Thermochimica Acta, 147 (1989) 291–302
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

MODELLING OF THE PROCESS IN DC EXPERIMENTS BY CONSIDERING THE LAYER OF AIR BETWEEN THE CALORIMETER AND HOLDER

J.Y. ARMAND, J. BOUZON and J.M. VERGNAUD

Laboratory of Materials and Chemical Engng., Faculty of Sciences, University of Saint-Etienne, 23 Dr. P. Michelon, Saint-Etienne 42100 (France)

(Received 12 October 1988)

ABSTRACT

Some emphasis has been placed upon the air layer between the calorimeter and holder, and upon its effect on the curing process in the case of calorimetry under isothermal conditions. Cylindrical samples of rather large dimensions (100–200 mg) have been considered, and the cure of epoxide resin was the reaction studied. Mathematical models based on numerical methods with finite differences have been used to describe the process: they take into account not only the rate of heat evolved from the reaction but also the heat transferred through the air layer, holder and sample.

As a result, heat flux–time histories in good agreement with experimental results and the profiles of temperature and state of cure developed in the sample have been obtained. A fuller insight into the process has been gained, enabling various conclusions to be drawn.

LIST OF SYMBOLS

C, C_1, C_2	specific heat of sample, holder and air respectively
E	activation energy
k_o	rate constant of reaction
n	order of overall reaction
Q_∞	enthalpy of reaction per unit mass
Q_t	enthalpy evolved up to time t
R	radius of sample
R_1, R_2	external radius of holder and air respectively
$\Delta r, \Delta r_1, \Delta r_2$	finite increment in radius of sample, holder and air respectively
SOC	state of cure reaction
Δt	finite increment in time
T_M	temperature of mould
T_j, TN_j	temperature of jth increment at time t and $t + \Delta t$ respectively

0040-6031/89/$03.50

$\lambda, \lambda_1, \lambda_2$	thermal conductivity of sample, holder and air respectively
ρ, ρ_1, ρ_2	density of sample, holder and air respectively

INTRODUCTION

As the process developed in calorimetry is controlled by the heat transferred to the holder surface and through the holder and sample, the time of the experiments is proportional to the square of the main dimension of the material in the case of samples which are a thin sheet or are cylindrical in shape, this main dimension being the thickness and radius respectively. Due to this basic fact, the tendency in calorimetry has been to use smaller samples which allow for faster rates of heating. Another important point is that when a small sample is used, if it is not pure or is a mixture, it is essential that all the constituents of the sample are very well dispersed. Dispersion problems occasionally arise and are generally observed to result in a lack of reproducibility in the calorimetric curves. The question which always arises is how representative of the homogeneity of the batch is a 5 mg sample taken from a large batch. For example, sulphur can be poorly dispersed in rubber either because of poor milling practices or because of large particles of sulphur not being broken down [1,2]. As a consequence of these basic facts, it is understandable that there are two types of calorimeter, one accommodating very small samples of 5 mg or less, the other for rather large samples of 150 mg or more [3,4], sometimes up to 10 g.

Very often, DSC and DC techniques are compared with each other, the second technique being sometimes preferred over the first one, perhaps because of the simpler operational conditions and the simpler mathematical treatment of the kinetics in DC experiments.

In fact, in spite of their advantages which are very well known and noteworthy, both DSC and DC techniques also suffer from drawbacks. The main important inconvenience is perhaps due to the temperature measurement in calorimetry. In a DSC experiment, the sample is scanned at a selected heating rate up to a temperature at which the full exotherm is complete. Because of the time required for heat to be transferred from the calorimeter to the inside of the sample, the temperature in the sample shifts with respect to that of the calorimeter, the difference in temperature being proportional to the heating rate and square of the main dimension [5–9]. For constant temperature operation in the DC mode, the calorimeter is stabilized at the desired temperature, and the sample previously at room temperature is introduced. Thus, the set calorimeter temperature is not the true sample temperature during the heating period or during the reaction period because of local heating arising from the exothermic reaction.

The purpose of this paper is to demonstrate that the quality of the contact between the calorimeter and the sample [10,11] must be widely studied, especially considering the presence of the air layer between the calorimeter and holder [12]. The air layer between the holder and the calorimeter is more important for heat transfer as was shown in a previous paper in which a temperature of 150 °C with epoxy resin was chosen [12]. The effect of this air layer with various other temperature values must be now be elucidated.

Another purpose of this paper is to determine the development of the profiles of temperature and state of cure through the sample and their modification by the presence of the air layer.

Mathematical models based on numerical methods with finite differences which consider, for example, the kinetics of the heat evolved from the reaction as obtained by DSC experiment, and the heat transferred through the air layer, holder and sample by conduction, have been used for this purpose.

THEORETICAL

Some assumptions have been made in order to clarify the problem:

(1) Only the radial heat transfer through the circular cross-section of the sample is considered, because of the cylindrical shape of the sample and the disposition of the sensitive heat cell of the calorimeter.

(2) The temperature of the sensitive heat cell of the calorimeter is kept constant during the process.

(3) The thin layer of air between the sample and the calorimeter oven has a constant thickness. In the same way, the thickness of the holder and the radius of the resin are assumed constant.

(4) The thermal parameters of the resin are constant. They do not change with the temperature or with the progress of the reaction.

(5) The partial enthalpy evolved up to time t as a fraction of the total enthalpy represents the conversion up to time t.

(6) The rate of the conversion is expressed by an Arrhenius equation with constant parameters.

Mathematical treatment

The rate of radial heat transfer through the circular cross-section of the sample is given by the general equation

$$\rho C\left[\frac{\partial T}{\partial t}\right]=\frac{1}{r}\frac{\partial}{\partial r}\left[r\lambda\frac{\partial T}{\partial r}\right]+\rho\frac{\mathrm{d}Q}{\mathrm{d}t} \tag{1}$$

where the heat transferred by transient conduction and the heat evolved from the reaction can be seen on the right-hand side of the equation. The

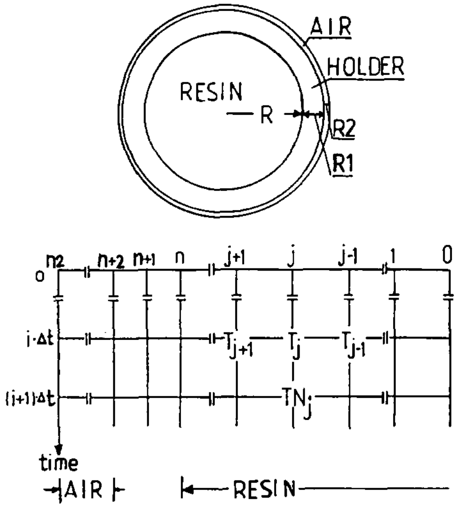

Fig. 1. Scheme of the sample and temperature–space diagram for numerical analysis.

initial and boundary conditions are

$$\left.\begin{array}{lll} t=0 & 0 \leqslant r \leqslant R & \text{sample} \\ & R \leqslant r \leqslant R_1 & \text{holder} \\ & R_1 < r < R_2 & \text{air layer} \\ & r = R_2 & \text{mould of calorimeter} \end{array}\right. \tag{2}$$

$$\left.\begin{array}{lll} t>0 & r < R_2 & T \text{ function of } r \text{ and } t \\ & r = R_2 & T \text{ of mould} \end{array}\right. \tag{3}$$

The rate of heat evolved from the cure reaction is as follows

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{Q_t}{Q_\infty}\right) = k_0\left(1 - \frac{Q_t}{Q_\infty}\right)^n \exp\left(-\frac{E}{RT}\right) \tag{4}$$

Numerical analysis

No analytical solution can be found for the problem because of the heat evolved from the reaction and the boundary conditions. A numerical method with finite differences has to be used (Fig. 1). From the first assumption, the circular cross-section of the sample, holder and air layer is considered with the radial heat transfer. The heat balance is calculated during the increment of time Δt within the annulus centred on the position r and having the thickness of Δr ($\Delta r/2$ on both sides of the centre r). The new temperature TN_j in this annulus at the time $(i+1)\ \Delta t$ can be obtained from the values of the temperature at the same position T_j and at the adjacent annuli T_{j-1} and T_{j+1} at the preceding time $i\Delta t$.

Calculations are made not only for the resin, but also for the metal holder and the air layer.

Within the resin: $1 \leqslant j \leqslant N-1$

$$TN_j = \frac{1}{M}\left[T_{j-1} + (M-2)T_j + T_{j+1}\right] + \frac{1}{j2M}\left[T_{j+1} - T_{j-1}\right] + \left[\frac{1}{C}\right]\left[\frac{\mathrm{d}Q}{\mathrm{d}t}\right]_j \Delta t \tag{5}$$

At the middle of the resin

$$TN_0 = T_0 + \frac{4}{M}(T_1 - T_0) + \left[\frac{1}{C}\right]\left[\frac{\mathrm{d}Q}{\mathrm{d}t}\right]_0 \Delta t \tag{6}$$

Within the metal holder

$$TN_j = \frac{1}{M_1}\left[T_{j-1} + (M_1-2)T_j + T_{j+1}\right] + \frac{\Delta r_1}{2M_1(R + \Delta r_1)}(T_{j+1} - T_{j-1}) \tag{7}$$

Within the air layer

$$TN_j = \frac{1}{M_2}\left[T_{j-1} + (M_2-2)T_j + T_{j+1}\right] + \frac{\Delta r_2(T_{j+1} - T_{j-1})}{2M_2[R_1 + (j - N_1)\,\Delta r_2]} \tag{8}$$

Interfaces between the sample and holder, the holder and air, and the air and the mould

More complex relations are obtained for these interfaces by calculating the heat balance during the increment of time Δt on the annuli located on both sides of each interface [12].

The values of the moduli shown in eqns. (5), (7) and (8) are given by

$$M = \frac{(\Delta r)^2 \rho C}{\Delta t \lambda} \qquad M_1 = \frac{(\Delta r_1)^2 \rho_1 C_1}{\Delta t \lambda_1} \qquad M_2 = \frac{(\Delta r_2)^2 \rho_2 C_2}{\Delta t \lambda_2} \tag{9}$$

with $M > 4$, $M_1 > 2$ and $M_2 > 2$ for the stability in the calculations.

Heat evolved from the cure reaction

The heat evolved from the cure reaction up to time $t = (i+1)\Delta t$ is obtained by the relation

$$Q_{i+1} = Q_i + \left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_i \Delta t \tag{10}$$

with

$$\left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_i = k_0\left(1 - \frac{Q_i}{Q_\infty}\right)^n Q_\infty \exp\left(-\frac{E}{RT_i}\right) \quad \text{and } Q_0 = 0 \tag{11}$$

The state of cure at time t is expressed by the partial enthalpy evolved up to time t as a fraction of the total enthalpy

$$\mathrm{SOC}_i = \left(\frac{Q_i}{Q_\infty}\right)100 \tag{12}$$

Heat flux emitted

The heat flux is calculated near the surface of the resin by considering two annuli with parabolic approximation

$$\mathrm{HF} = \lambda\left(\frac{3T_R - 4T_{R-\Delta r} + T_{R-2\Delta r}}{2\Delta r}\right) \tag{13}$$

EXPERIMENTAL

Apparatus

A DSC 111 (Setaram) was employed for this study using a rather large sample. This sample was representative of the heterogeneity of the batch from which it was taken.

The calorimeter was stabilized at the selected constant temperature (140, 150 or 160 °C), the sample at room temperature was introduced, and the time base recorded.

The dimensions are sample external radius, 0.25 cm; holder external radius, 0.30 cm; and air layer thickness, 0.027 cm.

Materials

An epoxide resin was used; its kinetic parameters were determined by DSC at the heating rate of 2 °C min^{-1}. The values of these kinetic parameters are: $Q_\infty = 38$ cal g^{-1}, $n = 1.56$, $k_0 = 2 \times 10^{23}$ (s^{-1}) and $E = 50018$ cal mol^{-1}.

The thermal parameters for the resin, metal holder and air are:
Resin $\lambda_r = 8 \times 10^{-4}$ cal cm^{-1} s^{-1} C^{-1}, $\rho_r = 1.47$ g cm^{-3}, $C_r = 0.3 + 5 \times 10^{-4} \times T$ (cal g^{-1} °C^{-1}) T(°C).
Metal $\lambda_m = 0.107$ cal cm^{-1} s^{-1}, $\rho_m = 7.86$ g cm^{-3}, $C_m = 0.108$ cal g^{-1} °C^{-1}.
Air $\lambda_a = 7.6 \times 10^{-5}$ cal cm^{-1} s^{-1}, $\rho_a = 944 \times 10^{-6}$ g cm^{-3} at 125 °C, $C_a = 0.24$ cal g^{-1} °C^{-1}.

RESULTS

The layer of air located between the calorimeter and holder has some effect not only on the heat flux–time histories obtained during the DC experiments but also on the temperature profiles developed through the system (air layer, holder and sample) and consequently on the profiles of state of cure developed through the sample. These two effects of the air layer were considered successively.

Determination of kinetic parameters with DSC experiments

DSC experiments with a selected heating rate which depends on the value of the enthalpy of reaction as previously shown [5–8], yielded the kinetic parameters for the cure reaction. The heat evolved from the overall reaction has been assumed to follow an Arrhenius equation, and the activation energy and order of reaction have been calculated from the heat flux–temperature curves using various classical techniques [13–15]. The main assumption made in this calculation is that the heating rate of the calorimeter is low compared with the rate of heat transfer through the system (air layer, holder and sample), so that the temperature is the same throughout the sample.

The validity of the parameters has been tested by comparing the experimental heat flux–temperature curves with the curves calculated by making the above-cited assumptions [12].

Heat flux–time profiles in DC experiments

Heat flux–time profiles with reaction

Various experiments were conducted in the DC mode with the calorimeter kept successively at 140, 150 and 160 ° C.

A good correlation was obtained between experimental and calculated curves, as shown at 150 ° C in a previous paper [12].

The three heat flux–time histories were drawn in Fig. 2 with the same time scale, but with two different scales for the heat flux.

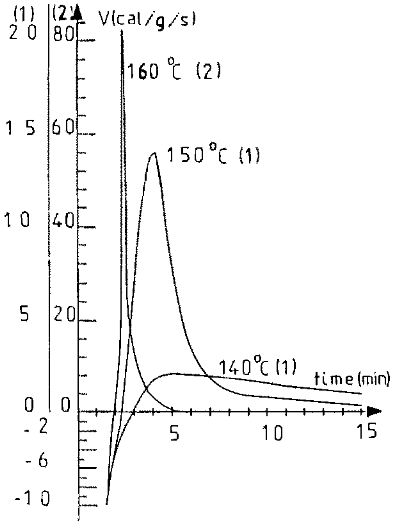

Fig. 2. Heat flux–time histories in DC experiments with internal reaction, at 140, 150 and 160 ° C.

There are three sections in these curves:

(1) The heating period of the sample from room temperature to that of the calorimeter. The temperature of the surface of the holder is the same as that of the calorimeter when the heat flux is 0. Of course, during this period, heat is transferred by conduction through the system (air layer, holder and sample) at a very high rate, and the air layer represents an important limiting factor. The presence of this air layer is responsible for the significant time required for thermal equilibrium to be established, this time ranging from 2 to 3 min according to the temperature of calorimeter.

(2) The development of the exothermic reaction in the sample which causes the temperature in the sample to increase. This is observed when heat flux is emitted from the sample to the calorimeter, being positive in this case.

(3) The heat flux–time curves pass through a maximum. As shown in Fig. 2, it takes a long time for the reaction to be completed in the case of the lowest temperature. In the case of the highest temperature, the heat-flux peak is high and sharp. From these experiments, a temperature window for the calorimeter is observed over which meaningful data can be obtained. In the case of epoxy resin, the temperature effect is very pronounced and this temperature window is narrow (20 ° C).

Heat flux–time with no reaction (reference baseline)

It is interesting to obtain the heat flux–time histories when no reaction occurs, these curves being used as reference baselines, especially for the determination of the enthalpy.

This experiment is done as follows: the sample is previously cured at the selected temperature up to a time at which the full exotherm is obtained; the sample is quenched and cooled down to room temperature and then dropped again in the calorimeter under conditions identical to the first cure.

These curves are easily obtained by calculation with the model, by putting the constant k_0 equal to 0. Of course, the thermal properties vary with the advance of the reaction: moreover, they are not the same for the solid cured resin and the liquid uncured resin [16]. However, these thermal properties have been kept constant in these calculations.

The endothermic curves obtained with the three temperatures are approximately the same, as shown in Fig. 3.

Comparisons between heat flux–times with and without reaction

Comparisons made between heat flux–time histories obtained with and without reaction can show that the reaction begins before the heat flux becomes exothermic. This interesting fact is worth noting and it will be studied in detail by considering the profiles of state of cure in the next section.

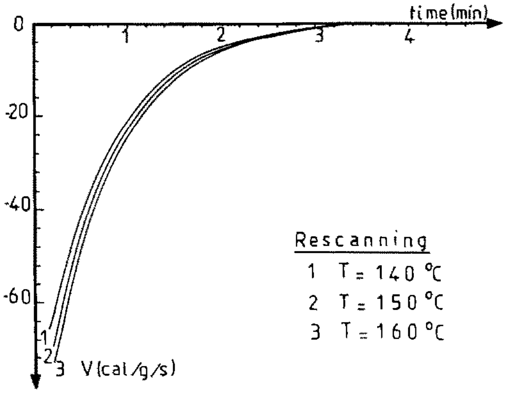

Fig. 3. Heat flux–time histories in DC experiments with no internal reaction, at 140, 150 and 160 °C.

Profiles of temperature and state of cure in the sample

The model can provide more information than the experiments—the profiles of temperature and state of cure developed throughout the sample during the reaction.

These gradients of temperature and state of cure are drawn for various temperatures of the calorimeter in Fig. 4 (140 °C), Fig. 5 (150 °C) and Fig. 6 (160 °C), at various times.

Some conclusions can be drawn from the temperature profiles developed through the sample:

(1) Very high temperature gradients are observed within the air layer for all these cases, especially during the heating period. They are due to the low thermal conductivity of air.

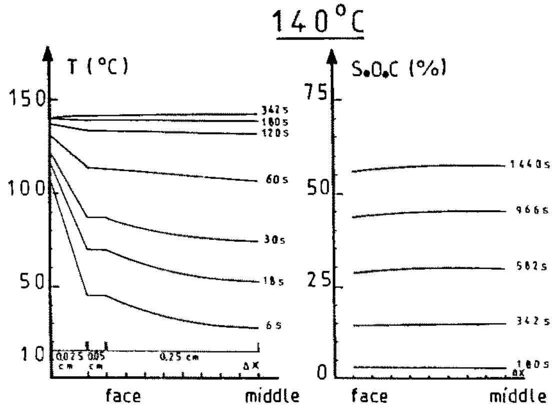

Fig. 4. Profiles of temperature (left) and state of cure (right) obtained in the sample (air layer–holder–material) at 140 °C.

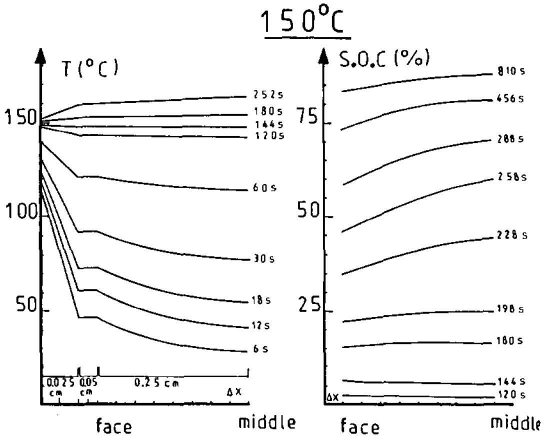

Fig. 5. Profiles of temperature (left) and state of cure (right) obtained in the sample (air layer–holder–material) at 150 °C.

(2) Because of the high thermal conductivity of the metal, the temperature gradient in the holder is flat.

(3) Significant temperature gradients exist throughout the sample during the heating period and the reaction period.

(4) The higher the temperature of the calorimeter, the steeper the temperature gradients: this is especially clear when the heat flux is maximum (342 s at 140 °C; 252 s at 150 °C; 144 s at 160 °C).

The profiles of state of cure developed throughout the sample are of great interest and various conclusions can be drawn from these curves:

(1) The effect of the temperature of the calorimeter on the gradients is very significant, for both the heating period and the reaction period. At

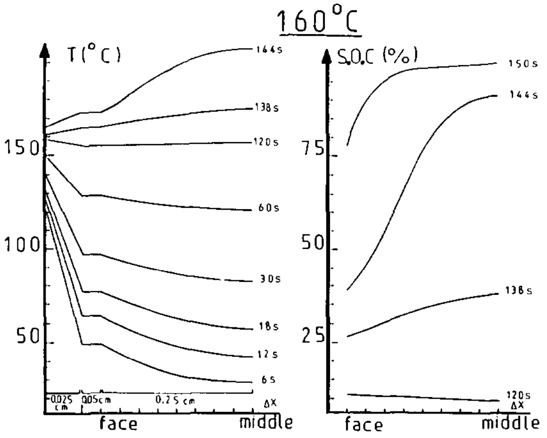

Fig. 6. Profiles of temperature (left) and state of cure (right) obtained in the sample (air layer–holder–material) at 160 °C.

140 ° C, the profiles of state of cure remain flat during these two periods. At 150 ° C, the profiles are flat only during the heating period. For the highest temperature (160 ° C), two profiles are developed during each of these two periods: one with a higher value on the surface (the heating period), and one with a higher value at the middle of the sample (the reaction period).

(2) The highest value for the gradient of state of cure is obtained when the heat flux is maximum.

(3) Part of the reaction has already occurred during the heating period. This fact is especially significant when the temperature of the calorimeter is high. For instance, at 150 and 160 ° C, more than 5% of the state of cure has been attained when the heat flux reaches the value of 0. This part of the enthalpy of cure is generally lost, especially when only the exothermic part of the heat flux is registered and taken into account. This is surely the main reason why the enthalpy of cure is lower when the constant temperature of the calorimeter is higher (3).

CONCLUSIONS

The modelling of the process developing in the sample has been carried out in the case of calorimetry under isothermal conditions. Mathematical models based on numerical methods with finite differences must take into account all the facts, not only the kinetics of the reaction (or rather the heat evolved from the overall reaction) but also the heat transferred through the air layer, the holder and sample.

The effect of the air layer located between the calorimeter and holder on the heat transfer is of significance, in spite of the fact that it is very thin.

Heat flux–time histories obtained either by experiment or calculation show that there is a temperature window of 20 ° C over which meaningful data can be obtained.

Profiles of temperature and state of cure can be calculated, as they develop through the sample. Interesting conclusions can be drawn from these profiles. Some of them can explain the decrease in the value of the enthalpy of cure obtained when the temperature of the calorimeter is increased.

A fuller insight into the process has been obtained in DC mode, in the case of a rather large sample (100–200 mg). However, the effect of the air layer is more pronounced with a small sample, especially when the sample is a thin sheet.

REFERENCES

1 D.W. Brazier, in N. Grassie (Ed.), Developments in Polymer Degradation, Vol. 3, Applied Science, London, 1981, Chapter 2, p. 27.

2 A. Accetta, J. Bouzon, A. Sadr-Bazaz and J.M. Vergnaud, J. Chim. Phys., 80(9) (1983) 691.
3 J.M. Vergnaud, Thermochim. Acta, 114 (1987) 15.
4 J.Y. Armand and J.M. Vergnaud, Thermochim. Acta, 116 (1987) 111.
5 J.Y. Armand, R. Gonnet, R. Jones, J. Bouzon, M. Touchard and J.M. Vergnaud, Thermochim. Acta, 103 (1986) 341.
6 J.Y. Armand, J. Bourgois, M. Touchard and J.M. Vergnaud, Thermochim. Acta, 108 (1986) 345.
7 J.Y. Armand and J.M. Vergnaud, Thermochim. Acta, 112 (1987) 313.
8 J.Y. Armand, J. Bourgois and J.M. Vergnaud, Thermochim. Acta, 116 (1987) 301.
9 H. Liu, J.Y. Armand, J. Bouzon and J.M. Vergnaud, Thermochim. Acta, 126 (1988) 81.
10 A. Khouider, J.B. Rochette and J.M. Vergnaud, Thermochim. Acta, 89 (1985) 81.
11 G. Chataing, M. Chater and J.M. Vergnaud, Thermochim. Acta, 89 (1985) 107.
12 H. Liu, J.Y. Armand, J. Bouzon and J.M. Vergnaud, Thermochim. Acta, 130 (1988) 355.
13 E.S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.
14 S.M. Ellerstein, in R.S. Porter and J.F. Johnson (Eds.), Analytical Calorimetry, Plenum Press, New York, 1968, p. 279.
15 K. Kretzschmar and K.W. Hoffmann, Thermochim. Acta, 83 (1985) 139.
16 M. Chater, J. Bouzon and J.M. Vergnaud, Plast. Rubber Process. Appl., 7 (1987) 199.