

EFFECT OF HEATING RATE AND SAMPLE SIZE ON HEAT TRANSFER THROUGH THE SAMPLE IN DSC

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ABSTRACT

As it is very often the first step of the process, heat transfer plays an important role, especially for systems heated in scanning mode. The problem is studied in the simple case when no reaction occurs. In the present case, heat is transferred through the cross-section of a cylinder heated on faces with a constant heating rate. The gradients of temperature through the sample when they are established are proportional to the heating rate on faces and to the square of the diameter of the cylinder. The shape of the gradients of temperature are obtained at different times when these gradients are not established and when they are constant. The heat flux emitted through the face–calorimeter interface are also determined. The value of heat flux is certainly the best parameter for testing the validity of the model.

INTRODUCTION

Heat transfer plays an important role in various cases for industrial reactions because it appears as the first limitation of the process. Of course, it is widely taken into account in industrial processes and it stands for a large part of chemical engineering. But it must also be considered in various other cases on a smaller scale, for instance, in laboratory applications.

As shown previously, several successive and simultaneous steps should be considered in pyrolysis of a fire retardant coating heated in air:

(i) Heat transfer by convection through air from the fire to the coating face and through the air–coating interface.

(ii) Heat transfer by conduction through the coating, followed by pyrolysis. As the temperature increases through the coating, pyrolysis takes place progressively from the heated face to the protected material. On the one hand, when the material initially at room temperature is put in the oven under isothermal conditions, heat is first conducted under transient condi-

tions and a long time is necessary to reach the stationary state [1]. On the other hand, when the material is heated by free convection in air in scanning mode, heat is transferred under transient conditions during the whole process, and very large gradients of temperature can be appreciated not only through the material but also through the air-material interface [2]. In fact, the problem is very often more complicated because of the effect of air velocity on heat transferred by convection through the air-material interface. So, while heat is transferred by free convection in the first two cases [1,2], it is now transferred by forced convection when air is in motion. In this last case, the heat transfer at the interface is higher, and the higher the air velocity, the higher the heat transfer [3]. Another case of interest is concerned with the heating by conduction when the material is put in contact with heated metal. A classical application is when the material plays the role of the coating for heating metal. Even if the heating rate is not large ($< 50^{\circ}\text{C min}^{-1}$), appreciable gradients of temperature through the material are shown, with following gradients for the mechanical properties [4]. Moreover, intempesive gradients of temperature and degradation by pyrolysis have been obtained by experiment and calculation when higher heating rates have been used in flash pyrolysis [5].

Obviously, heat transfer is also the most important step in industrial processes, as has been shown in rubber cure [6] and epoxide reticulation [7]. Because of the low thermal properties of rubber (conductivity and diffusivity), higher gradients of temperature are developed within the rubber mass when the rubber initially at room temperature is put in a heated mold, and they are responsible for an important heterogeneity in the sample as far as the state of cure is concerned [8]. In order to shorten the time of this heating period and also to reduce these gradients of temperature and the following gradients of state of cure through the rubber mass, an injection molding process has been developed. But, although the temperature of the injected rubber is higher than the room temperature, this temperature must be lower than that of the mold because of intempesive cure reactions in the storage bulb, and some problems remain concerned with the heterogeneity of the sample [9,10].

The problem of heat transfer limitation also appears in calorimetry, and its role is decisive for this technique. In both DSC and DC techniques, the enthalpy changes accompanying the chemical reaction or physical change in the sample are monitored, the result being a profile of the rate of enthalpy change as a function of temperature (DSC) or time (DC). Some sources of error arise from heat transfer from the specimen to the reference cell [11,12], which apply particularly for reactions of high enthalpy. The applied temperature is the set calorimeter and not the true temperature during cure, because of local heating arising from exothermic reactions and low heat transfer through the sample [6-8]. Moreover, reactions do present some specific problems both in sample handling and in obtaining reproducible experimen-

tal results. On the one hand, it is imperative in sample preparation that good contact is made between the sample, the sample holder and the oven, and we had to introduce a new coefficient able to describe the quality of this contact [13–15]. On the other hand, the small sample size used in DSC necessitates that all the ingredients in the sample are well dispersed. Dispersion problems do occasionally arise and will generally be observed by lack of reproducibility, especially for very small samples. The question which arises is how representative is a 1–5 mg sample, taken from a large batch, of the homogeneity of the batch. But for larger samples (> 100 mg), as a result of high heating rates and the size of samples, intempestive gradients of temperature are developed through the mass, provoking some disturbances for the kinetic treatment of reactions [13–18]. The presence of these large gradients of temperature obtained in DC has shown that methods coupling DSC and DC techniques [15,17] or DSC technique are of greater interest for kinetic studies of reactions, especially those of high enthalpy. Lastly, the effect of the value of the heating rate on various factors in DSC has been studied quantitatively for the separation of two different phenomena taking place in the reaction and for the sensitivity of the technique by considering the value of heat flux [19].

As the tendency in industry is to look for processes able to shorten the cycle in order to increase the productivity, higher and higher heating rates are being used. The same tendency is followed in pyrolysis with the expected result of the flash pyrolysis. In our opinion, the best way for progressing is to get a sufficient knowledge on the process, and especially heat transfer. So, we have to give a valuable answer to some questions about the simultaneous effect of the heating rate and sample size on heat transfer, in the case of polymeric material of low thermal properties heated under scanning mode. Of course, other parameters are of interest, such as the value of thermal properties, the mode of heating (convection, conduction) and in the case of conduction the quality of contact between the sample and heated metal holder, and at last but not the least, the reaction taking place in the material.

Our purpose in this paper is to study the simultaneous effect of heating rate and sample size on heat transfer through cylindrical samples, when they are heated at a constant heating rate. In order to simplify the rather complicated problem, no reaction will take place in the sample, and the radial heat is transferred by conduction through the cross-section of the cylinder. The choice of the cylinder is of interest in our studies, because we can obtain experimental values from calorimetry, giving especially the heating rate as a function of time or temperature. For calculating the gradients of temperature developed through some samples of various sizes, we have used a model described previously [3,10]. This model, based on an explicit method with finite differences is able to take into account every kind of heat transfer, that by conduction in the problem at hand, and especially the quality of contact between the heated holder and the material.

THEORETICAL

Assumptions

Some assumptions are made:

- (i) Radial heat by conduction through the circular cross-section of the cylindrical sample only is considered.
- (ii) Thermal properties of the material such as thermal conductivity and diffusivity are constant during heating.

Mathematical treatment

With the above assumptions, the equation for heat conduction through the cross-section reduces to

$$\frac{\partial T}{\partial t} = \alpha \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \cdot \frac{\partial T}{\partial r} \right) \quad (1)$$

$$\frac{dT}{dt} = \text{constant on the holder} \quad (2)$$

The initial and boundary conditions are

$$t = 0 \quad 0 \leq r \leq R \quad T = T_o \text{ sample} \quad (3)$$

$$t > 0 \quad r > R \quad T = T_m \text{ calorimeter} \quad (4)$$

$$0 \leq r < R \quad T = T_{i,r} \text{ sample}$$

Numerical analysis

The problem has been solved by a numerical method with finite differences.

Let us consider the following circles of radius, r , $r + \Delta r$, $r + 2\Delta r$, etc., taken on the circular cross-section, r being between 0 and the radius of the sample R .

The heat balance determined for the ring between $r + \Delta r/2$ and $r - \Delta r/2$ gives the important relation

$$T_{i+1,r} = \frac{1}{M} [T_{i,r+\Delta r} + (M-2)T_{i,r} + T_{i,r-\Delta r}] + \frac{\Delta r}{2Mr} [T_{i,r+\Delta r} - T_{i,r-\Delta r}] \quad (5)$$

where $T_{i+1,r}$ is the temperature on the circle of radius r and at time $(i+1)\Delta t$.

For the middle of the cylinder ($r=0$), the following equation is suitable for calculating the temperature

$$T_{i+1,0} = \frac{4}{M} [T_{i,\Delta r} - T_{i,0}] + T_{i,0} \quad (6)$$

Another equation has been tested for the calorimeter-sample interface

$$T_{i+1,R} = \frac{1}{2} [T_{i,m} + T_{i,R}] \quad (7)$$

The dimensionless number M is a function of the increments of time and space

$$M = \frac{(\Delta r)^2}{\Delta t} \cdot \frac{1}{\alpha} \quad (8)$$

The heat flux transferred to the calorimeter vessel and detector is obtained by the following equation

$$\text{HF} = \lambda \frac{T_R - T_{R-\Delta r}}{\Delta r} \quad (9)$$

EXPERIMENTAL

Calorimeter

The apparatus (DSC 111, Setaram) is used in scanning mode, with various values for the heating rate ranging from 2°C min^{-1} to $20^\circ\text{C min}^{-1}$.

The holder has a radius of 0.25 cm. Heat flux is continuously recorded as a function of time and temperature.

Material

A commercial epoxide resin has been used. Of course, this resin has been cured previously. The thermal properties of the material are described in Table 1. They do not vary with the temperature in this case, but the model is available for temperature-dependent parameters.

Calculations

Calculations of the profiles of temperature are obtained with the help of eqns. (5–8). They are carried out for various values of the radius of the sample ranging from 0.125 to 1 cm.

The values chosen for the parameters are: $M = 5$, $\Delta r = 0.0125$ cm, $\Delta t = 0.05$ s. The number of slices is proportional to the value of the radius.

TABLE 1

Thermal properties of the resin

Thermal diffusivity	$\alpha = 0.25 \times 10^{-2} \text{ (cm}^2 \text{ s}^{-1}\text{)}$
Thermal conductivity	$\lambda = 10^{-3} \text{ (cal s}^{-1} \text{ cm}^{-1} \text{ K}^{-1}\text{)}$

RESULTS

When a material, cylindrical in shape, for instance, is heated on its cylindrical faces, the heat is transferred progressively from the faces to the middle. So, if the faces are heated at a constant heating rate, the temperature at the middle follows in a retarded way, and it may take a long time for the rate of heating at the middle to reach the constant value. As a result, the temperature at the middle is always lower than that on the faces.

The problem can be solved by a mathematical treatment. The heating rate on the circle of radius x is as follows, for a long cylinder of radius R

$$\frac{\partial T}{\partial t} = \frac{\alpha}{x} \cdot \frac{\partial}{\partial x} \left(x \cdot \frac{\partial T}{\partial x} \right) \quad (10)$$

while the heating rate b on the face is constant

$$T(R, t) = b \cdot t + k \quad (11)$$

A simple solution for eqns. (10) and (11) is of the form

$$T = ax^2 + ct + d \quad (12)$$

and it gives

$$T(R, t) - T(0, t) = \frac{bR^2}{4\alpha} = \Delta T \quad (13)$$

So, the difference ΔT between the temperature on the face and at the middle varies as a function of the heating rate and the square of the radius.

The purpose of this paper is to show that the experimental values obtained with the calorimeter are in agreement with these results, as well as the values obtained by calculation with the help of our model. Moreover, the model is able to predict the time necessary for the difference in the temperatures ΔT to reach the constant value, as a function of the heating rate and the radius of the cylinder. The model can also give some information of interest on the profiles of temperature developed through the material. And, at last, the model can take into account the particular parameter H qualifying the quality of the contact between the holder and the material.

Determination of the maximum values of the gradients of temperature (ΔT)

Two parameters are of interest: the radius of the cylindrical sample, and the heating rate on the cylinder face.

The temperature-time history on the face and at the middle of the cylinder is described in Figs. 1-3 for different heating rates ranging from 5 to 20°C min⁻¹ and various values of the radius between 0.125 and 1 cm.

As proved in Fig. 4, where the values of $\log \Delta T$ are plotted against the logarithm of the radius, the slopes obtained for these straight lines are equal to 2.

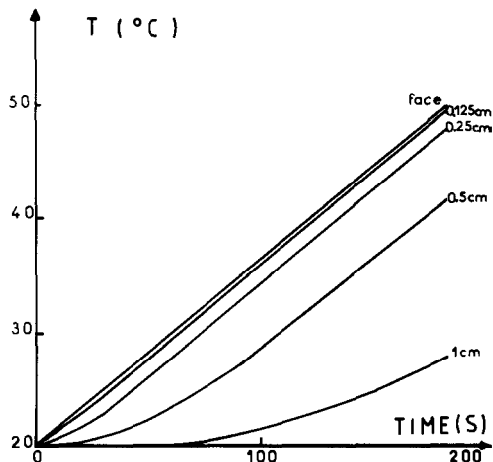


Fig. 1. Temperature-time history in various places through the sample, for different thicknesses. Heating rate = $5^{\circ}\text{C min}^{-1}$.

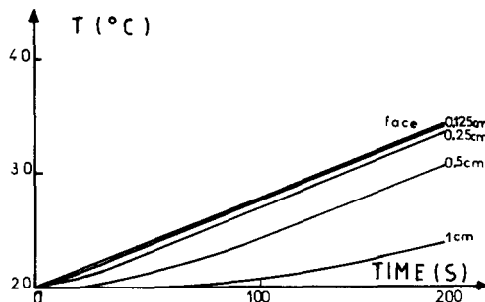


Fig. 2. Temperature-time history in various places through the sample, for different thicknesses. Heating rate = $10^{\circ}\text{C min}^{-1}$.

In the same way, straight lines are obtained by plotting $\log \Delta T$ as a function of $\log V$, the slope being 1 (Fig. 5).

Experiments carried out with the calorimeter and samples of 0.25 cm for the radius give about the same result as those obtained by calculation with the value of 1 given to the coefficient H for the quality of the contact between the holder and sample.

As a conclusion, the theoretical result shown in eqn. (13) is verified, for the values of ΔT corresponding with the higher gradients of temperature through the sample. Of course, this result is of interest, especially for calorimetric techniques working in scanning mode. When the heating rate is the same at the midplane and on the face, the difference in the temperatures on the face and at the middle is the higher, and then the value of ΔT varies with the heating rate and the square of the radius.

Profiles of temperature developed through the sample

Equations (5)–(7) are available for determining the profiles of temperature developed through the cross-section taken in the sample as a function of time.

Figures 6 and 7 illustrate the shape of these profiles of temperature obtained through two samples of 0.5 and 2 cm for the diameter, respectively, while the heating rate on the face is $20^{\circ}\text{C min}^{-1}$. As shown in the Fig. 6, these profiles are parallel to each other for times higher than 30 s. On the contrary, because of the larger thickness, the profiles of temperatures in Fig.

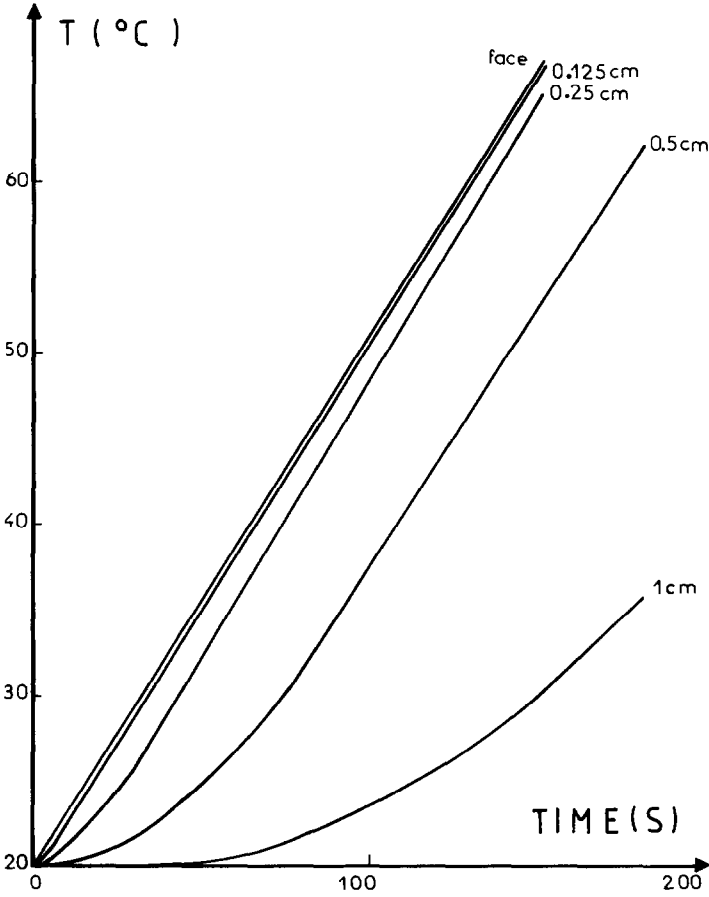


Fig. 3. Temperature–time history in various places through the sample, for different thicknesses. Heating rate = $20^{\circ}\text{C min}^{-1}$.

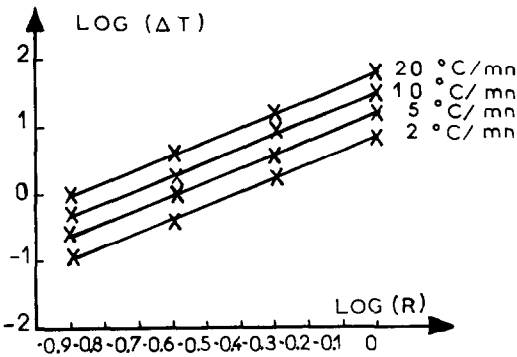


Fig. 4. $\text{Log } \Delta T$ as a function of $\text{log } R$, for various heating rates.

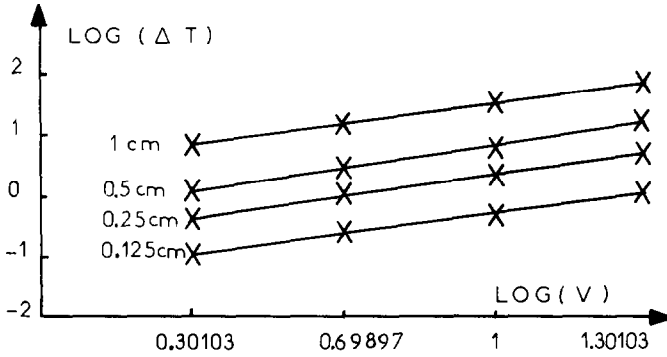


Fig. 5. Log ΔT as a function of log (heating rate), for various thicknesses.

7 are only parallel to each other for times higher than 90 s. The curves drawn in Fig. 7 are of interest to see how the heat progresses through the sample.

Heat flux as a function of time

The great interest of the model described above is to be able to give the heat flux emitted through the sample-calorimeter interface as a function of

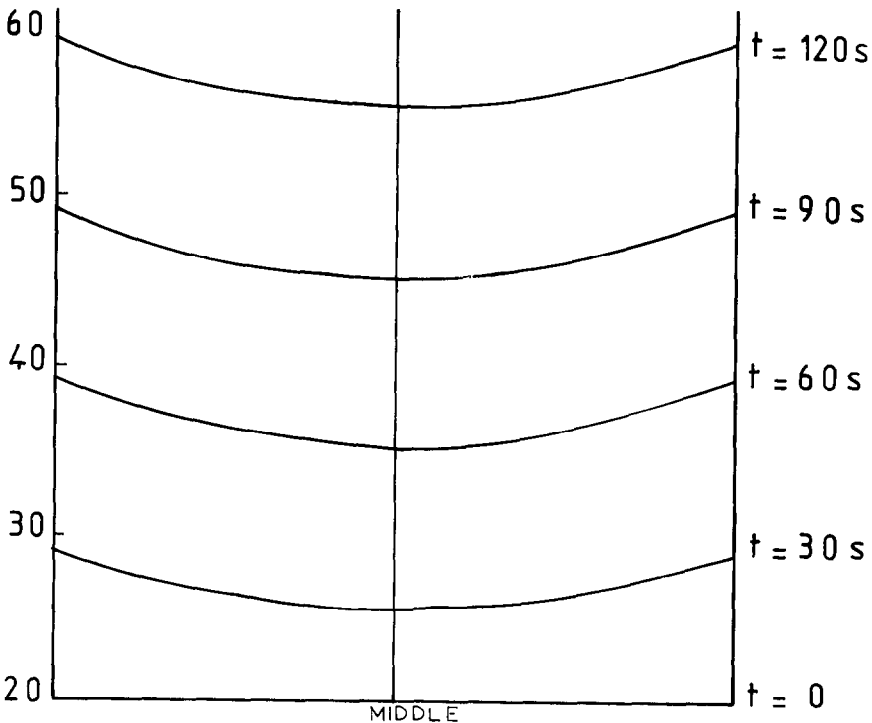


Fig. 6. Profiles of temperature developed through the sample (0.25 cm for diameter) at various times. Heating rate = $20^{\circ}\text{C min}^{-1}$.

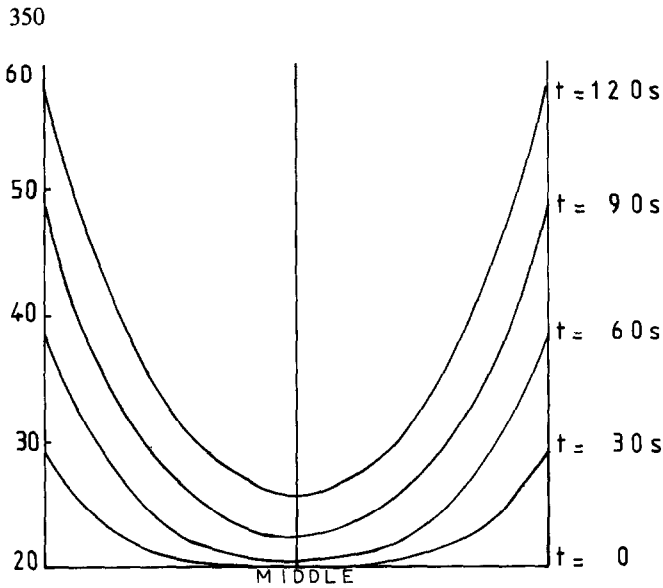


Fig. 7. Profiles of temperature developed through the sample (1 cm for diameter) at various times. Heating rate = $20^{\circ}\text{C min}^{-1}$.

time, by using eqn. (9). In fact, the heat flux can be measured with high accuracy by calorimetry. As shown previously [13–15], experimental values for heat flux are in good agreement with the corresponding calculated ones. This agreement is certainly the best proof for the validity of the model.

CONCLUSIONS

In the framework of studies devoted to the reaction taking place in samples heated with a scanning mode, as that occurs for instance in a calorimeter, the present work deals with the effect of some parameters of interest on the heat transfer through the sample. As an extension of the theoretical results, some results obtained in this paper can afford further insight into the nature of phenomena taking place in the sample. This information is necessary, heat transfer being the slower phenomenon. For instance, when the cylindrical sample is heated with a constant heating rate, the temperature at the middle increases very slowly at the beginning of the operation. After a particular elapse of time, the heating rate at the middle becomes equal to that imposed by the calorimeter. After this time, the difference in the temperature between the face and the middle (or the gradient of temperature) is proportional to the heating rate and the square of the diameter. The profiles of temperature developed through the cross-section of the cylindrical sample is also obtained as a function of time. The validity of the model is tested not only by temperature measurements at the middle of the sample but also and essentially by comparing calculated and experimental values of the heat flux emitted through the calorimeter.

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