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MODELLING IN CALORIMETRY WORKING UNDER ISOTHERMAL CONDITIONS OR IN SCANNING MODE.

J.M. VERGNAUD
Lab. of Materials and Chemical Engng. - U.F.R. of Sciences
23, Dr. P. Michelon - University of St-Etienne - St-Etienne 42100 - France.

ABSTRACT

Models based on numerical method with finite differences were applied to the study of the methods of calorimetry working under various conditions : isothermal or scanning mode. These models took into account not only the heat evolved from the reaction but also the heat transferred by conduction through thematerial and the oven-holder interface. As a result, heat flux emitted through the oven-holder interface could be obtained by calculation, as well as the profiles of temperature and state of cure developed through the material. A coefficient determining the quality of the contact between the holder and oven was introduced. These informations obtained for cure of low enthalpy as in rubber and of high enthalpy as in thermoset, were useful for explaining the properties of the materials cured in calorimetry and the changes in the enthalpy determined under isothermal conditions or in scanning mode.

INTRODUCTION

A general survey of the pertinent literature on industrial processes pointed out that modelling was already playing an important role on the description of these processes in flowsheets and on the optimization of the productivity. Of course, in this last case, the mathematical simulation of the process used in order to find out the best operational conditions were usually faster and cheaper than real experiments undertaken on the large scale. Before operating this simulation, some experiments on a small scale were generally useful and done by varying each of all parameters, in turn and separately. In this above case, the model had to account for all the facts intervening in the process, and particularly the kinetics of reactions and all heat and matter transfers.

Modelling was especially studied for gaining a fuller insight on the process, and thus for allowing the optimization of operational conditions, when the process was complicated, as shown in case of rubber (1-4) and thermosets (5-6). The absorbing facts in both these cases were that in addition to some complex reactions taking place in the material and especially in rubber, some important problems of heat transfer played the role of a limitation in the rate of the process. For instance, in the cure of the rubber

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the kinetic of reaction was determined by considering the change in some mechanical properties of the rubber, either the viscosity of the rubber during the cure with the help of rheometer (7) or the swelling of the final product in a solvent (2), or the heat evolved from the overall reaction (8). An additional difficulty for the problem at hand was due to the fact that the thermal properties of the rubber were found to vary largely with the temperature (9-10) and perhaps also with the state of cure of the material. In case of thermosets, the problem was complicated by these following two facts : on the one hand, thermosets exhibited low thermal properties, and on the other hand the enthalpy of cure was very high. So that the process of cure followed three steps : heating of the components of the resin generally in liquid form, reaction of cure with high evolving of heat, and cooling of the material with the help of the mold (5,6). Each of these above three steps was responsible for the development of intempestive gradients of temperature, and especially the second one. These high gradients of temperature were in turn responsible for other high gradients of the rate of cure and of state of cure, as well as for high internal stress provoking deformations of the final product and playing a role for high change in mechanical and physical properties.

In case of the reaction taking place in the calorimeter, modelling could be of help affording a further insight into the nature of the process and of the final cured material. In calorimetry, two points were worth noticing:
i - The small sample size used in these techniques necessitated that all ingredients in the sample were well dispersed. Dispersion problems did occasionally arise and would generally be observed by lack of reproducibility. The question which always arised for rubber and thermosets was how representative could be a 1-5 mg. sample, taken from a large batch, of the homogeneity of the batch.
ii - The applied temperature was the set calorimeter temperature and not the true sample temperature during the cure, because of low heat transfer through the sample (3,8) and of local heating arising from the exothermic reaction. As a result, very high gradients of temperature were developed within the sample during the heating and the cure period, provoking some following profiles of state of cure. These profiles were found to depend largely on both the sample size and the heating rate (11).

Of course, modelling of calorimetric techniques had to be done by considering not only the kinetic of heat evolved from the cure reaction but also heat transferred through the calorimeter-holder and the material by conduction. These models were built either for isothermal calorimetry (DC) or for differential scanning calorimetry (DSC), by using rather large samples of

100-200 mg., cylindrical in shape with a diameter of about 5 mm, with reactions of low enthalpy as those taking place in rubber (12-14) or with reactions of high enthalpy with epoxy resin (15-17). This large size was chosen for the holder, because of the above considerations on the distribution of components in the material and by reminding that rubbers and thermosets were complex mixtures.

The model above described (12-17) for the calorimetry techniques was based on a numerical method with finite differences applied to the cylindrical sample and took into account heat evolved from the reaction and from conduction. The heat flux emitted through the sample-calorimeter interface was calculated as a function of time in DC and of temperature in DSC, as well as the profiles of temperature and state of cure developed in the sample at the same time.

Moreover, a particular coefficient had to be considered accounting for the quality of the contact between the holder and oven.

An additional purpose of this paper was to show that these above informations given by simulating the process with the help of the model, were of interest for comparing the techniques of calorimetry running under isothermal conditions and in scanning mode. These results were able to explain some facts which were not understandable otherwise, as the difference in the enthalpies determined in DC and DSC, and the change in the properties obtained for the materials when they were cured in DC and DSC.

THEORETICAL

Assumptions

The following assumptions were made :

i - As the sample was cylindrical in shape with a circular cross-section, the heat flow was considered as radial, by neglecting the longitudinal heat transfer.

ii - Although the reactions of cure were complex, the heat evolved from the overall cure reaction was expressed by an equation with constant parameters.

iii - The quality of the contact between the calorimeter and sample holder was accounted for by a coefficient.

iv - The heat was transferred by convection through the material and the material-oven interface.

Fundamental equations

The transient heat conduction through the circular cross-section of the sample was expressed by the classical equation

$$\rho c \frac{\partial T}{\partial t} = \frac{1}{r} \cdot \frac{\partial}{\partial r} \left(r \lambda \frac{\partial T}{\partial r} \right) + \rho \cdot \frac{dQ}{dt} \qquad (1)$$

where the contribution of heat transferred by conduction and heat evolved from the cure could be seen.

The overall rate of cure was given by the simple equation :

$$\frac{1}{Q_\infty} \cdot \frac{dQ}{dt} = k_0 \left(1 - \frac{Q_t}{Q_\infty}\right)^n \cdot \exp - \frac{E}{RT} \qquad (2)$$

Initial and boundary conditions were as follows :

$t = 0$ $\quad 0 \leqslant r \leqslant R$ $\quad T = Tr$ sample space (3)

$t \quad 0$ $\quad r > R$ $\quad T = Tm$ oven space (4)

$\quad 0 < r < R$ $\quad T = Tr,t$ sample space

Numerical Analysis

As equations (1) and (2) could not find an analytical solution with the above conditions (internal heat from the cure reaction, quality of contact at the oven-holder interface), the problem was solved by using a numerical method with finite differences.

By considering the various circles of radius with the successive values, r, r+Δr, r+2Δr, dividing the circular cross-section, with Δr being a constant radius increment, the temperature for each annulus was considered as constant $T_{i+1,r}$. The heat balance enabled one to obtain for these temperatures

$$T_{i+1,r} = \frac{1}{M} \left[T_{i,r+\Delta r} + (M-2)\, T_{i,r} + T_{i,r-\Delta r} \right] + \frac{\Delta r}{2Mr} \left[T_{i,r+\Delta r} - T_{i,r-\Delta r} \right] + \frac{1}{C} \cdot \frac{dQ}{dt} \cdot \Delta t \qquad (5)$$

In the middle of the sample, eq. 5 was indeterminated, and the temperature was calculated with another equation :

$$T_{i+1,0} = \frac{4}{M} \left[T_{i,\Delta r} - T_{i,0} \right] + \frac{1}{C} \cdot \frac{dQ}{dt} \cdot \Delta t \qquad (6)$$

In both these Eq., the dimensionless number M was expressed as a function of the increments of time and space

$$M = \frac{(\Delta r)^2}{\Delta t} \cdot \frac{1}{\alpha_s} \qquad (7)$$

On the sample face, the heat balance allowed one to write :

$$T_{i+1,R} = \frac{H}{1 + H} T_{i,m} + \frac{1}{1 + H} T_{i,R} \qquad (8)$$

the coefficient H qualifying the contact between the holder and oven.

The coefficient was obtained as follows (18)

$$H = \left(\frac{\alpha_m}{\alpha_s}\right)^{0.5} \cdot \frac{\lambda_s}{\lambda_m} \qquad (9)$$

The heat flux emitted through the holder–calorimeter interface was obtained by Eq. 10.

$$HF = \lambda s \, \frac{T_R - T_{R-\Delta r}}{\Delta_r} \qquad (10)$$

The heat evolved from the cure reaction during the increment of time at the time iΔt was calculated by the recurrent relation :

$$\left(\frac{dQ}{dt}\right)_{i+1} \cdot \Delta t = Q_{i+1} - Q_i = (Q_\infty - Q_t)^n \cdot Q_\infty^{1-n} \cdot k_0 \cdot \exp - \frac{E}{RT} \qquad (11)$$

and

$$Q_0 = 0 \quad \text{and} \quad Q_i = \sum_{i=0}^{i} \left(\frac{dQ}{dt}\right)_i \cdot \Delta t \qquad (12)$$

EXPERIMENTAL

Apparatus

The apparatus chosen in this work (DSC 111 - Setaram) can work either in isothermal or in scanning mode. The heat flux detector emitted a signal which was proportional to the heat transferred per unit of time.

About 100-200 mg of the mixture was encapsulated in the holder. The holder was cylindrical in shape with a diameter of 5 mm. A smaller size would necessitate that all ingredients in the sample were perfectly dispersed.

The calorimeter was coupled with a micro-computer (HP 86) which stored all the data, determined the kinetic parameters with the help of various methods (18). The validity of these kinetic data was usually controlled by superimposing heat flux-time curves obtained by calculation and experiments.

Materials

The formulations used in this study were composed of 2605 epoxy resin (which contained DGEBA epoxy molecules, an anhydride hardener, and tertiary amine as catalyst (CDF-Chimie). The formulations investigated contained 80 parts of hardener per hundred parts of resin, by weight.

The values of the kinetic and thermal parameters were shown in Table 1.

TABLE 1

Values of Parameters

Kinetic of reaction $k_0 = 0.4 \times 10^{12}/s.$ $E = 27{,}140$ cal/mole

$n = 1.5$ $\Delta H = 76$ cal/g

Thermal properties

$\lambda = 1.85 \times 10^{-3}$ cal/cm.s.deg. $C = 0.5$ cal/g.deg.

RESULTS

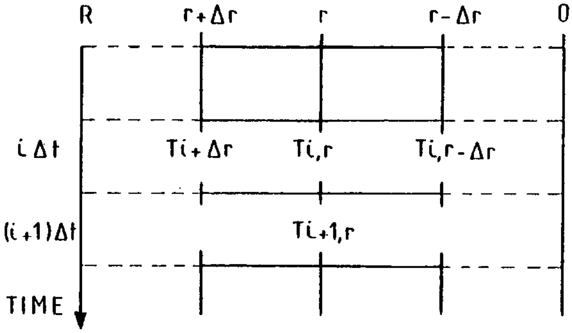

Fig. 1. Scheme of temperature-time history for numerical analysis

1 - Determination of kinetic parameters in DSC

The epoxy resin mixture was heated in the calorimeter from 30 to 250°C by using a constant heating rate of 2°C/min. After cooling the calorimeter and sample to 30°C, the sample was heated again under the same conditions in order to obtain the baseline for heat flux-time curves.

As shown in Fig. 2, the heat flux-time curves obtained by experiment and calculation were very well superimposed, the good agreement between these above curves proving the validity of kinetic parameters. It was necessary in fact to draw a third curve corresponding with the difference between these heat flux as a function of time for appreciating some slight divergence.

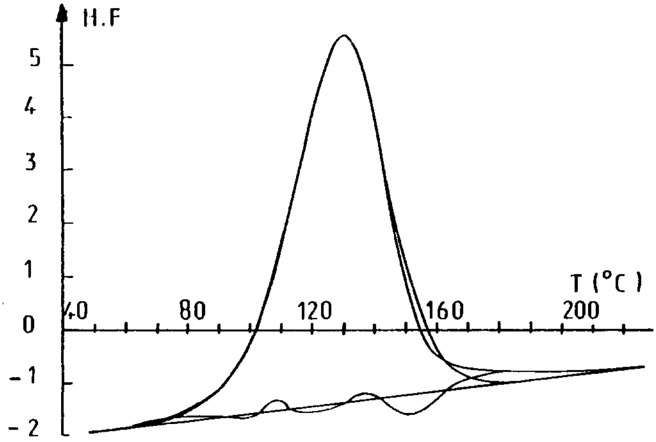

Fig. 2. Comparison between experimental and calculated heat flux-time curve in DSC for epoxy resin.

2 - Determination of heat flux in DC

Fig. 3 illustrated the typical curve obtained for the cure of epoxy resin with the calorimeter working under isothermal conditions at 150°C. As shown in this Fig., the heat flux could be recorded only after about a minute, and it was usually admitted that only the positive part of the heat flux was of interest and worth studying for determining either the kinetic of the reaction or the enthalpy of cure. A good agreement between the experimental curve and the calculated one with the help of the model were found to be in good agreement (15). As indicated previously, the value of the coefficient H qualifying the quality of contact between the resin and holder and between the holder and calorimeter, was about 20, corresponding with a contact like that occuring between iron and resin. This value given for H had a quantitative effect on the value of heat flux obtained in calorimeter, but not on the shape of this curve and the kinetic parameters (15).

The whole part of the heat flux-time curves corresponding with the heating of material and cure reaction, and with the heating of material only, could be easily obtained with the help of the model : the first curve with the rate constant of the reaction, and the second when this rate constant was zero (Fig. 4). Both these curves appeared to be superimposed at the beginning of the process for times lower than 30 s. Then after this time these curves were found to diverge because of the internal heat from cure, so that the difference between these curves did not correspond exactly with the heat flux generally recorded (heat flux in Fig.3). This difference was drawn in Fig. 3 and could be compared with the heat flux recorded. Of course, the whole enthalpy of cure was not proportional to the surface under the heat flux-time curve, but to the surface under the above difference between these heat flux-time curves, this fact explaining the lower value of enthalpy obtained by DC than by DSC.

The same results were obtained for the resin at 170°C in Fig. 5 and 6, exhibiting a higher divergence between the positive heat flux recorded and calculated, and the difference between the calculated heat flux.

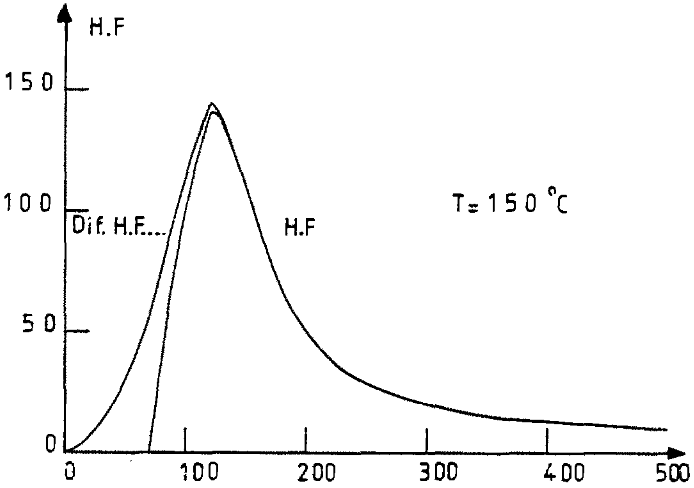

Fig. 3. Heat flux (HF)-time curve for epoxy resin in DC (calc. and exp.)
Difference in Heat flux obtained with cure reaction and without cure.

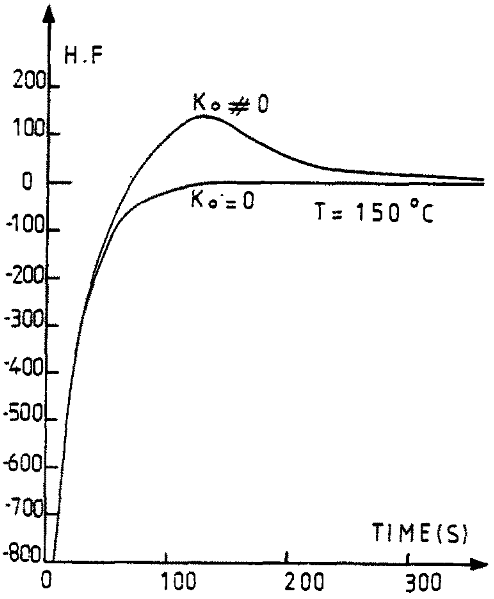

Fig. 4. Heat flux-time curves obtained with cure ($k_0 \neq 0$) and without cure ($k_0 = 0$) in DC for epoxy resin at 150°C.

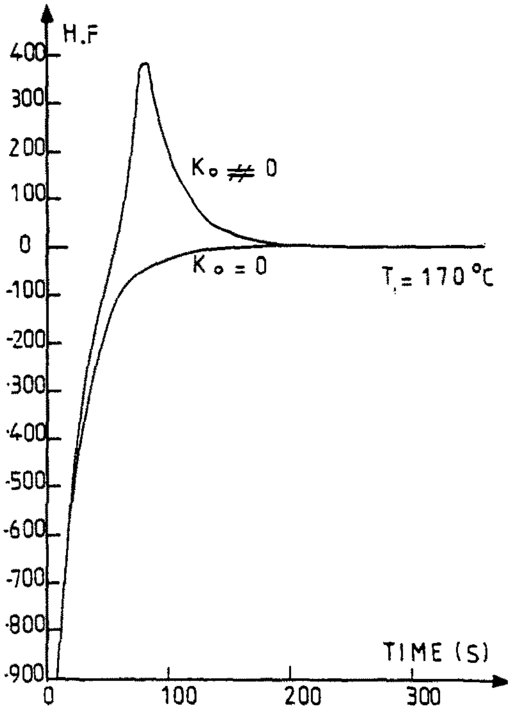

Fig. 5. Heat flux-time curves obtained with cure (k_0=0) in DC at 170°C for epoxy resin.

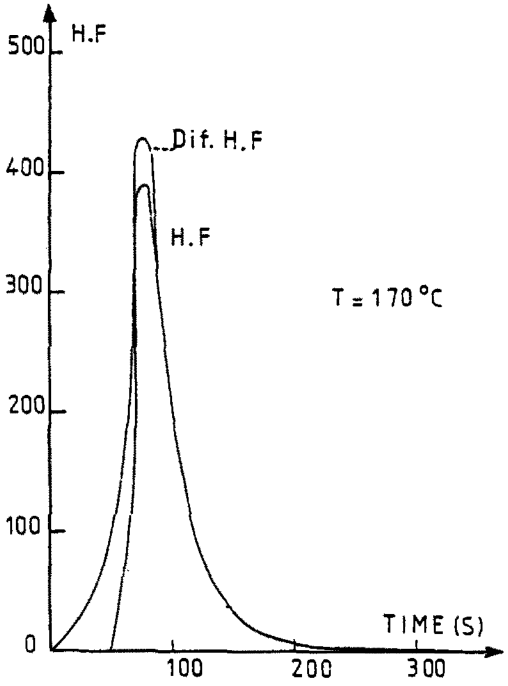

Fig. 6. Heat flux(HF)-time curve for epoxy resin in DC (calc. and exp.).

Difference in Heat flux obtained with cure and without cure.

3 - Determination of the profiles of temperature and SOC

The model was also able to give information on the temperature and state of cure at any place and time within the sample. Although it was difficult at the present time to make some experiments on the temperature and state of cure, the validity of the model was tested by comparing the heat flux-time curves determined either by calculation or experiments. A good agreement between these curves was obtained when the data concerned with the kinetic and thermal parameters were convenient.

Some profiles of temperature developed within the radius of the cross-section of the cylindrical sample were illustrated in Fig. 7 when the temperature of the calorimeter was 150°C and in Fig. 8 at 170°C. Some facts of interest were worth noticing :

i - the temperature in the sample took about 60-70 s to reach the value of the calorimeter at 150°C, and about 60s. when this temperature was of 170°C.

ii - During this first heating period, some high profiles of temperature were developed through the sample, corresponding with the very high endothermic heat flux emitted from the calorimeter to the sample.

iii - At the present time, a determination of the kinetic of cure reaction was practically unfeasible during this heating period.

iv - A second period corresponding with the cure reaction was found to start at about 60-70 s. for the lower temperature of the calorimeter. During this period, the temperature was higher at the middle of the sample, because of the heat generated by the cure reaction.

v - A third period occured after the maximum of heat flux was raised.

The profiles of the state of cure could also be calculated with the help of the model, as they were developed through the sample. As shown in Fig. 7 at 150°C and Fig. 8 at 170°C, the state of cure was not the same within the sample, these profiles of SOC following the profiles of temperature shown previously. Some facts of interest could be pointed out :

i - The reaction of cure did not start for times lower than 30-40 s.

ii - Some profiles of SOC were developed through the sample, the SOC being higher on the heated face of the sample during the heating period, and then higher at the middle of the sample during the cure period.

iii- The highest gradients of SOC was obtained when the heat flux raised its maximum value.

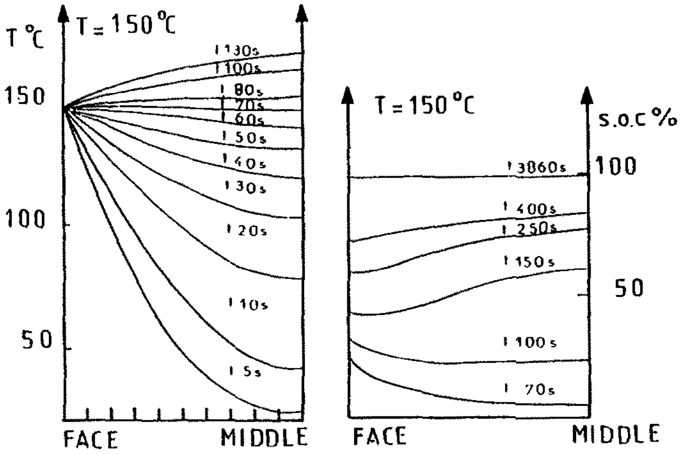

Fig. 7. Profiles of temperature and SOC through the radius of sample in DC at 150°C, for various times.

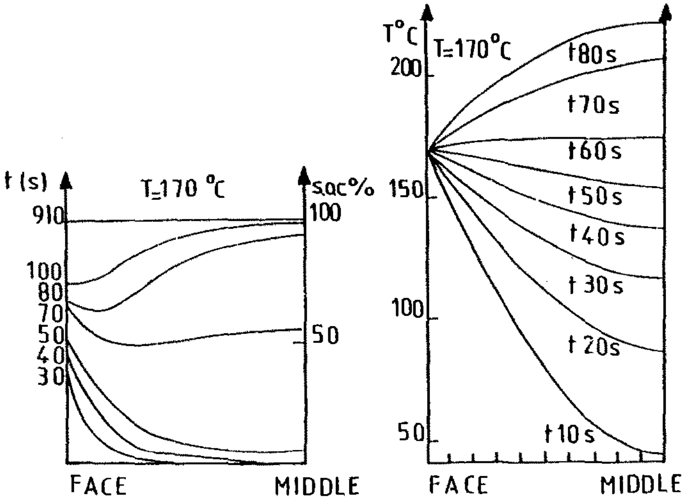

Fig. 8. Profiles of temperature and SOC through the radius of sample in DC at 170°C, for various times.

4 - Determination of the enthalpy of cure in DC

The enthalpy of cure obtained by using DSC with a heating rate of 2°C/min was 76 cal/g (19). This value was about the same as those determined by using the difference between the heat flux shown in Figs 3 and 5. However the value of enthalpy obtained by integrating the positive part of the heat flux was slightly lower. This divergence between the values was found to depend largely on the temperature chosen for isothermal calorimetry as shown in Table 2.

TABLE 2

Values of enthalpy obtained in DC

Temperature (°C)	150	160	170
Enthalpy (cal/g)	66.9	61.3	53.4
Difference (%)	12	19.4	29.8

CONCLUSIONS

Modelling of process was surely of interest, because it enabled the user to get a fuller insight on the process, providing a knownedge on the profiles of temperature and state of cure, as well as heat flux-time history. But building a model was sometime a tedious work, not only because of the difficulty of mathematical treatments especially in case of interfaces,but also because of the pressing need of data of high accuracy.

Reactions taking place in calorimeters were very often complicated, in the way that various phenomena could be observed : heat transfer by conduction or convection, reaction and heat flux. So modelling these processes could be of help in order to give more information on the process. The temperature of the calorimeter was not the temperature of the sample, and moreover some profiles of temperature were developed through the sample. As a result, the state of cure was not the same throughout the sample, this point being of importance when a definite material was desired.

However, calorimetry techniques, and especially those working in scanning mode were of great interest, allowing the user to record the rate of reaction as a function of time or temperature. Some apparatus able to work with rather large samples had to be run with lower heating rates, but they might be useful for providing the user with definite samples, these samples being of high interest for studying other properties of the material related to their state of cure.

REFERENCES

1 G.A. Prentice and M.C. Williams, Rubber Chem. Technol., 53 (1980) 1023.
2 D. Hands and F. Horsfall, Gummi, Asbest. Kunstst., 33 (1980) 440.
3 A. Accetta and J.M. Vergnaud, Rubber Chem. Technol., 56 (1983) 689.
4 A. Sadr, R. Granger and J.M. Vergnaud, J. Appl. Polym. Sci., 29 (1984) 955.
5 S.Y. Pusatcioghu, J.C. Hassler, A.L. Frickle and H.A. Mc Gee, J. Appl. Polym. Sci., 25 (1980) 381.
6 J.A. Nixon and J.M. Hutchinson, Plast. and Rubber Proc. and Appl., 5 (1985) 337.
7 P. Di Mauro, Intern. Rubber Conf., Kyoto, Oct. 17, 1985.
8 A. Accetta, P. Le Parlouer and J.M. Vergnaud, Thermochim. Acta, 59 (1982) 149.
9 S.D. Gehman, Rubber Chem. Technol., 40 (1967) 36.
10 D. Hands, Rubber Chem. Technol., 50 (1977) 480.
11 G. Chataing, M. Chater and J.M. Vergnaud, Thermochim. Acta, 97 (1986)281.
12 A. Khouider, J.B. Rochette and J.M. Vergnaud, Thermochim. Acta, 89 (1985) 81.
13 A. Khouider, J.B. Rochette and J.M. Vergnaud, Thermochim. Acta, 89 (1985) 93.
14 A. Khouider, J. Bouzon and J.M. Vergnaud, Thermochim. Acta, 98 (1986)285.
15 G. Chataing, M. Chater and J.M. Vergnaud, Thermochim. Acta, 89 (1985)107.
16 M. Chater,G. Chataing and J.M. Vergnaud, Thermochim. Acta, 89 (1985) 119.
17 M. Chater, G. Chataing and J.M. Vergnaud, Thermochim. Acta, 90 (1985)135.
18 G. Chataing and J.M. Vergnaud, Thermochim. Acta, 94 (1985) 379.
19 M. Chater, D. Lalard, F. Michel-Dansac and J.M. Vergnaud, Europ. Polym.J. in press.

LIST OF SYMBOLS

Q_t, Q_∞ : heat evolved from reaction up to time t, total enthalpy of cure.

i,n : integers for the time and space

H : coefficient characterizing the quality of heat transfer at the oven-holder interface

M : dimensionless number
Δt : increment of time
Δr : increment of space
$T_{i,n}$: temperature at time i and space n
α : thermal diffusivity of the material
λ : thermal conductivity of the material
C : heat capacity