSC, with eight different functions (homogeneous law, Johnson–Mehl–Avrami, power law, diffusion) for selection of the appropriate mechanism. The multiple linear regression method [6,7] was added to this software.

2.3. Differential scanning calorimetry

Measurements were performed in the scanning mode on a DSC 111 instrument (Setaram) with a heating rate of 5°C min^{-1}. For the different sets of experimental samples studied, the reproducibility of the results was ≈ 8–10%. The activation energy value of the Kissinger method was determined using three different heating rates (1, 2 and 5°C min^{-1}) [1].

3. Results

The accuracy of modelling was evaluated with a parameter called LSM [1,4,5], the difference between the experimental and the calculated thermograms, defined as

$$\mathrm{LSM} = \frac{1}{N}\sum_i (Y_{i,\mathrm{exp}} - Y_{i,\mathrm{calc}})^2$$

where N is the number of experimental values and Y represents the heat flow measured (exp) or calculated (calc) from the kinetic parameters. The idea is that the method which will be selected as the most suitable is that which gives the lowest LSM and therefore the best fit between the calculated and experimental data.

In addition to the methods previously described [5], we have also used the multiple linear regression method [6,7]. The logarithmic form of the reaction rate equation is expressed (for the kinetic homogeneous law) as $\ln(\mathrm{d}\alpha_i/\mathrm{d}t) = \ln k_0 - E_a/RT_i + n\ln(1-\alpha_i)$, where α is the degree of conversion, k_0 is the pre-exponential factor, E_a is the activation energy, R is the universal gas constant, T is the absolute temperature and n is the reaction order. This equation is solved using multiple regression analysis.

First, the kinetic parameters were calculated over a range of 10–90% conversion ($0.1 < \alpha < 0.9$) as in our previous work [1]. Table 1 allows comparisons between the multiple linear regression and the Achar–Brindley–Sharp methods [2]. These methods do not lead to such good agreement between experimental and computed data as we have generally observed (LSM value > 1).

The method given by Málek [4] is the only one to propose a way of selecting the proper $f(\alpha)$ function to describe the kinetic mechanism from among three different models: the Johnson–Mehl–Avrami model, the reaction order model (that is to say, the reaction can be fitted by the kinetic homogeneous law) and the general Šesták–Berggren model, limited by Málek to the use of only two kinetic exponents. This method, based on the standardized curve shape $y(\alpha)$ and on the degree of conversion at the top of the peak (here 43.82%), requires the use of the activation energy, previously calculated by the Kissinger method as 60.23 kJ mol^{-1} [1]. Málek had shown that $y(\alpha)$ depends on the mechanism involved and expresses the $f(\alpha)$ shape. From the $y(\alpha)$ shape of the polymerization ($\alpha_{\max} = 10.39\%$), we might decide in the kinetic interval chosen (10–90%) on a reaction order model, i.e. $f(\alpha) = (1-\alpha)^n$, because the curve is strictly decreasing whereas, considering the whole

Table 1
Kinetic parameters using the Achar–Brindley–Sharp (ABS) and multiple linear regression (MLR) methods in the 10–90% interval

	n	$\ln k_0$	E_a	r	LSM
ABS	2.18	20.02	77.80	−0.99943	7.51
MLR	2.13	19.38	75.92		8.31

Key: n, kinetic exponent; k_0, pre-exponential factor (s^{-1}); E_a, activation energy (kJ mol^{-1}); r, correlation coefficient; LSM, fit of the experimental curve with the calculated one.

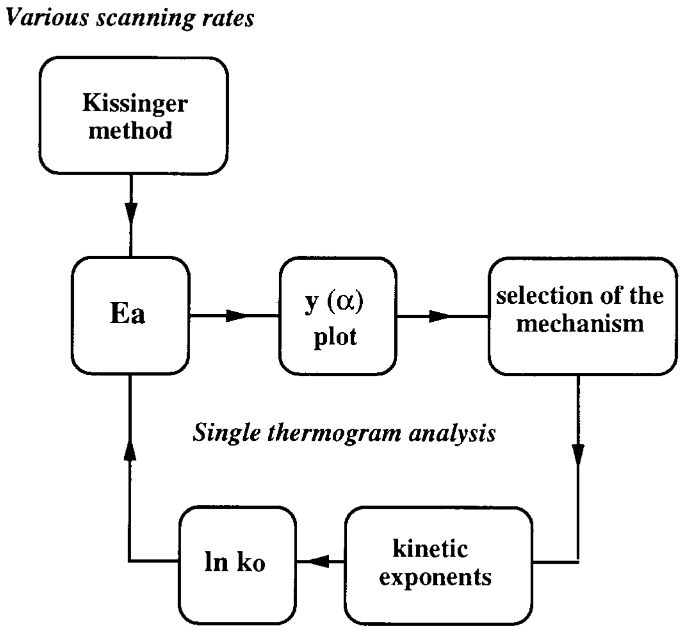

Fig. 1. Modification of the Málek method.

thermogram, the method would point to a more general model, that of Šesták–Berggren involving a more complex $f(\alpha)$ function. This function describes the kinetic mechanism with two exponents: the kinetic exponents m and n, where $f(\alpha) = \alpha^m(1-\alpha)^n$. The reaction order model led to poor modelling with an LSM value of 442.547 (!), whereas better agreement was obtained (LSM value = 17.554) with the more general model of Šesták–Berggren.

As we proposed in the description of the software equations [5], we have modified the Málek method by introducing a succession of calculation iterations (Fig. 1). The activation energy is computed by means of the Kissinger method and the plot of the $y(\alpha)$ function allows the selection of the kinetic mechanism, as proposed by Málek [4]. The kinetic exponents and ln k_0 may then be found. The kinetic parameters are computed again from this scheme in the form of an iterative calculation stopped when a convergence criterion defined as

$$\text{convergence} = \frac{E_a(i) - E_a(i-1)}{E_a(i)}$$

is found to be low enough. We have shown [8] that these iterations may lead to the best modelling of the recorded phenomenon; meanwhile, the parameters obtained may have no physical meaning. After 300 iterations, using the activation energy of the Kissinger method as initial value, the activation energy was stabilized (Fig. 2). Furthermore, this method allows the real determination of m and n in a reasonable time for a given heating rate, whereas the usual Šesták–Berggren method is

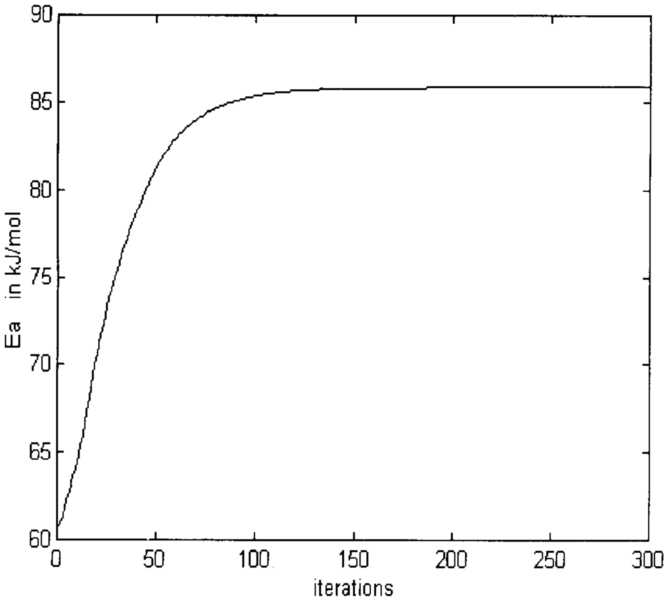

Fig. 2. Evolution of the activation energy vs. the number of iterations in the Šesták–Berggren model of the modified Málek method.

time-consuming. In the case of the reaction order model (that of the Málek method), one iteration has led to an important decrease of the LSM (to 7.865), giving a value similar to those obtained by the Achar–Brindley–Sharp and the multiple linear regression methods, without later significant modification of the fit when increasing the number of iterations.

Meanwhile, in the case of the Šesták–Berggren model of the Málek method, Table 2 does not show the expected decrease in the LSM when increasing the number of iterations. In addition, there is an unexpected increase in the value of m, whereas m should decrease to a value of zero in the case of a reaction order model.

Table 2
Kinetic parameters using the Šesták–Berggren model of the Málek method in the 10–90% interval with the degree of conversion corresponding to the top of the peak $\alpha_p = 43.42\%$. Parameters as in Table 1

Line	E_a	m [a]	n [a]	$\ln k_0$	r	LSM
1 [b]	60.23	0.227	1.955	14.41	−0.99934	17.55
2 [c]	60.00	0.227	1.955	14.29	−0.99903	6.89
300 [d]	23.42	0.600	1.404	2.37	−0.99494	7.34

[a] m and n are kinetic exponents. [b] E_a determined by Kissinger method allows calculation of m and n of the Málek method. [c] E_a obtained by the modified Málek method determined with m and n parameters previously obtained in line 1 for a chosen heating rate (5° C min^{-1} here). [d] Parameters obtained by the modified Málek method after 300 iterations.

To account for this induced increase, we have considered a possible reflection of two or more applicable reaction mechanisms and/or bad modelling by a single reaction order model for the studied polymerization in the usual kinetic interval ($0.1 < \alpha < 0.9$). The differences observed in Table 2 between the kinetic parameters obtained before and after iterations caused us to consider the possible existence of local minima, leading to similar LSM values for very different kinetic parameters. This agrees with the conclusions of other authors [9,10] with regard to the application of the Šesták–Berggren or multiple linear models and with the proviso that any thermal analysis curve may be interpreted within the scope of several apparent kinetic models. These variations also confirm the strong correlations existing between kinetic parameters [9,11].

The existence of additive phenomena is not evident on the basis of the thermogram shape analysis at 5°C min^{-1} (Fig. 3). To check this hypothesis, the kinetic parameters were calculated using a reduced range of 10–80% conversion ($0.1 < \alpha < 0.8$). The results calculated with the Šesták–Berggren model of the Málek method and the modified one are listed in Table 3. From these results it can be seen that, in this reduced interval, m now has a limiting value near to zero, and there is excellent agreement between the experimental and the model results obtained with the modified method (LSM = 0.57). We note that the Šesták–Berggren model of the modified Málek method leads to interesting information on the profile, suggesting the presence of more than one component in the usual kinetic interval of 10–90%. Even if the value of m is not exactly zero, the polymerization seems to be governed mainly by the homogeneous law in the reduced interval.

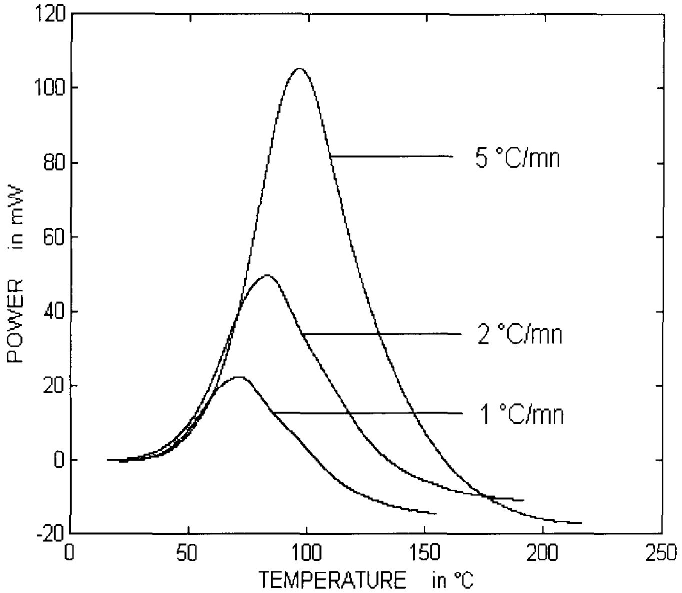

Fig. 3. Experimental thermograms of cure at three different heating rates.

Table 3
Kinetic parameters using the Šesták–Berggren model of the Málek method in the 10–80% interval with the degree of conversion corresponding to the top of the peak $\alpha_p = 43.42\%$. Parameters as in Table 1

Line	E_a	m [a]	n [a]	ln k_0	r	LSM
1 [b]	60.23	0.235	2.029	14.42	−0.99976	2.41
2 [c]	60.54	0.235	2.029	14.52	−0.99977	2.30
300 [d]	85.90	0.006	2.463	22.85	−0.99996	0.57

Footnotes as in Table 2.

As the reaction now fulfils the kinetic homogeneous law in the new kinetic interval, it is possible to treat the experimental data by the Freeman–Carroll and the Ellerstein method, methods supported only by the kinetic homogeneous law [12,13]. We can compare the results obtained (Table 4) from these methods, which are widely used in thermal analysis because of their relative simplicity in the performance of the computations. The Freeman–Carroll and Ellerstein methods proceed in two stages: in the first, a difference–differential equation gives the activation energy E_α and the kinetic exponent n (with a correlation coefficient denoted by r_1). Afterwards, the pre-exponential factor k_0 is deduced from these values, according to the equation used in the Borchardt–Daniels method [14] (with a correlation coefficient r_2). As we previously noted in our experimental solid–plastic transition study [8], Table 4 shows that the fit expressed by the LSM is of poor accuracy, and the correlation coefficient r_2, often the only one given in such computations, does not reflect the accuracy of correlation between the kinetic parameters and the phenomena experimentally observed in DSC. Analysis of the correlation coefficient r_1 seems to reflect better the difference existing between the theoretical parameters and the experimental values. In order to test the Freeman–Carroll method differently, we have estimated the absolute error in the reaction order value Δn established by Jerez [15] according to the expression $\Delta n = \sigma_y(1 - r^2)^{1/2}$, where σ_y represents the standard deviation of the ordinates. The value obtained for Δn is large (64%), and if we consider the value of n obtained by the Achar–Brindley–Sharp or the multiple linear regression method as reference

Table 4
Kinetic parameters obtained by the Freeman–Carroll (FC) and Ellerstein (EL) methods in the 10–80% interval. Parameters as in Table 1

Method	Step 1			Step 2		LSM
	n	E_a	r_1 [a]	ln k_0	r_2 [a]	
FC	2.33	82.60	−0.95881	21.43	−0.99989	435.87
EL	2.36	83.33	−0.98474	21.77	−0.99992	214.32

[a] r_1 and r_2 are correlation coefficients of the two steps.

Table 5
Kinetic parameters using the Achar–Brindley–Sharp (ABS) and multiple linear regression (MLR) methods in the 10–80% interval. Parameters as in Table 1

	n	$\ln k_0$	E_a	r	LSM
ABS	2.47	23.02	86.41	−0.99996	0.57
MLR	2.47	23.02	86.42		0.57

(Table 5) this represents 14% of the absolute difference between these methods and that of Freeman–Carroll. Even in the 10–80% interval, where the kinetic homogeneous law seems to predominate, the Freeman–Carroll and Ellerstein methods do not allow a good fit between experimental and calculated data.

In Table 5, we can see that the Achar–Brindley–Sharp and the multiple linear regression methods in the reduced interval now provide good curve-fitting, and the apparent kinetic parameters of cure (n, $\ln k_0$, E_a) are in perfect agreement with those obtained by the Šesták–Berggren model of the modified Málek method.

4. Conclusions

Using essentially the LSM values, the Šesták–Berggren model of the modified Málek method, the Achar–Brindley–Sharp method and the multiple linear regression method were used to obtain similar kinetic parameters by DSC in a reduced kinetic interval (10–80%).

However, our wish is to evaluate the accuracy of each method, for a phenomenon of the same order of magnitude and for a given kinetic mechanism, so as to allow an evaluation of the different methods themselves. For example, it has not been possible to obtain a good agreement between experimental and calculated data from the reaction order model of the Málek method. The problem is to ascertain whether this method can lead to accurate fitting, because the polymerization studied may or may not involve more complex processes. It will be useful for this purpose to perform simulations on theoretical thermograms fulfilling a given kinetic mechanism (for example, the kinetic homogeneous law).

In the 10–90% kinetic interval, the existence of additive phenomena is not evident on the basis of the thermogram shape analysis in DSC at 5°C min^{-1}; meanwhile, a more complex mechanism is obvious using the Šesták–Berggren model of the modified Málek method by means of the kinetic parameters obtained after several calculation iterations. Although more work needs to be done on the possibility of solving the kinetic analysis in the case of two or perhaps more stages of reaction, the Šesták–Berggren model of the modified Málek method may be employed to establish whether the kinetic interval is governed by a single mechanism, so avoiding erroneous kinetic analyses.

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References

[1] N. Sbirrazzuoli, Y. Girault and L. Elégant, Angew. Makromol. Chem., 211 (1993) 195.

[2] B.B. Achar, G.W. Brindley and J.H. Sharp, in Heller and Weiss (Eds.), Proc. Int. Clay Conf. Jerusalem, 1 (1966) 67.

[3] J. Šesták and G. Berggren, Thermochim. Acta, 3 (1971) 1.

[4] J. Málek, Thermochim. Acta, 138 (1989) 337.

[5] N. Sbirrazzuoli, D.Brunel and E. Elégant, J. Therm. Anal, 38 (1992) 1509.

[6] G.J. Widman, J. Therm. Anal., 25 (1982) 45.

[7] K.W. Hoffmann, K. Kretzschmar and C. Koster, Thermochim. Acta, 94 (1985) 205.

[8] N. Sbirrazzuoli, Y. Girault and E. Elégant, Thermochim. Acta, 202 (1992) 233.

[9] J. Málek and J.M. Criado, Thermochim. Acta, 203 (1992) 25.

[10] J. Šesták, Solid State Ionics, 63–65 (1993) 245.

[11] N. Koga, J. Šesták and J. Málek, Thermochim. Acta, 188 (1991) 333.

[12] E.S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.

[13] S.M. Ellerstein, in R.S. Porter and J.F. Johnson (Eds.), Analytical Chemistry, Plenum Press, New York, 1968, p. 279.

[14] H.J. Borchardt and F. Daniels, J. Am. Chem. Soc., 79 (1957) 41.

[15] A. Jerez, J. Therm. Anal., 26 (1983) 315.