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Kinetic study of solid–plastic transitions. Part 1. Comparison of methods describing the transition by differential scanning calorimetry

N. Sbirrazzuoli [a], Y. Girault [b] and L. Elegant [a]

[a] *Laboratoire de Thermodynamique Expérimentale, Université de Nice-Sophia Antipolis, Parc Valrose, 06034 Nice Cedex (France)*
[b] *Laboratoire de Chimie Physique Organique, Université de Nice-Sophia Antipolis, Parc Valrose, 06034 Nice Cedex (France)*

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Abstract

Following our research on organic phase-change materials, we tested the different kinetic methods, described in previously established software, on the solid–plastic transition of pentaerythritol using criteria based on the minimization of the difference between experimental and calculated thermograms obtained by differential scanning calorimetry. The good modelling of the Achar–Brindley–Sharp method, which does not require long calculation times, led to its selection from other differential methods. The Freeman–Carroll and Ellerstein methods are not appropriate for modelling the transition.

INTRODUCTION

In the course of our studies on organic phase-change materials, the very high disparity between the values obtained by thermal analysis and the literature data [1–8], for temperatures as well as for enthalpies relating to solid–plastic transitions prompted us to attempt an investigation of the phenomenon responsible for those variations.

A detailed kinetic knowledge of the transformation would be useful to optimize the conditions of use of these phase-change materials and to afford a further insight into the nature of the process observed during solid–plastic transition. Among the numerous equations proposed in kinetics, we aim to identify the ones which can better model the phenomenon observed in differential scanning calorimetry during the transformation of phase-change materials involving a high enthalpy in a low temperature range. In our previous study [9] we reported that the kinetic treatment

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Correspondence to: N. Sbirrazzuoli, Laboratoire de Thermodynamique Expérimentale, Université de Nice-Sophia Antipolis, Parc Valroze 06034 Nice Cedex, France.

methods used did not allow selection between results obtained by different methods from examination of the correlation coefficients. In this paper we present a more extensive and comprehensive treatment of the phenomena observed during the transformation of a solid–solid transition material by modelling of thermograms observed by differential scanning calorimetry using software (already described) that collects data from the different kinetic methods [10].

EXPERIMENTAL

High purity (99 + %) 2,2-dihydroxymethyl-2,3-propanediol or pentaerythritol (PE) from Aldrich Chemical Company was used.

In order to reduce the effect of dependence of kinetic parameters on the sample mass, we decided, as suggested by Guarini et al. [11] and Pokol et al. [12], to carry out the experiments with small sample quantities (approximately 25–28 mg). Pentaerythritol gives anisothermal transition thermograms, with shapes very sensitive to experimental conditions; samples for thermal analysis were therefore carefully weighed, powdered and packed to prevent thermal conductivity effects. All the scans were performed with a Setaram DSC 111 differential heat flux scanning calorimeter (with the ordinate scale in power units), maintained in a vertical position in order to obtain good reproducibility in the disposition of the sample in open aluminum pans (in order to operate at constant pressure).

The data obtained by acquisition with the HP 86 calculator of the DSC apparatus processed on a 386 AT microcomputer using the software previously described [10].

RESULTS

The modelling, carried out in a 20–80% interval (except in the Coats–Redfern method, where the treatment interval is reduced to 45–55%), leads to accurate setting out of Arrhenius lines. Table 1 summarizes the physical characteristics and experimental data for the studied samples **1–3**.

TABLE 1

Transition enthalpy (ΔH_{Tr}), top of peak temperature (T_{p}) and degree of conversion corresponding to the top of the peak (α_{p}) for different scanning rates (V)

Sample	V (°C min^{-1})	ΔH_{Tr} (J g^{-1})	T_{p} (°C)	α_{p} (%)
1	1	286.67	190.15	46.64
2	2	286.03	190.99	46.58
3	5	283.92	192.99	45.94

TABLE 2

Activation energy E_a and correlation coefficient R by integral methods

Method	E_a (kJ mol^{-1})	R		
Kissinger	974.45	−0.98855		
Ozawa	933.99	−0.98872		
Satava	979.28	−0.99605	$n^a \to 0$	20–80% [b]
Coats–Redfern	984.57	−0.99991	$n^a \to 0$	45–55% [b]

[a] n, kinetic exponent.

[b] Kinetic interval.

Table 2 gives the activation energy for the pentaerythritol transition from the Coats–Redfern, Satava, Ozawa, and Kissinger integral methods, obtained with the same software [10].

In the case of the Coats–Redfern method, the limits of application of the approximation on the exponential integral p(x) imply an interval of treatment of the peak (45–55%) which is comparatively restricted, and preclude the comparison of the correlation coefficient R obtained with that of the other methods. The Coats–Redfern, and Satava methods do not permit, in our case, the determination of the kinetic exponent n, the calculations for that parameter tending to zero value.

The Kissinger method was realized for samples **1**, **2** and **3** (see Table 1), for which the degree of conversion corresponding to the top of the peak, α_p, is constant. The methods of top of peak temperature analysis (Kissinger, and Ozawa) give low correlation coefficients, but the chief virtue of these methods is to yield the activation energy without the knowledge of the conversion function $g(\alpha)$.

Tables 3–6 give the kinetic parameters of the pentaerythritol transition at 2°C min^{-1} for the differential methods. Among the eight functions of the Achar–Brindley–Sharp method, we present in Table 3 the three functions giving the best modelling of the thermogram. The best modelling

Table 3

Kinetic modelling by the Achar–Brindley–Sharp (ABS) method for sample **2** by treatment of 125 points of the thermogram corresponding to the 20–80% interval

$f(\alpha)$	n [a]	ln k_0 [a]	E_a [a]	R [a]	LSM [a]
A: $(1-\alpha)^n$	1	169.60	671.37	−0.99965	0.1740
B: $n(1-\alpha)[\ln(1-\alpha)]^{1-1/n}$	1	169.60	671.37	−0.99965	0.1740
C: α^n	0.9	−185.29	−698.04	+0.99980	0.11321

[a] n, kinetic exponent; α, degree of conversion; 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.

TABLE 4

Kinetic parameters for Freeman–Carroll (FC) and Ellerstein (EL) methods

Method	Step 1			Step 2		LSM [a]
	n [a]	E_a [a]	R_1 [a]	ln k_0 [a]	r_2 [a]	
FC	1.18	819.92	−0.95832	202.71	−0.99930	1702.9
EL	1.01	703.88	−0.96914	171.20	−0.99965	1712.9

[a] For abbreviations see Table 3.

is retained when taking into account minimization of the difference (LSM) between the calculated and experimental thermograms, expressed as [13]

$$\mathrm{LSM} = \frac{1}{n}\sum_{i=1}^{n}\left(\mathrm{Y}_{\mathrm{exp}} - \mathrm{Y}_{\mathrm{i\,calc}}\right)^2$$

where Y_{exp} is the heat flow experimental data, i.e. $\mathrm{d}H/\mathrm{d}t$, Y_{calc} is the heat flow obtained with kinetic parameters and n is the kinetic exponent.

The function C which gives the best correlation coefficient and LSM leads to a negative value of the activation energy. We therefore retain the functions A and B that are equivalent here, because the kinetic exponent n is equal to unity.

The experimental results of Table 4 seem to confirm that the Ellerstein method is the more precise for the determination of the kinetic exponent [10]. The Freeman–Carroll, and Ellerstein methods proceed in two stages [10]. A difference–differential equation gives the activation energy E_a and the kinetic exponent n (with a correlation coefficient R_1) and from these values the pre-exponential factor k_0 is deduced, according to the same equation as that used in the Borchardt–Daniels method [14] (correlation coefficient R_2). As the values of these two coefficients are in our case very different, it is important to be specific as to which correlation coefficient the calculation involves. Indeed, if the ln k_0 calculation leads to an acceptable R_2 value, this is very different from the R_1 value obtained in the previous determination of the activation energy and the kinetic exponent.

TABLE 5

Kinetic parameters obtained by the Šesták–Berggren (SB) method

Line	m [a]	n [a]	p [a]	ln k_0 [b]	E_a [b]	R [b]	LSM [b]
1 [c]	0.1	0.4	0.6	−121.77	−452.65	0.99987	0.04754
2 [d]	0.10	0.50	0.48	−70.97	−256.67	0.99979	0.03728
3 [e]	0	1	0	169.60	671.37	−0.99965	0.17403

[a] m, n, p are exponents.

[b] For abbreviations see Table 3.

[c] Precision exponent, 10^{-1}.

[d] Precision exponent, 10^{-2}.

[e] Supplement condition $E_a > 0$.

TABLE 6

Kinetic parameters obtained by the Malek method with the degree of conversion corresponding to the top of the peak $\alpha_p = 0.4658$

Line	E_a [a]	m [b]	n [b]	ln k_0 [a]	R [a]	LSM [a]
1 [c]	974.45	0.2364	1.6214	248.77	−0.99436	75.67662
2 [d]	951.36	0.2364	1.6214	242.81	−0.99372	5.03827
3 [e]	215.63	0.2855	0.6533	51.47	−0.99920	0.06314

[a] For abbreviations see Table 3.

[b] m, n are Kinetic exponents.

[c] E_a determined by the Kissinger method permits calculation of m and n.

[d] E_a determined with the m and n parameters previously obtained with the Šesták–Berggren model.

[e] Parameters obtained after 1000 iterations [10].

The commercial software used in an earlier study [9] operates in a different way: it is first limited to the case where the kinetic exponent n is equal to unity, and in fact involves seeking manually the interval of the degree of conversion α for which n will be equal to unity. The value of n is computed on the basis of differences between successive points, and E_a and ln k_0 values are obtained from the equation used in the Borchardt–Daniels (BD) method [14]. It is in fact a feature of the Borchardt–Daniels method that we set $n = 1$. The correlation coefficient given by the commercial software is often very good because it relates to the calculation of E_a and ln k_0 with this equation (BD), which is not the equation of a difference–differential method. Table 4 permits us to appreciate the differences between R_1 and R_2 obtained with the Freeman–Carroll method using our program (which is not limited to the value of $n = 1$). The commercial software modified to compute every value of n gives, for the 20–80% interval, 2.37 for the kinetic exponent and an activation energy of 1588.1 kJ mol^{-1}. This would lead to an LSM value of 287.33! Even if the kinetic parameter values are not fundamentally different from those we obtain with the Achar–Brindley–Sharp (function A) method, they are inadequate for modelling the phenomenon observed in differential scanning calorimetry (LSM close to 1700: see Table 4).

The Šesták–Berggren (SB) method, however, allows a very good modelling of the phenomenon (Table 5), and gives an example of the fact that the lowest LSM value is not always obtained for the exponent giving the best value of R. Line 1 corresponds to a calculation with a precision exponent of 10^{-1} and line 2 with 10^{-2}. If we consider only the positive values for the activation energy, the calculations (in line 3) give the same results as those obtained with the Achar–Brindley–Sharp (A) method.

The Málek method, based on the standardized curve shape $y(\alpha)$ and on the value of the degree of conversion at the top of the peak α_p (here 0.4658), shows that the phenomenon studied can be described by the

Šesták–Berggren model that involves two parameters, the kinetic exponents *m* and *n*. The results obtained (line 1, Table 6), lead to poor modelling. As we proposed in the description of the software equation [10], we proceed in a succession of calculation loops until the value of the activation energy is stabilized. Line 2 in Table 6 corresponds to a first LSM amelioration, and after 1000 iterations (line 3) we observe the closest fit of the experimental curve with the calculated one.

CONCLUSIONS

The Coats–Redfern, and Satava integral methods did not allow determination of the kinetic exponent *n* necessary for modelling the solid–plastic transition of polyols.

The selection among the various differential methods proposed to model the solid–plastic transition was achieved by evaluating the difference between the calculated and the experimental thermograms (LSM parameter). Taking into account these LSM values, the Freeman–Carroll, and Ellerstein methods do not seem to be suitable for modelling this kind of phenomenon, even if the Ellerstein method affords a difference of only 4.8% for the activation energy compared with that from the Achar–Brindley–Sharp method. The Šesták–Berggren method allows good modelling of the phenomenon but leads to unconventional kinetic parameters. If we restrict the investigation to kinetic parameters giving positive activation energy values, the method leads to kinetic parameters in line with those of the Achar–Brindley–Sharp method. The Málek method as modified by us, proceeding by calculation loops, is the one allowing the best modelling of the phenomenon observed in differential scanning calorimetry with positive values of the activation energy, but requires prolonged calculation times. Thus the Šesták–Berggren and Malek methods make the physical interpretation of the kinetic exponents found and the comparisons between several kinetic parameters obtained under different experimental conditions difficult.

The Achar–Brindley–Sharp method, which does not require lengthy calculations, gives a good model of the phenomenon from a type A or B function (here, they are similar because *n* is equal to unity). Now that we have a suitable tool for studying the solid–plastic transitions of phase-change materials, we propose in future work to effect comparative studies under different experimental conditions, and to show the effects in the use of differential scanning calorimetry.

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