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EFFECT OF THE LAYER OF AIR BETWEEN THE CALORIMETER AND CYLINDRICAL SAMPLES IN DC EXPERIMENTS

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ABSTRACT

When using cylindrical samples in calorimetry a thin space is left between the calorimeter and holder so that the holder may be moved. The layer of air in this space must be considered in calorimetry when working under isothermal conditions (differential calorimetry) in order to obtain calculated heat flux–time histories which can be compared with the experimental values. The model used here is a numerical method with finite differences. It takes into account not only the heat evolved from the reaction, but also heat transferred by conduction through the holder and sample and through the thin layer of air. The assumption made about the heat conduction through the layer of air is proved to be correct. This layer of air is found to be responsible for a retardation in the reaction and for lower profiles of temperature and state of cure through the sample, exhibiting an almost constant rate of reaction at any location in the sample. However, the location of the sample in the calorimeter is of great interest, as is the constancy of the thickness of the layer of air.

LIST OF SYMBOLS

C, C_1, C_2	specific heat of sample, holder and air, respectively
E	activation energy
H	proportionality factor
K_0	rate constant of reaction
n	order of overall reaction
Q_∞	enthalpy of reaction
Q_t	enthalpy evolved up to time t
R	radius of sample
R_1, R_2	radial thickness 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

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T_j, TN_j	temperature of jth increment at time t and $t + \Delta t$, respectively
$\lambda, \lambda_1, \lambda_2$	thermal conductivity of sample, holder and air, respectively
ρ, ρ_1, ρ_2	density of sample, holder and air, respectively

INTRODUCTION

Both differential scanning calorimetry (DSC) and differential calorimetry (DC) are used for measuring the enthalpy change accompanying a chemical reaction or a physical event in a sample. The DC technique, running under isothermal conditions, is sometimes preferred to DSC, either because of the simpler conditions or because of the simpler mathematical treatment of the kinetics.

In fact, the DC technique is not simple at all. The principle is plain: in a DC experiment, the enthalpies of the reactions occurring at a constant applied temperature are determined up to a given time. Detailed kinetic analysis of these enthalpy profiles is possible either in the case of simple reactions or by considering the overall reaction [1–4]. If we consider the process, the applied temperature is the set calorimeter temperature (if it does not change during the introduction of the sample) and not the true temperature of the sample during the reaction. This is because (i) the sample (at room temperature) is introduced into the calorimeter and a certain time is required for it to establish thermal equilibrium (very high gradients of temperature and large changes in the heat flux are observed during this heating period, so that the induction period for some cure reactions cannot be determined [5–8] and (ii) during the reaction, other gradients of temperature are developed through the sample, because of local heating arising from exothermic reactions and low heat conductivity.

Other drawbacks of the technique are obvious.

(i) A temperature window is generally observed and meaningful data can only be obtained over a range of about 30 °C. The lowest temperature is determined by the sensitivity of the calorimeter. The highest temperature at which measurements can be made is very often determined by the first part of the reaction period, which cannot be recorded and determined experimentally, and by the high gradients of temperature, especially for reactions of high enthalpy.

(ii) If a small sample is used a lack of reproducibility of the enthalpy profiles is sometimes observed, because problems of dispersion arise for the components in the sample. Thus calorimeters are often run with rather large samples in order to reduce this inconvenience.

(iii) The quality of the contact between the oven and the sample is certainly a factor of interest as previously observed [5,6]. A special parameter has been introduced in this work to qualify this contact. It cannot necessarily be assumed that this coefficient is the same for different samples.

The main purpose of this work is to determine the effect of the quality of contact between the sample and the oven on the profiles of temperature and state of cure. As a thin layer of air is present between the holder and the calorimeter it has to be taken into account. In order to attain this aim, the process of heating and reaction is studied, not only by experiment, but also by modelling with the help of numerical methods with finite differences. These models take into consideration the kinetics of the heat evolved from the reaction and the heat transferred through the various parts of the sample (thin layer of air, holder and sample).

EXPERIMENTAL

A DSC III (Setaram) was used under isothermal conditions. The sample of epoxide resin (150 mg) was encapsulated in the stainless steel holder. The dimensions were sample, external diameter = 0.5 cm; holder, external diameter = 0.7 cm; thickness of the air layer = 0.027 cm. The values of the kinetic parameters were previously determined by DSC using a convenient heating rate of 2° C min^{-1}. The values of the thermal parameters were noted for the air layer and for the resin sample. The kinetic properties determined by DSC were $n = 1.56$, $k_0 = 2 \times 10^{23}$ (s^{-1}), $E = 50\,018$ cal mol^{-1} and $Q_\infty = 38$ cal g^{-1}. The thermal properties of the resin were $\lambda = 8 \times 10^{-4}$ cal cm^{-1} s^{-1} deg^{-1}, $\rho = 1.47$ g cm^{-3} and $C_p = 0.3 + 5 \times 10^{-4} \times T$ (cal g^{-1} deg^{-1}) (T in °C).

THEORETICAL

Assumptions

The following assumptions were made to clarify the problem and to simplify the process.

(i) Because of the cylindrical shape of the sample and of the disposition of the sensitive heat cell, only radial heat through the circular cross-section was considered.

(ii) The thermal conductivity was taken to be constant.

(iii) The kinetics of the cure reaction of the resin were described by a simple reaction with a constant activation energy.

(iv) The temperature of the heated oven was considered to be constant, when the sample (previously at room temperature) was introduced.

(v) The thin layer of air located between the oven and the sample was cylindrical in shape, with a constant thickness. This was obtained by placing the sample carefully.

(vi) The sample was placed in a holder with a constant thickness surrounding the resin.

Mathematical treatment

Following the above assumptions, the increase in temperature of the sample is given by the general equation of transient heat conduction

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

where the contribution of the internal heat generated by the exothermic reaction can be seen.

The initial and boundary conditions are

$$\begin{array}{lll} t = 0 & 0 \leqslant r \leqslant R & T \text{ sample} \\ & R < r \leqslant R_1 + R & T \text{ holder} \\ & R + R_1 < r < R_2 + R_1 + R & T \text{ air layer} \\ & r = R_2 + R_1 + R & T \text{ mould} \end{array} \tag{2}$$

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

The rate of heat evolved from the cure reaction up to time t is expressed by

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

Numerical analysis for the model

As no analytical solution could be found to the problem a numerical method with finite differences was used. The circular cross-section of the sample, holder and air layer is shown in Fig. 1. By considering the circles of radius $r - \Delta r$, r and $r + \Delta r$, the heat balance is calculated in the ring between the circles $r - \Delta r/2$ and $r + \Delta r/2$. As a result, the temperature within the ring after time Δt can be obtained from the temperature at the preceding time in the same ring and in the two adjacent rings. Calculations are made in the resin, in the holder and in the layer of air.

Within the resin ($1 \leqslant j \leqslant N - 1$)

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

At the middle of the resin, a simpler equation must be used

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

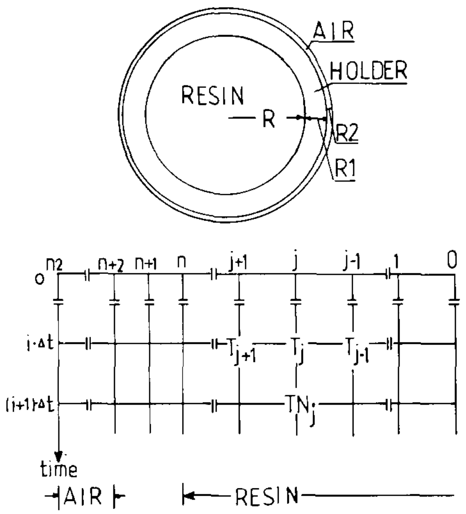

Fig. 1. Scheme of the temperature–space diagram for numerical analysis.

Within the metal holder

$$TN_{N+1} = \frac{1}{M_1}\left[T_N + (M_1 - 2)T_{N+1} + T_{N+2}\right] + \frac{\Delta r_1}{2M_1(R + \Delta r_1)}(T_{N+2} - T_N) \tag{7}$$

Within the layer of air ($\mathrm{N} + 3 \leqslant \mathrm{j} \leqslant \mathrm{N}2 - 1$*)*

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

At the interface between the sample and metal ($j = N$)

$$TN_N = T_N + \left\{V(T_{N-1} - T_N) - V_1(T_N - T_{N+1}) - U(TN_{N-1} - T_{N-1}) - U_1(TN_{N+1} - T_{N+1})\right\}/\left\{3(U + U_1)\right\} + W\left[\left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_N \frac{3}{4} + \left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_{N-1}\left(\frac{1}{4}\right)\right] \tag{9}$$

where the coefficients V, V_1, U and U_1 are

$$V = \frac{8\,\Delta t\lambda}{\Delta r}\left(R - \frac{\Delta r}{2}\right) \quad V_1 = \frac{8\,\Delta t\lambda_1}{\Delta r_1}\left(R + \frac{\Delta r_1}{2}\right) \quad U = \frac{\Delta r}{2}\left(2R - \frac{\Delta r}{2}\right)\rho C$$

$$U_1 = \frac{\Delta r_1}{2}\left(2R + \frac{\Delta r_1}{2}\right)\rho_1 C_1 \quad W = \left(R - \frac{\Delta r}{2}\right)\frac{4\,\Delta r\,\Delta t\rho}{3(U + U_1)} \tag{10}$$

At the interface between the air and metal ($j = N + 2$), we have

$$TN_{N+2} = T_{N+2} + \{V_2(T_{N+1} - T_{N+2}) - V_3(T_{N+2} - T_{N+3}) - U_2(TN_{N+1} - T_{N+1}) - U_3(TN_{N+3} - T_{N+3})\}/\{3(U_2 + U_3)\} \qquad (11)$$

where the coefficients are

$$V_2 = \frac{8\,\Delta t\lambda_1}{\Delta r_1}\left[R + R_1 - \left(\frac{\Delta r_1}{2}\right)\right] \qquad V_3 = \frac{8\,\Delta t\lambda_2}{\Delta r_2}\left[R + R_1 + \left(\frac{\Delta r_2}{2}\right)\right]$$

$$U_2 = \frac{\Delta r_1}{2}\left[2R + 2R_1 - \left(\frac{\Delta r_1}{2}\right)\right]\rho_1 C_1 \qquad U_3 = \frac{\Delta r_2}{2}\left[2R + 2R_1 + \left(\frac{\Delta r_2}{2}\right)\right]\rho_2 C_2 \qquad (12)$$

At the interface between the mould of the calorimeter and the layer of air, we have the simple equation ($j = N2$)

$$TN_{N2} = \frac{H}{1+H}T_{\mathrm{m}} + \frac{1}{1+H}T_{N2-1} \qquad (13)$$

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

$$M = \frac{(\Delta r)^2 \rho C}{\Delta t \lambda} \qquad M_1 = \frac{(\Delta r_1)^2 \rho_1 C_1}{\Delta t \lambda_1} \qquad M_2 = \frac{(\Delta r_2)^2 \rho_2 C_2}{\Delta t \lambda_2} \qquad (14)$$

Some stability conditions must be used for the problem

$$3(U + U_1) - V - V_1 > 0$$
$$3(U_2 + U_3) - V_2 - V_3 > 0 \qquad (15)$$
$$M > 4 \qquad M_1 > 2 \qquad M_2 > 2$$

Heat evolved from the cure reaction

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

$$Q_{i+1} = Q_i + \left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_i \Delta t \qquad (16)$$

with

$$\left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_i = k_0\left(1 - \frac{Q_i}{Q_\infty}\right)^n Q_\infty \exp\left(\frac{-E}{RT_i}\right) \qquad \text{and } Q_0 = 0 \qquad (17)$$

The state of cure at time $t = i\Delta t$ is obtained from the ratio

$$\mathrm{SOC}_i = \left(\frac{Q_i}{Q_\infty}\right)100 \qquad (18)$$

and the heat flux is determined near the surface of the resin

$$\mathrm{HF} = \lambda\left(\frac{3T_R - 4T_{R-\Delta r} + T_{R-2\Delta r}}{2\ \Delta r}\right) \tag{19}$$

RESULTS

The effect of the layer of air located between the holder and the calorimeter is studied by considering the heat flux–time histories obtained with the same calorimeter operated in DSC and DC modes.

Heat flux–temperature history in DSC

In the DSC experiment, the sample is heated at a selected heating rate from room temperature up to a temperature at which the reaction exotherm is complete. The heat flux–temperature history obtained describes the reaction process taking place in the sample. The reference baseline is obtained by scanning under conditions identical to the initial scan with the sample previously cooled to room temperature.

If the heat evolved from the cure reaction is assumed to be described by the Arrhenius equation, the activation energy and the order of reaction can be obtained from the experimental curves by using various techniques [9,10]. The validity of the kinetic parameters previously obtained (as well as the constant k_0) can be tested by superimposing the calculated and experimental curves [11]. The main assumption made in this calculation is that the thermal conductivity of the material is so high that the temperature is the same throughout the sample [12,13].

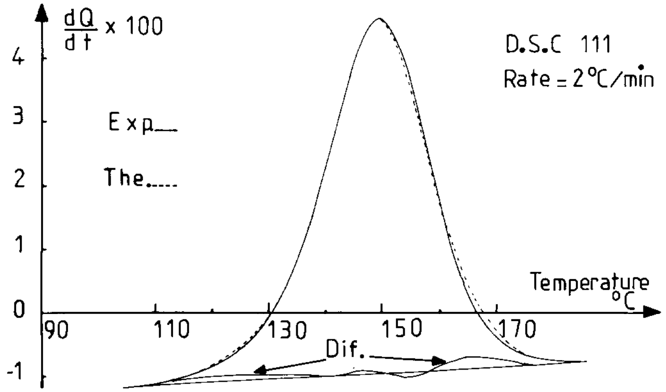

Fig. 2. Temperature–enthalpy profile with and without reaction in DSC (heating rate is 2° C min^{-1}): ———, experiment; — — —, calculation.

As shown in Fig. 2, a good correlation is obtained between the theoretical and experimental curves for a low heating rate of 2° C min^{-1}. This demonstrates the validity of the kinetic parameters.

DC experiments. Calculation by considering the heat transfer and the layer of air

Experiments were performed under isothermal conditions at 150 ° C using the same apparatus (DSC III, Setaram), samples and material.

Two kinds of results are shown: the heat flux–time profile obtained when the fresh uncured resin (previously at room temperature) is placed into the calorimeter retained at a constant temperature (Fig. 3) and the heat flux–time profile with the reference baseline, which is obtained by dropping the cured sample previously cooled at room temperature into the calorimeter at 150 ° C (Fig. 4).

The mathematical model described above was used for calculating both these heat flux–time histories. The first (Fig. 3) is calculated by considering the heat transfer by conduction through the sample and holder and the kinetics of the heat evolved from the cure reaction. The second (Fig. 4) is attained by using the same model and a value of zero for the rate constant k_0, which eliminates the reaction heat. In both cases, the layer of air located between the calorimeter and holder is considered. The assumption made about the heat transferred through this layer of air is that it is controlled by conduction.

As shown in Fig. 4, good agreement is obtained between the experimental and theoretical curves when the layer of air is between 0.025 and 0.03 cm.

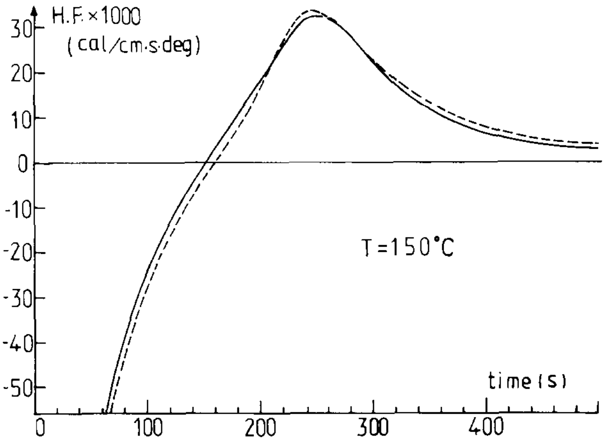

Fig. 3. Temperature–heat flux profile with reaction and taking into account the layer of air in DC (150 ° C); ———, experiment; — — —, calculation.

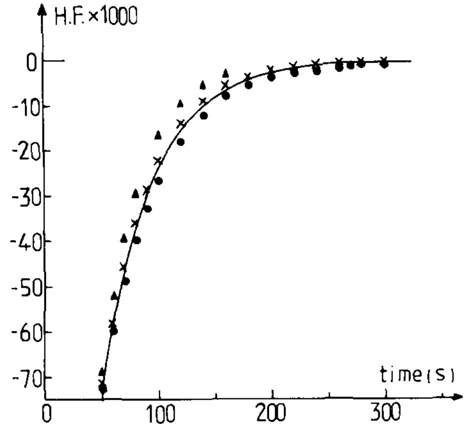

Fig. 4. Temperature–heat flux profile without reaction and taking into account the layer of air in DC (150 °C) Thicknesses of the air layer are: ▲▲, 0.020 cm; × ×, 0.025 cm; ●●, 0.030 cm; ———, experiment.

The same thickness of the layer of air is retained for the calculation of the heat flux–time profile in the case of the reaction (Fig. 3) and good superimposition is obtained.

The model is able to provide more information than experiment: the profiles of temperature and state of cure can thus be attained by calculation. Some temperaure gradients are developed within the sample, e.g. a higher temperature is observed on the face of the sample at the beginning of the process, during the heating period. When the reaction takes place, for instance after 200 s, other temperature gradients are observed, with higher temperatures in the middle of the sample (Fig. 5, left). The profiles of the state of cure shown in Fig. 5 (right) are also of interest.

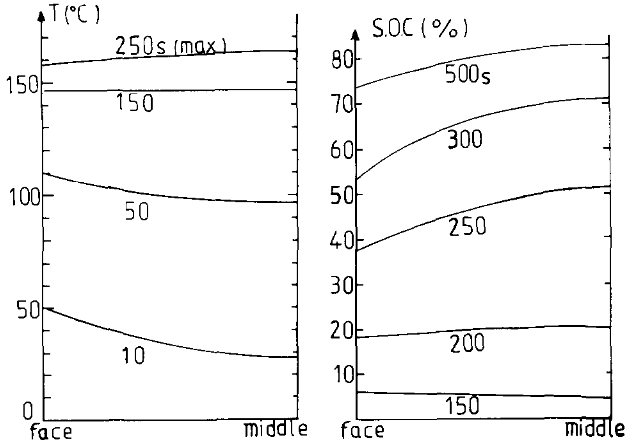

Fig. 5. Distribution of temperature (left) and SOC (right) through the sample when the air layer is considered. The number in the figure is the time (s).

The following conclusions can be drawn from these curves.

(i) The layer of air located between the calorimeter and holder must be taken into consideration, heat being transferred by conduction through this layer.

(ii) A period of time of around 150 s is necessary for the heat flux to reach a value of zero as shown in Figs. 3 and 4.

(iii) During this heating period, high gradients of temperature are developed through the sample.

(iv) The reaction starts to take place during the heating period. For instance at the end of this period, a state of cure ranging from 4 to 5% is attained through the sample, following a low gradient through the sample.

(v) During the period of reaction, other gradients of temperature and state of cure develop within the sample, with a higher value of temperature and state of cure in the middle of the sample [13].

Heat flux–time profiles calculated by considering heat transfer but not the layer of air

The heat flux was calculated with the help of the model by considering the heat transfer through the sample with the heat of reaction and without the heat of reaction. In both cases, the layer of air was not taken into account.

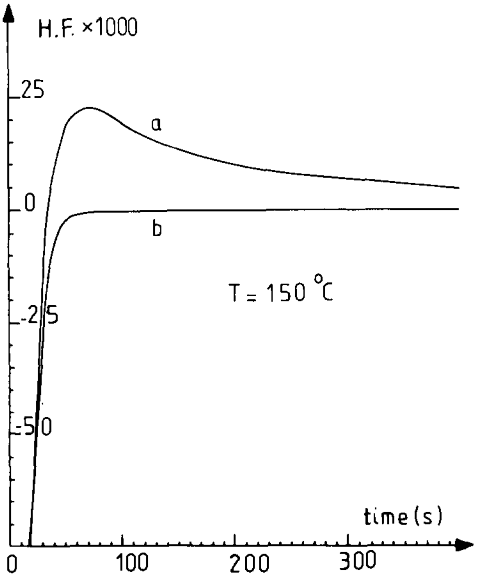

Fig. 6. Profile of temperature–heat flux history with (a) and without (b) reaction from calculation.

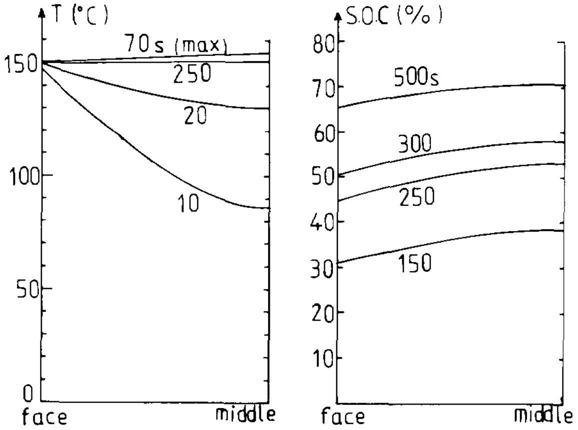

Fig. 7. Distribution of temperature (left) and SOC (right) through the sample when the layer of air is not considered.

As shown in Fig. 6, the heat flux–time profiles obtained in these cases cannot be superimposed on the experimental curves. A time of only about 40–50 s is necessary for the heat flux to reach zero.

The effect of the layer of air can be appreciated in Fig. 7, where the profiles of temperature and state of cure developed through the sample are shown.

Some facts of interest are worth noting, especially if the temperature profile obtained when the layer of air is considered is compared with that obtained when the layer of air is not taken into account.

(i) High temperature profiles are obtained in the case of a sample in good contact with the calorimeter. These temperature profiles are rather low when the layer of air is considered.

(ii) Higher profiles of state of cure are developed within the sample when no layer of air is present.

(iii) The presence of the layer of air is responsible for a retardation in the reaction, especially at the beginning of the reaction when the maximum heat flux is not attained. In this case, lower profiles of temperature and state of cure develop through the sample, the reaction proceeding at about the same rate everywhere in the sample. Of course, it takes a longer period of time to reach the maximum heat flux when the layer of air is considered (250 s instead of 70 s).

(iv) The presence of the layer of air is also responsible for a higher increase in the temperature and state of cure after the maximum heat flux has passed. This fact can be seen in Fig. 5 (right) and Fig. 7 (right) for times of 300 and 500 s.

CONCLUSIONS

Large samples must be used in calorimetry when complex mixtures are studied. In this case, the presence of a thin layer of air located between the calorimeter and sample holder is necessary for moving the holder in the calorimeter.

A mathematical model based on a numerical method with finite differences is able to give heat flux–time histories in good agreement with experimental values when this layer of air is considered. The assumption of heat conduction through this layer of air is proved to be correct.

By comparing the profiles of temperature and state of cure calculated with and without the layer of air, it is clear that this layer of air is responsible for a retardation in the reaction, lower profiles of temperature through the sample, and lower profiles of state of cure at the beginning of the process before the maximum heat flux has been reached. These last two results are of interest in the case of DC experiments, and show that the rate of reaction is about the same everywhere in the sample.

However, the position of the sample in the calorimeter is certainly of great importance, and the sample must not be in contact with the calorimeter. The dimensions of the various holders have to be constant in order to maintain the thickness of the air layer at a constant value.

Cylindrical samples have been considered in this paper, but the problem of the quality of the contact between the holder and calorimeter surely arises in plane samples and could perhaps be highly significant in the case of very small samples.

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