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# TRANSIENT TECHNIQUE FOR DETERMINING SIMULTANEOUSLY THE THERMAL PARAMETERS AS A FUNCTION OF TEMPERATURE. A MATHEMATICAL TREATMENT

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ABSTRACT

The development of the industry of materials necessitates a good knowledge of the thermal parameters of these materials. This problem becomes very important when these materials must be heated. Two parameters are of great interest: the thermal conductivity and specific heat. Moreover, the information on the variation of these parameters with temperature is very often in great demand. A method using a calorimeter working under transient conditions is studied in a mathematical way. The technique involves a recurrent two-step process: the calorimeter is heated at a constant heating rate during the first step, and then the temperature is stabilized during the second step. An increase of a few degrees may be chosen for each step. The mathematical treatment is carried out by considering the heat flux emitted through the calorimeter–holder interface, in the case where both the holder and calorimeter are cylindrical in shape.

## INTRODUCTION

The rate at which heat can pass into and out of materials, especially polymers, is a measure of how efficiently it can be transferred. Therefore, it affects the design of processing machinery and controls the speed of many mixing, extruding and moulding operations. Heating and cooling are essential processes in the forming of most rubber and plastic articles. For instance, the control of heat is exceedingly important for costs and the quality of rubber vulcanizates. In the curing of rubber, there are two main requirements: on the one hand, the heating and curing cycle must be kept as short as possible for efficiency, and on the other hand, the temperature gradients in the article must be minimized for uniformity in the finished products. A simple compromise is obtained by trial and error leading to crude rule-of-thumb methods. The best compromise is attained by calculating the temperature distribution, and these results depend largely on a good knowledge of the appropriate thermal properties at the relevant temperature.

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Values of the thermal conductivity and heat capacity are needed for heat-flow calculations, but hardly any thermal diffusivity exists, and the reported values of thermal conductivity show very large scatter [1] as shown, for instance, for polystyrene and natural rubber. In fact not only do the values differ at some temperatures by more than 100%, and in the case of rubber by almost 300%, but also different trends are indicated throughout the temperature range [2]. It is clear that errors of this size cannot by due to variations in the sample, and they give some indication of the experimental difficulties associated with thermal property measurements. This lack of data is surprising in view of the importance of these basic material properties.

Firstly, it needs to be stressed that the thermal properties are very temperature dependent. For instance, it has been shown that the thermal conductivity of black-loaded natural rubber compounds decreases with increasing temperature, this decrease being as much as 45% over the temperature range from ambient to 200 °C [3]. Secondly, carbon black increases thermal conductivity in all elastomers, and generally additives modify that value for all materials. There is usually a break in the thermal conductivity–temperature curves at $T_g$ (the temperature of glass transition) for amorphous polymers. Moreover, cross-linking and the vulcanization additives usually do somewhat increase the thermal conductivity of a polymer [4].

Although various methods for the measurement of thermal conductivity are well documented in the literature, including the ASTM procedure [5], there remains a demand for rapid and versatile techniques for routine research with less stringent temperature equilibration and instrument operation. Some earlier attempts to utilize differential scanning calorimetry (DSC) have been made [6,7]. In contrast to the ASTM procedures, which require large samples and hours or days for one determination, the DSC procedure requires a relatively small amount of materials and takes only a few minutes for each determination of thermal conductivity. A further advantage of this last technique is that the specific heat can be readily determined by the same unit, allowing the calculation of the thermal diffusivity if the specific gravity is known.

Although a dynamic method would have the advantage of readings at different temperatures from one experiment giving thermal conductivity as a function of temperature, the isothermal method was usually adopted for its simplicity of operation and better reproducibility [6,7].

The purpose of this work is to show by means of a mathematical study that measurements can be simultaneously obtained for thermal conductivity and specific heat by using a transient method for calorimetry in scanning mode. The method of heating is a recurrent two-step process with the following cycle: in the first step the temperature is increased at a constant rate for a definite time, and in the second step the temperature is kept constant for another definite period of time. The time necessary for these steps is attained when the heat flux emitted through the calorimeter reaches equilibrium, either with an endothermic value in the first step or a zero value for the second step.

The experimental study is made by considering a rather large sample, cylindrical in shape, because of the interest we have found previously in these samples [8–9] for various materials as rubber of thermosets.

## THEORETICAL

### *Assumptions*

The following assumptions are made.

(i) The sample is cylindrical in shape.

(ii) The contact between the sample and the mould of the calorimeter is supposed to be perfect, without an air layer.

(iii) The heat flux is measured at the middle of the length of the sample so that the heat flux is radial only.

(iv) The thickness of the holder is neglected with regard to the radius of the sample.

(v) The calorimeter is treated according to the following two-step process: (a) the calorimeter is heated with a constant rate for a definite time, allowing the heat flux to become constant; (b) the temperature of the calorimeter is stabilized at constant temperature for another definite time necessary for the heat flux to reach the zero value.

By considering the cylindrical cross-section of the sample, the heat transfer is radial and the increase in temperature at the position $r$ is

$$\frac{\partial T}{\partial t} = \frac{1}{\rho C} \frac{1}{r} \frac{\partial}{\partial r}\left(\lambda r \frac{\partial T}{\partial r}\right) \tag{1}$$

and becomes

$$\frac{\partial T}{\partial t} = \frac{\alpha}{r} \frac{\partial}{\partial r}\left(r \frac{\partial T}{\partial r}\right) \tag{1a}$$

when the thermal conductivity $\lambda$ is constant (temperature independent). The diffusivity $\alpha$ is assumed to be constant within the range of temperature.

### *Study of the heating stage*

The following function of $r$ and $t$:

$$T = \frac{b}{4\alpha}(r^2 - R^2) + bt + c \tag{2}$$

where $b$ and $c$ are constant, is a solution of eqn. (1a), and the initial condition and boundary conditions during the heating of the sample are respectively

$$T(r,0) = \frac{b}{4\alpha}(r^2 - R^2) + c \quad \text{initial condition} \tag{3}$$

$$T(R,t) = bt + c \quad \text{boundary condition} \tag{4}$$

The profile of temperature within the cross-section is parabolic, and this curve is translated when the time is increased.

The heat flux can be written as

$$F = \lambda \frac{\partial T}{\partial r}(R,t) = \lambda \frac{bR}{2\alpha} = \frac{1}{2} bR\rho C \tag{5}$$

The other solutions $U$ of eqns. (1a) and (4) are obtained by adding together the particular solution (2) and an arbitrary solution of eqn. (1a) having zero value at the interface.

$$\frac{\partial U}{\partial t} = \frac{\alpha}{r} \frac{\partial}{\partial r}\left(r \frac{\partial U}{\partial r}\right) \tag{1a}$$

$$U(r,0) = f(r) \quad \text{with } f(R) = 0 \text{ and } f'(0) = 0 \tag{3a}$$

$$U(R,t) = 0 \tag{4a}$$

This classical problem has been solved [10]:

$$U = \sum_{n=1}^{\infty} \beta_n \exp\left(-\frac{\alpha t}{R^2} j_{0,n}^2\right) J_0\left(\frac{r}{R} j_{0,n}\right) \tag{6}$$

where

$$\beta_n = \frac{2}{R^2 J_1^2(j_{0,n})} \int_0^R x f(x) J_0\left(\frac{x}{R} j_{0,n}\right) \mathrm{d}x \tag{7}$$

$j_{0,n}$ being the $n$th positive root of the Bessel function $J_0$.

All solutions of the system of eqn. (1a) and the boundary conditions shown in eqn. (4) are in the form

$$V = T + U \tag{8}$$

The initial condition of $V$ then becomes

$$V(r,0) = f(r) + \frac{b}{4\alpha}(r^2 - R^2) + c \tag{3b}$$

Therefore the function $f(r)$ must be as follows:

$$f(r) = \frac{b}{4\alpha}(R^2 - r^2)$$

when the initial temperature in the sample is the same as the calorimeter temperature.

Then, for $\beta_n$ we have

$$\beta_n = \frac{bR^2}{2\alpha} \gamma_n$$

with

$$\gamma_n = \frac{1}{J_1^2(j_{0,n})} \int_0^1 u(1-u^2) J_0(u j_{0,n})\, \mathrm{d}u$$

where $u = x/R$.

The function $T$ verifying $T(r,0) = c$ for each $r$ is

$$T = c + bt + \frac{b}{4\alpha}(r^2 - R^2) + \frac{bR^2}{2\alpha} \sum_{n=1}^{\infty} \gamma_n \exp\left(-\frac{\alpha t}{R^2} j_{0,n}^2\right) J_0\left(\frac{r}{R} j_{0,n}\right) \tag{9}$$

The flux emitted through the calorimeter–sample interface becomes

$$F = \lambda \frac{bR}{2\alpha} + \gamma \frac{bR}{2\alpha} \sum_{n=1}^{\infty} \gamma_n j_{0,n} J_0'(j_{0,n}) \exp\left(-\frac{\alpha t}{R^2} j_{0,n}^2\right) \tag{10}$$

This flux function may be written in the following form:

$$F = \frac{1}{2} bR\rho C \phi\left(\frac{\lambda t}{\rho C R^2}\right) \tag{10a}$$

which has a limit for infinite time:

$$F = \frac{1}{2} bR\rho C \tag{11}$$

The rate of heat flow into a truncated cylinder of unit height is

$$D = 2\pi RF \qquad D = \pi R^2 b\rho C \phi\left(\frac{\alpha t}{R^2}\right) \tag{12}$$

This function $\phi$ is a purely mathematical function which is always the same whatever the values of the parameters. We shall study it in more detail later.

*Study of the isothermal stage*

During the heating stage with the constant heating rate $b$, the function $U$ decreases down to zero, and the profile of temperature tends to

$$T(r,t) - bt - c = \frac{b}{4\alpha}(r^2 - R^2) \tag{13}$$

Then at time $t_1$, the external temperature is stabilized at its final value: $T_1 = T(R,t_1) = bt_1 + c$. Thus, this final profile becomes the initial profile for the isothermal stage. The temperature in the cylinder increases as described by the function $-U$, opposite to the previous function:

$$T(r,t) = T_1 - U(r,t-t_1) \tag{14}$$

The flux emitted through the lateral surface of the cylinder becomes

$$F = \frac{bR\rho C}{2}\left\{1 - \phi\left[\frac{\alpha}{R^2}(t - t_1)\right]\right\} \tag{15}$$

with the same function $\phi$ defined above.

*Study of the function $\phi$ and its reciprocal function $\phi^{-1}$*

Let

$$\theta = \frac{\alpha t}{R^2} \qquad F_{\mathrm{L}} = \lim_{t \to \infty} F = \frac{bR\rho C}{2} \qquad y = \frac{F}{F_{\mathrm{L}}}$$

The dimensionless variables $\theta$ and y are linked by the relation

$$y = \phi(\theta)$$

where $\phi$ has been shown above. The value $y$ of the function $\phi$ increases from 0 to 1 when $\theta$ is increased from 0 to $+\infty$.

From eqn. (10), $\phi$ is expressed explicitly by its development in series by means of Bessel functions $J_0$ and $J_1$:

$$\phi(\theta) = 1 + \sum_{n=1}^{\infty} \gamma_n j_{0,n} J_0'(j_{0,n}) \exp(-\theta j_{0,n}^2) \tag{16}$$

In order to obtain its numerical values, it is easier to choose

$$R = 1 \qquad \rho C = 1 \qquad \lambda = 1 \qquad b = 2 \qquad c = 0$$

and solve numerically the system

$$\left.\begin{aligned} &\frac{\partial T}{\partial t} = \frac{1}{x}\frac{\partial}{\partial x}\left(x\frac{\partial T}{\partial x}\right) \\ &T(1,t) = 2t \quad t \geqslant 0 \\ &T(x,0) = 0 \quad 0 \leqslant x \leqslant 1 \end{aligned}\right\} \tag{17}$$

$$\phi(t) = \frac{\partial T}{\partial x}(1,t) \tag{18}$$

For the system (17), we have used the explicit numerical method with finite differences, which we have explained previously [8,11,12]. The radius is divided into $N$ equal parts, the increment of abscissa is $\Delta x = 1/N$, the increment of time is $\Delta t$, and $T(n,i)$ is the temperature at abscissa $n\Delta x$ and time $i\Delta t$.

$M = \Delta x^2/\alpha\Delta t$ is a dimensionless number, then

$$\left.\begin{aligned} T(n,i+1) &= \left[\left(1 + \frac{1}{2n}\right)T(n+1,i) + (M-2)T(n,i)\right. \\ &\qquad \left. + \left(1 - \frac{1}{2n}\right)T(n-1,i)\right]\frac{1}{M} \qquad 1 \leqslant n \leqslant N-1 \\ T(0,i+1) &= T(0,i) + (T(1,i) - T(0,i))\frac{4}{M} \\ T(N,i) &= 2i\Delta t \end{aligned}\right\} \tag{19}$$

The coefficient of $T(n,i)$ and $T(0,i)$ must be positive for calculation stability, and then $M > 4$.

TABLE 1

Calculated values of the function $\phi$

| Function $\phi$ | | | | | | | |
|---|---|---|---|---|---|---|---|
| $\theta$ | $y \times 100$ | $\theta$ | $y \times 100$ | $\theta$ | $y \times 100$ | $\theta$ | $y \times 100$ |
| 0.001 | 7.01 | 0.010 | 21.54 | 0.100 | 60.58 | 0.550 | 97.13 |
| 0.002 | 9.87 | 0.020 | 29.85 | 0.150 | 70.81 | 0.600 | 97.85 |
| 0.003 | 12.04 | 0.030 | 35.97 | 0.200 | 78.21 | 0.650 | 98.39 |
| 0.004 | 13.86 | 0.040 | 40.96 | 0.250 | 83.70 | 0.700 | 98.79 |
| 0.005 | 15.44 | 0.050 | 45.21 | 0.300 | 87.80 | 0.750 | 99.10 |
| 0.006 | 16.86 | 0.060 | 48.94 | 0.350 | 90.86 | 0.800 | 99.32 |
| 0.007 | 18.16 | 0.070 | 52.27 | 0.400 | 93.16 | 0.850 | 99.49 |
| 0.008 | 19.36 | 0.080 | 55.29 | 0.450 | 94.88 | 0.900 | 99.62 |
| 0.009 | 20.48 | 0.090 | 58.05 | 0.500 | 96.16 | 0.950 | 99.72 |
| | | | | | | 1.000 | 99.79 |

TABLE 2

Calculated values of the reciprocal function of $\phi$

| Reciprocal function of $\phi$ | | | | | |
|---|---|---|---|---|---|
| $y \times 100$ | $\theta$ | $y \times 100$ | $\theta$ | $y \times 100$ | $\theta$ |
| 5.00 | 0.00051 | 40.00 | 0.03794 | 80.00 | 0.21472 |
| 10.00 | 0.00205 | 45.00 | 0.04947 | 85.00 | 0.26435 |
| 15.00 | 0.00471 | 50.00 | 0.06306 | 90.00 | 0.33442 |
| 20.00 | 0.00856 | 55.00 | 0.07900 | 95.00 | 0.45427 |
| 25.00 | 0.01369 | 60.00 | 0.09764 | 96.00 | 0.49285 |
| 30.00 | 0.02021 | 65.00 | 0.11950 | 97.00 | 0.54259 |
| 35.00 | 0.02825 | 70.00 | 0.14535 | 98.00 | 0.61270 |
| | | 75.00 | 0.17639 | 99.00 | 0.73256 |

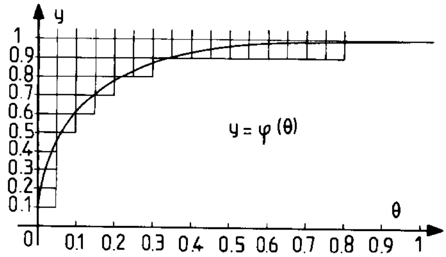


Fig. 1. A plot of $y$ vs. $\theta$.

For eqn. (18) we have used the parabolic approximation

$$\frac{\partial T}{\partial x}(1,t) = \left[3T(1,t) - 4T\left(1 - \frac{1}{N}, t\right) + T\left(1 - \frac{2}{N}, t\right)\right]\frac{N}{2} \tag{20}$$

In this case, this parabolic approximation is recommended, because the profile of temperature within the radius is developed from a straight line to an arc of a parabola.

By using $N = 200$ and $\Delta t = 5 \times 10^{-6}$, the function $\phi$ and its reciprocal, $\phi^{-1}$, have been calculated as shown in Tables 1 and 2 and in Fig. 1.

*Application for the determination of the thermal parameters*

During the interval of heating, the flux $F$ per unit area is registered experimentally as a function of time. The asymptotic value for the flux $F_L$ gives the specific heat per unit volume of the sample:

$$\rho C = \frac{2F_L}{bR}$$

From the relative heat flux $y$ measured at various times, it is easy to obtain from Table 2 the value of $\theta$ (where $\theta = \phi^{-1}(y)$) and then the thermal diffusivity and conductivity:

$$\alpha = \frac{\theta}{t}R^2 \qquad \lambda = \rho C R^2 \frac{\theta}{t}$$

Several facts of interest are worth pointing out.

(i) If the initial time $t_0$ (at which the flux is zero) is not zero and is not known precisely, we can write

$$\phi^{-1}(y) = \frac{\alpha}{R^2}(t - t_0)$$

The variable $z = \phi^{-1}(y)$ as a function of time is linear, with a slope $p = \alpha R^{-2}$. Thus, the whole curve can be determined when a part of it is known, or even when two points are very well known.

(ii) The preceding equations have been determined for constant thermal parameters. Otherwise an additional term taking into account the variation of $\lambda$ with temperature must be added to eqn. (1a):

$$\frac{1}{\rho C}\frac{d\lambda}{dT}\left(\frac{\partial T}{\partial x}\right)^2$$

As the gradient of temperature is approximately proportional to the heating rate, the additional term shown above becomes very small when the heating rate is low enough.

(iii) Of course, the heat flux must be measured around the circular section taken at the half height of the cylinder in order to obtain a radial heat transfer.

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