

A PULSE METHOD FOR DETERMINATION OF SPECIFIC HEAT AND THERMAL DIFFUSIVITY OF PLASTICS

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Abstract. *In this paper a pulse method of simultaneous determination of the specific heat and the thermal diffusivity of plastics by using double-layer sample "metal-plastics" has been presented. Investigations have been carried out using a sample made of polytetrafluoroethylene (PTFE) of diameter 12 mm with glued molybdenum foil of thickness 0.1 mm. The temperature range of investigations has 290 ÷ 400 K.*

1. Introduction

The relationship between the basic thermophysical parameters of solids, as the thermal conductivity λ , thermal diffusivity a , specific heat c_p and the density ρ is as follows

$$\lambda = \rho a c_p \quad (1)$$

Determination by means of an experiment of the three of the above parameters allows for the evaluation of the forth of them from formula (1)

Nowadays, the most common used methods of the thermal diffusivity a measurements of the opaque solids are the laser pulse methods [1,2,3]. On the other hand using these methods for the thermal diffusivity measurements of the materials semitransparent for the laser pulse radiation always causes technical and interpretative problems [5,6,8]. A pulse laser, usually made of neodymium, is used in these methods to generate the surface (in case of the opaque solids) or the volume (in case of the semitransparent solids) heat sources on the surface or in the volume of the investigated sample, respectively.

Plastics are usually materials semitransparent for pulse laser radiation. This leads to substantial complications when evaluating heat diffusivity by means of pulse methods. The evaluation of specific heat c_p involves even greater problems. In practice the thermal diffusivity of the semitransparent solids can be measured in two different ways [6,8]. Both versions of the pulse method are based in the experimental part on the measurement of the temperature difference $\Delta\Theta(t)$ on the front and rear surfaces of the sample after one of them has absorbed the laser pulse radiation. The second one concerns the pulse method with the pulse radiation shielding of the inside of the sample. Thin metal foil glued on the front sample surface or thin metal

coatings sputtered on this surface are used as the shields. It is connected with the model of the heat transfer in the adiabatic, flat – parallel, double - layer sample in which the initial temperature distribution is given in consequence of the laser pulse absorption. As opposed to the first version, here it is possible to record the temperature change $\Delta\Theta(t)$ and temperature Θ_p of the investigated layer of the sample as well as Θ_m of the metal foil during the same measurement. The second version can almost automatically be used to simultaneous determination of thermal diffusivity a and specific heat c_p of the plastic.

2. Description of the method

2.1. Measurement of the thermal diffusivity of the semitransparent to laser pulse radiation samples.

Measurement of the thermal diffusivity of the semitransparent to laser pulse radiation samples gives the best results by means of screening interior of the sample against the laser pulse. Thin foil glued on to the front surface of the sample or thin metal coating sputtered on this surface is used as the shields (Fig.1a). In this case the model of the heat exchange in the double-layer sample is shown in Fig. 1b.

A formula for the thermal diffusivity was derived by Larson and Koyama [4] in the form of the dimensionless temperature distribution

$$U(x,t; X, H, \vartheta_2, \gamma_2) = \Theta(x,t; X, H, \vartheta_2, \gamma_2) / \Theta_\infty \quad (2)$$

inside the layer $i = 2$, of the double-layers sample ([5], Eq. (43)).

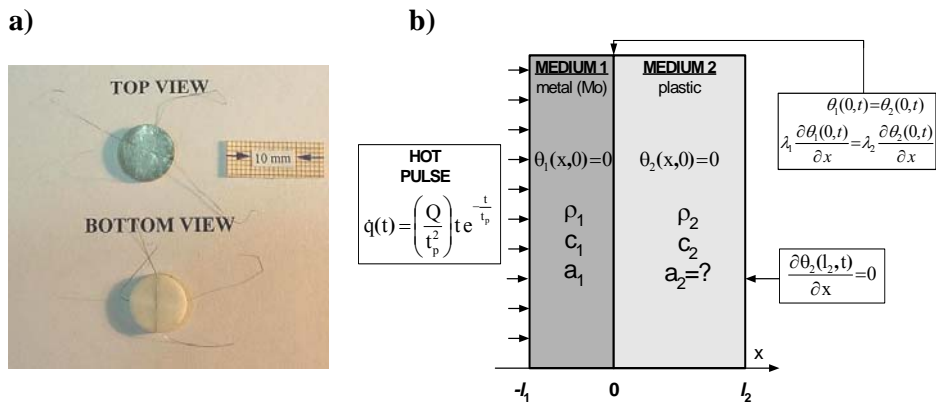


Fig.1: a) View of the double-layer sample with thermocouples; b) model of the heat exchange used for the thermal diffusivity and specific heat determination.

The solution given by Larson and Koyama can be transformed into a simpler form for the temperature difference between the opposite surfaces of the second layer of the sample (in our case PTFE). It can be expressed in the form

$$\Delta\Theta(t) = \Theta(x=0,t) - \Theta(x=l_2,t) = 2\Theta_\infty \sum_{k=1}^{\infty} B_k \exp(-b_k^2 \frac{t}{\tau}), \quad (3)$$

where:

$$- \quad B_k = \frac{\cos(\beta_k) - 1}{\cos(\beta_k X) \cos(\beta_k) - \Omega(X) \sin(\beta_k X) \sin(\beta_k)} ; \quad (3a)$$

- $\beta_1 = b_0 \pi$ is the first and $\beta_k = b_k \beta_1$ ($k \geq 2$) are the next positive roots of equation

$$H \sin(\beta X) \cos(\beta) + X \cos(\beta X) \sin(\beta) = 0 ; \quad (3b)$$

- τ – is the characteristic time of the 2-nd layer of the double-layer sample, according to [5] it is equal to

$$\tau = \frac{l_2^2}{\beta_1^2 a_2} = \left(\frac{1}{b_0^2} \right) \frac{l_2^2}{\pi^2 a_2} ; \quad (3c)$$

whereas coefficient $1/b_0^2$ takes into account the double-layer character of the investigated sample;

- X, H, Ω – the dimensionless coefficients in equations (3a) and (3b)

$$\left. \begin{aligned} X &= (l_1/l_2)(a_2/a_1)^{0.5}, \\ H &= (\rho_1 c_1 l_1)(\rho_2 c_2 l_2)^{-1}, \\ \Omega(X) &= (X + HX^{-1})(H + 1)^{-1}. \end{aligned} \right\} \quad (3d)$$

The dependence (3) was derived under assumption:

$$l_2^2 (a_2 t_p)^{-1} \gg \beta_k^2 . \quad (4)$$

The thermal diffusivity is evaluated as follows:

- in the first stage the thicknesses of the individual layers l_1 and l_2 is determined. Then the thermophysical parameters $\rho_1, c_1, a_1, \rho_2, c_2$ are measured or are given from the literature (all in the temperature in which the thermal diffusivity $a(T) = a_2(T)$ is evaluated);
- in the second stage on the basis of the expression (3) the experimental initial value of the thermal diffusivity $a'(T) = a_{2,0}(T)$ of the two layers sample is obtained (assuming the homogeneous and the opaque sample to laser radiation). Necessary for the evaluation $a'(T) = a_{2,0}(T)$ and c_p , the characteristic time τ and the temperature increase $\Theta_p = \Theta_\infty$ of the sample after the time equalisation on its opposite surfaces are determined according to [8], on the basis the measuring signal of the temperature

difference between opposite surfaces of the sample after the laser shot $\Delta\Theta'(t)$, from the formulas

$$\tau = (t_2 - t_1) \ln \frac{\Delta\Theta(t_1)}{\Delta\Theta(t_2)}, \quad \Theta_\infty = 0.25 \exp(y_{\max}) \quad (5)$$

where: $y_{\max} = \lim_{t \rightarrow 0} \Delta\Theta(t)$.

The thermal diffusivity is calculated from

$$a = \frac{l^2}{\pi^2 \tau}. \quad (6)$$

- in the third stage under the assumption that $a(T) = a_{2,0}(T)$, the values of X , H , $\Omega(X)$ and the first five characteristic numbers β_k are evaluated from the equation (3b). Now the equation (3) can be transferred into the expression for $\Delta\Theta_1(t)$, in which the two layers of the sample are taken into account. This dependence is the basis to fit again the theoretical curve $\Delta\Theta(t)$ from the collection $\Delta\Theta_1(t)$ into the experimental curve $\Delta\Theta'(t)$, which is a way to evaluate the new value of the thermal diffusivity $a'(T) = a_{2,1}(T)$;
- in the fourth stage on the basis of the value $a(T) = a_{2,1}(T)$ (obtained in the third stage) the procedure is repeated again.

In practise the two evaluations are sufficient to obtain the results accurate enough for the technical purposes.

2.2. Measurement of the specific heat

Measurement of the specific heat c_p by this method can be brought up to measure the following quantities:

- the temperature increase Θ_m of the metal foil acting as a shield against a direct absorption of the laser pulse radiation in the second layer (plastic) just after the laser shot. The temperature increase Θ_m of the metal foil is determined at the time t_m when it is accepted that the foil temperature along the thickness of the sample has been equalised and heat exchange between the foil and its surroundings as well as the second layer (plastic) is small to such an extent that it can be neglected. Assuming that the following relation $a_m \gg a_p$ and $l_m \ll l_p$ occurs in the samples, where a_m and l_m stand for the thermal diffusivity and the thickness of the metal layer, respectively and a_p and l_p concern the sample, so just after the laser shot there is such a time interval t_m when the metal layer may be regarded approximately as adiabatic one and just then the temperature excess Θ_m is measured;
- the temperature increase $\Theta_p = \Theta_\infty$ of the double-layer sample after the transient process ($t \geq 5\tau$) due the laser shot over the metal foil. The temperature increase Θ_p of the double-layer sample is determined while the thermal diffusivity of the plastic is evaluated and calculated at the known

specific heat c_m of the metal foil and known densities and thicknesses of the metal layers (ρ_m i l_m) as well as the plastic (ρ_p i l_p), using the relation $Q_m = \rho_m A l_m c_m \Theta_m$, the laser pulse energy being absorbed by the metal layer and then by the two-layer sample $Q_s = (\rho_m l_m c_m + \rho_p l_p c_m) A \Theta_p$.

The specific heat c_p of the plastic is calculated according to $Q_m = Q_s$ and it is equal

$$c_p = \frac{\rho_m l_m}{\rho_p l_p} \left(\frac{\Theta_m}{\Theta_p} - 1 \right) c_m \quad (7)$$

Realised here measurement of the specific heat c_p of the plastic is of calorimetric character.

Heat exchange from the metal foil due to heat conduction to the next layer of the sample, that is the loss of heat of the first layer during time interval between the laser shot and the temperature equalisation in that layer can be estimated approximately in the following way:

- a minimum time necessary to make the temperature of the sample layer even is equal to

$$t_m = 5\tau = 5 \frac{l_m^2}{\pi^2 a_m} \quad (8)$$

where τ is the characteristic time of the first layer of the sample, a_m is the thermal diffusivity of the metal foil and l_m is the thickness of the foil;

- thus if the temperature increase Θ_m of the metal foil is taken during experiment for $t_m < t < 20 t_m$ that is in the range $\Delta t_m = 20 t_m$ and there is temperature derivate $d\Theta_m(t)/dt$ known, than it is possible to estimate the measurement error of the specific heat c_p due to uncertainty of $\Theta_m(t)$ determination.

3. Apparatus

A block diagram of the apparatus is shown in Fig. 2. A pulse heat source is generated on the front surface (Mo foil) of the double-layer sample by means of a pulse neodymium laser with the beam about 14 mm in diameter and the pulse energy 5 ÷ 15 J. A typical duration time of the laser radiation pulse generated by the neodymium laser applied for the laboratory stand is about 1 ms. Inside the furnace a vacuum of order 10^{-4} Pa was maintained in time of the measurements.

In case of non-metals thickness l of the investigated samples is of order of 1 ÷ 2 mm. For the double-layer samples (metal – plastic) the quantities T_2 and $\Delta\Theta'(t)$ are measured by using the 50 μ m in diameter thermocouples from iron and CuNi electrically welded to Mo foil (front surface) and directly glued to the rear surface of the sample (Fig. 1a)

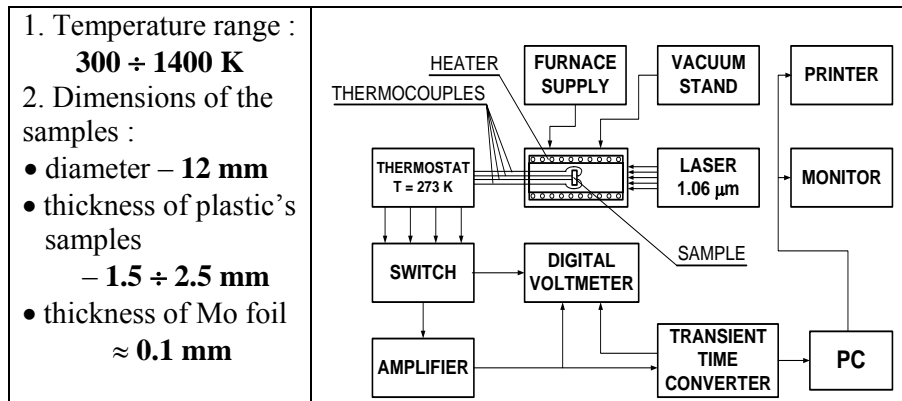


Fig.2. A block diagram of the laboratory stand for the thermal diffusivity and specific heat determination of solids.

Typical temperature difference changes on the opposite sample's surfaces, the base for the thermal diffusivity determination by means of this method are shown in Figure 3 (double-layer sample). The same figure presents the final effect of the data processing in the form:

- time range (t_1 and t_2), where the quantity τ and its value were determined (see Eqs (3c), (5) and (6));
- evaluated numerically value of θ_∞ (see Eqs (2), (3), (5) and (7));
- experimental results $\Delta\theta'(t)$ and its approximation by means of the $\Delta\theta(t)$ curve, which is received from the set of the theoretical solutions of the problem.

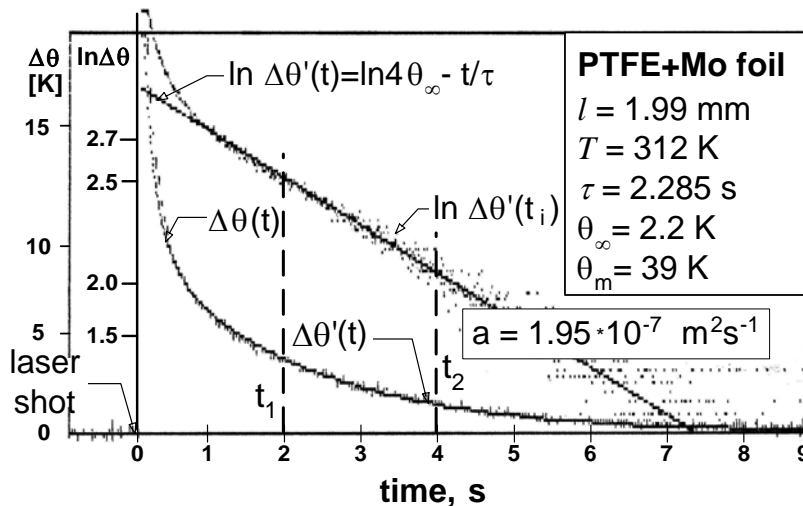


Fig. 3. Typical example of a digital recording of the temperature difference $\Delta\theta'(t)$ on the sample's opposite surfaces of the double-layer sample "PTFE-Mo foil" together with final processing of the signal during the thermal diffusivity and specific heat evaluation.

The real value of the thermal diffusivity a in the double-layer samples was calculated according to procedure described in the 2 chapter. Values of the

thermal diffusivity of the investigated samples were calculated using the expressions:

$$a_{PTFE}(l_2 = 1.56mm) = a_{2,PTFE} = \frac{l^2}{\beta_1^2 \tau} = 1.11 \frac{l^2}{\pi^2 \tau} \quad (9)$$

$$a_{PTFE}(l_2 = 2.18mm) = a_{2,PTFE} = \frac{l^2}{\beta_1^2 \tau} = 1.10 \frac{l^2}{\pi^2 \tau} \quad (10)$$

where the thickness l of the sample is given by [6, see (49)].

Results of preliminary investigations of the thermal diffusivity and specific heat for the PTFE, by means of application of the methods described above, are shown in Figure 4 and 5. The investigations were carried out in temperature range 290 - 400 K.

It was found from [8] that the error of the thermal diffusivity measurements was less than 6 % and the error of the specific heat measurements was less than 15 % in the whole range of the temperature changes.

The following data : : $l_m = 10^{-4}$ m, $l_p = 1.99 \cdot 10^{-3}$ m, $\rho_m = 10200$ kg/m³, $\rho_p = 2200$ kg/m³ and $c_m = c_{Mo} = 255$ J/kgK were accepted to determine the specific heat c_p and thermal diffusivity of PTFE to make calculations possible. For example, of temperature 312 K it was obtained $\Theta_p = 2.2$ K and $\Theta_m = 39$ K (see Fig.3).

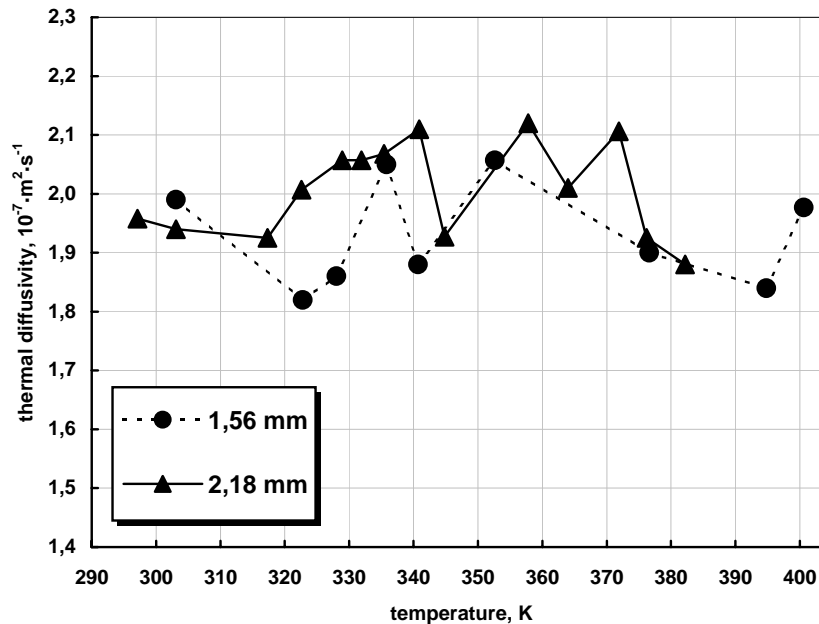


Fig.4. Results of the thermal diffusivity investigation of the polytetrafluoroethylene (PTFE) obtained for the double-layer sample “PTFE –Mo foil”

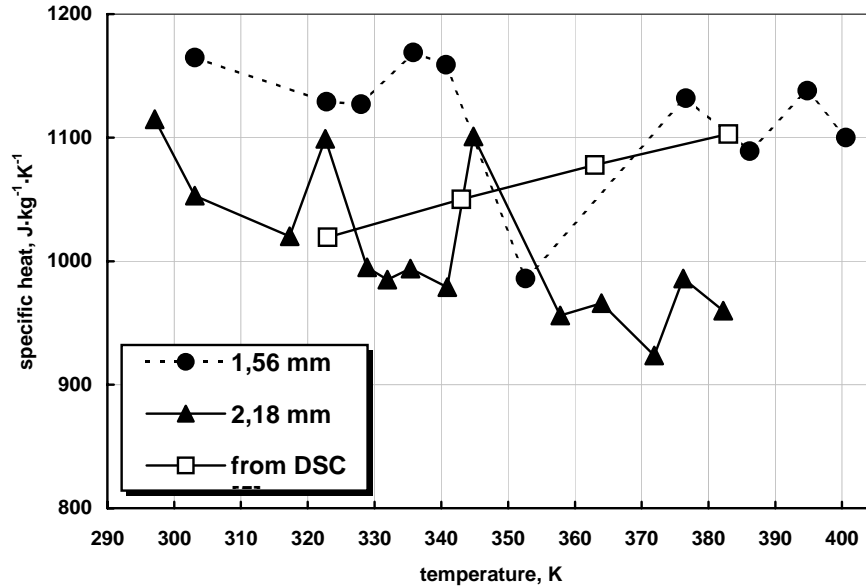


Fig.5. Results of the specific heat investigations of the polytetrafluoroethylene (PTFE) obtained for the double-layer sample “PTFE –Mo foil”

Thus

$$c_p(312K) = \frac{10^{-4} \cdot 10200}{1.99 \cdot 10^{-3} \cdot 2200} \left[\frac{39}{2.2} - 1 \right] \cong 994 \text{ J / kgK}$$

On the other hand, the minimum time necessary to even the temperature the molybdenum foils equals

$$t_m = 5\tau = 5 \frac{l_m^2}{\pi^2 a_m} = \frac{5 \cdot 10^{-8}}{3.14^2 \cdot 52.7 \cdot 10^{-6}} \cong 0.1 \text{ ms}$$

Results of preliminary investigations of the specific heat of polytetrafluoroethylene (PTFE) by the method briefly described in this paper are shown in Fig. 5, together with the results obtained by the both methods. one can conclude that the method of the author can be applied to the rapid but rough measurements of specific heat. It seems that the method permits obtaining more precisely results like DSC after its improvement.

4. Summary and conclusions

In this work an effective pulse method of simultaneous determination of the specific heat and thermal diffusivity of plastics has been presented. The method is based on known solution of the heat transfer model in a double-layer adiabatic sample in which one of its face surfaces is exposed to a laser pulse radiation. The response of the sample to such an input function in a shape of the recorded temperature difference at the interfaces was a base to determine both the thermal diffusivity and specific heat.

Advantages of the method are as follows:

- a comparatively high accuracy of measurement – of about 5 % for the thermal diffusivity and about 15 % for the specific heat;
- a possibility to measure both the specific heat and the thermal diffusivity of transparent as well as opaque laser radiation plastics;
- a possibility to take into account heat losses from the sample interfaces upon the thermal diffusivity and the specific heat determination.

Drawbacks of the method are as follows:

- the method can be used in such temperature range where glue keeps its properties, practically up to 150 °C;
- time- and labour-consuming preparation process of flat-parallel layer of plastic - diameter 12 mm and thickness 1÷2 mm (* precise glutination of a metallic layer (≈ 0.1 mm) to a plastic, so that the two surfaces of the now double-layered sample are flat-parallel and the glue film – as thin as possible, * at the interfaces of sample – electric welding of thermocouple wires ($\phi = 40 \mu\text{m}$) to the metal surface and mechanical sticking to glueing the plastic surface).

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