

Hot-Wire Parallel Technique: A New Method for Simultaneous Determination of Thermal Properties of Polymers

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ABSTRACT: The hot-wire parallel technique standardized for determining the thermal conductivity of ceramic materials was employed in the determination of the thermal properties of polymers. For these materials, additional care must be taken considering the low melting point of polymers, when compared with that for ceramic materials. Samples can be prepared either in the shape of bricks or in the shape of half-cylinders. The thermal conductivity and the specific heat were simultaneously determined from the same experimental thermal transient, and the thermal diffusivity is derived from these properties. Five different polymers with different structures at room temperature were selected, and measurements were carried out from room temperature to approximately the maximum service operating temperature. A nonlinear least-squares fitting method was employed in the calculations, so that all the experimental points obtained are considered in the thermal properties' calculations. The apparatus used in this work is fully automatic. The reproducibility is very good with respect to the thermal conductivity, even with a defective experimental arrangement with respect to the theoretical model. However, deviations from the theoretical model have a severe influence on the specific heat values and, consequently, on the thermal diffusivity. Experimental results were compared with those available in the literature, showing the applicability of this technique for the determination of thermal properties of polymers. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1779–1786, 2002

Key words: polymers; thermal properties; heat capacity; calculations; hot wire

INTRODUCTION

Thermal conductivity, thermal diffusivity, and specific heat are the three most important physical properties of a material that are needed for

heat-transfer calculations. The equation relating these properties is given by

$$\alpha = \frac{k}{\rho c_p} \quad (1)$$

where α is the thermal diffusivity (m^2/s); k , the thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$); ρ , the bulk density (kg/m^3); and c_p , the specific heat ($\text{J kg}^{-1} \text{K}^{-1}$).

Thermal conductivity assumes a critical role in the performance of materials in many applications. Low thermal conductivity values are required when the purpose is to minimize heat ex-

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changes. On the other hand, when heat transfer from one site to another is desirable, materials with higher thermal conductivities must be chosen. So, reliable thermal conductivity values are essential in a selection of a material to get the best performance in a specific application.

Thermal conductivity is the property that determines the working temperature levels of a material, and it is an important parameter in problems involving steady-state heat transfer. However, it is one of the physical quantities whose measurement is very difficult and it requires high precision in the determination of the parameters involved in its calculations.

The specific heat (heat capacity per unit mass) is also a critical property in many applications. It is a thermodynamic quantity that is relatively simple to be determined for small and homogeneous samples. However, for heterogeneous materials having different phases, where the quantity to be measured is the specific heat of the bulk of the body, including all present phases, it is almost impossible to prepare a small and representative sample, so that the measurement of this property must become particularly troublesome.

Thermal diffusivity is a measure of rapidity of the heat propagation through a material. It is an important property in all problems involving non-steady-state heat conduction.

As for ceramic materials, reliable thermal property values are essential for polymers, both in steady and non-steady-state situations. A typical example of a non-steady-state problem, common in polymer engineering, is the extrusion process. Since through this process the polymer experiences a complicated thermal history, knowledge of the thermal properties of the polymer is crucial in the description and analysis of the entire extrusion process.¹ In steady-state situations, the thermal conductivity is essential for a suitable application like insulators.

HOT-WIRE PARALLEL TECHNIQUE

The hot-wire parallel technique is an absolute, non-steady-state and direct method, and, therefore, it makes the use of standards unnecessary. The hot-wire method was described by Schieirmacher in 1888,² and its first practical application was reported in 1949 by Van der Held and Van Drunen,³ in the determination of the thermal conductivity of liquids. However, it was Haupin⁴ who, in 1960, first used this method to measure

the thermal conductivity of ceramic materials. Nowadays, the hot-wire method is considered as an effective and accurate means of determining the thermal conductivity of ceramic materials. However, it is not possible to use this method for electrical conductor materials, unless some process of electric insulation between the hot wire and the sample is developed. It is a very suitable technique for the purpose of this work since it is possible to measure thermal conductivities at room temperature, which is impossible when using calorimetric methods. In addition, with the hot-wire technique, the concept of "mean temperature" between hot and cold faces of a sample on thermal conductivity calculations is eliminated, since the measurement is carried out at a fixed temperature. The temperature gradient across the sample is very low, and this is another virtue of this technique, since an ideal method for measuring thermal conductivity would be one capable of measuring this property across a zero-temperature gradient throughout the sample.

In the mathematical formulation of the method, the hot wire is assumed to be an ideal infinitely thin and long heat source which is in an infinite surrounding material whose thermal conductivity is to be determined. This assumption implies that the temperature transient that is picked up by the thermocouple joint, at the measuring point, during the experiment cannot be altered by the fact that the actual sample has finite dimensions. These considerations mean some restrictions in the applicability of the hot-wire technique in terms of possible sample sizes and thermal conductivity allowable ranges.

Applying a constant electric current through the wire, a constant amount of heat per unit time and unit length is released by the wire and propagates throughout the material. This propagation of heat throughout an infinite medium generates a transient field of temperatures, which is logarithmically dependent on the time. In practice, the theoretical infinite linear source is approached by a thin electric resistance and the infinite solid is replaced by a finite sample. The difference between the actual and the theoretical time-temperature curves, when one of the possible variations (hot-wire standard technique) is used, is shown in Figure 1. Nonlinearity in the early part of the real curve is caused by contact resistance between the wire and the sample and the heat capacity of the wire, and the departure from linearity in later part of the curve is due to the finite sample size. The intermediate region of

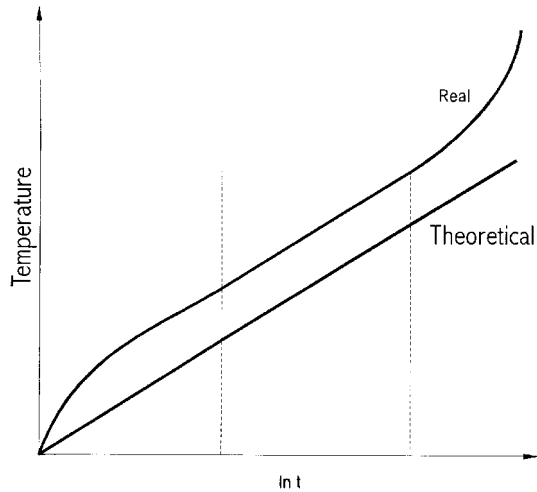


Figure 1 Theoretical and actual temperature–time curve.

the curve, where real and theoretical plots have the same behavior, defines the time limits to be considered in any measurement. To get accurate and consistent results, some theoretical aspects must be considered⁵.

1. The heating wire must approximate as closely as possible the theoretical line source.
2. The duration of the test must be limited, since a finite-size sample cannot affect the measured temperature. The maximum measuring time, t_{\max} , must be within the intermediate region of the temperature–time curve.
3. The early part of the curve must be neglected in calculations to ensure that the contact resistance is not affecting the measurement. So, the correct choice of t_{\min} , the minimum time considered in calculations, is very important.
4. The contact between both samples and wire must be as best as possible since the theoretical model assumes the hot wire as a line source in a surrounding material without any interface between the samples.

Four variations of the hot-wire method are known⁶: the hot-wire standard technique, hot-wire resistance technique, two thermocouple techniques, and the hot-wire parallel technique. The theoretical model is the same, and the basic difference among these variations lies in the tem-

perature measurement procedure. Two pieces are required whatever is the variation to be used.

In 1996, de Carvalho et al.⁷ employed the hot-wire standard technique in the determination of the thermal conductivity of four commercial polymers at room temperature. In the present work, the variation employed is known as the hot-wire parallel technique. The great advantage of this variation compared with the standard technique is that, in this case, the thermal conductivity, the specific heat, and the thermal diffusivity are simultaneously determined from the same experimental thermal transient.

With the hot-wire parallel technique, it is possible to measure thermal conductivities up to $25 \text{ W m}^{-1} \text{ K}^{-1}$,⁸. Samples may be prepared either in the shape of rectangular parallelepipeds or half-cylinders. In the case of the choice of half-cylinder-shaped samples, the radius and height of the cylinder should correspond to the height and length of the parallelepiped. The minimum dimensions required for the samples, to fulfil the theoretical model requirements, depend on the thermal diffusivity of the material to be tested. For ceramic materials, this technique was standardized for samples in the shape of bricks with the dimensions of $(230 \times 114 \times 64) \text{ mm}$. The effect of the finite sample size reported by Cintra and Santos⁹ in 2000 for ceramics is also valid for polymer materials, and the errors involved, due to the sample finite dimensions, can be estimated.

Between two equal specimens, the heating wire and the thermocouple are placed in two parallel ground grooves. The depth of the grooves is approximately the same as that of the wire diameters to be embedded. The recommended distance r between the hot wire and the thermocouple is from 15 to 17 mm. The comparison junction is kept elsewhere at a fixed temperature, and that is the reference temperature. By applying a constant electric current throughout the wire and recording the temperature increase at the measuring point M_p located at a distance r of the hot wire, the thermal conductivity is calculated according the following equation⁸:

$$k = \frac{-q'}{4\pi T(t)} E_i\left(\frac{-\rho c_p r^2}{4kt}\right) \quad (2)$$

where k is the thermal conductivity of the material ($\text{W m}^{-1} \text{ K}^{-1}$); q' , the linear power density (W m); ρ , the material bulk density (kg/m^3); c_p , the specific heat of the material ($\text{J/kg}^{-1} \text{ K}^{-1}$); the

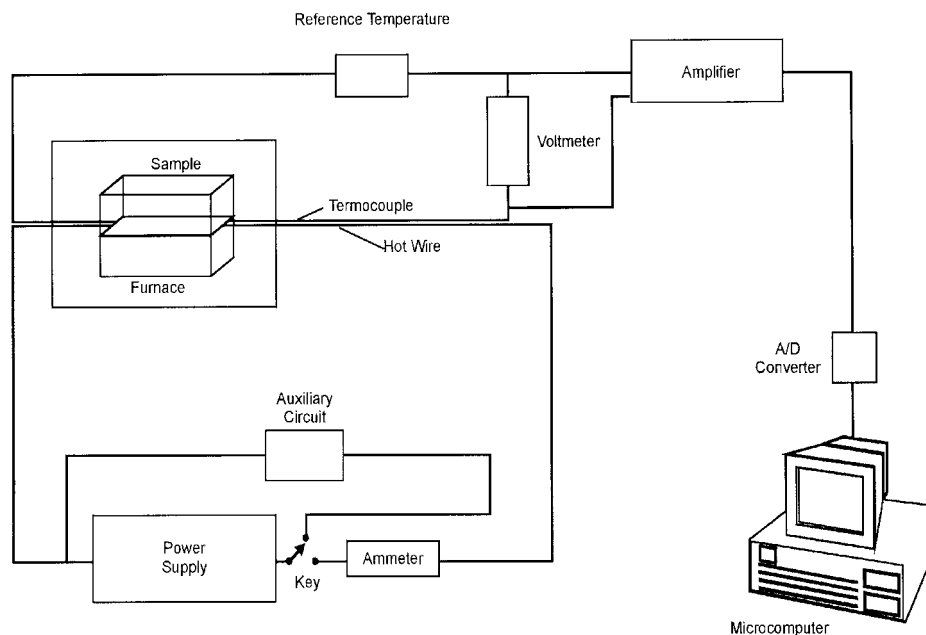


Figure 2 Schematic of hot-wire parallel equipment.

distance between the hot wire and the thermocouple (m); t , the elapsed time after the beginning of the heat release (s); $T(t)$, the temperature increase registered by the thermocouple related to the initial reference temperature (K); and $-E_i(-x)$, the exponential integral function.

This variation of the hot-wire method was standardized in 1978 by DIN-51046 Standard-Part 2, for ceramic materials.^{10,11} The thermal conductivity is determined for several pairs of selected t and $2t$ times, using eq. (2) and the several values obtained are then averaged. In our work, a different procedure was adopted. The calculations, starting from the recorded temperature transient in the sample, are carried out using a nonlinear least-squares fitting method.¹² Both the thermal conductivity and the specific heat in eq. (2) are fitted to obtain the best possible approximation between the thermal transient experimentally registered and that one predicted by the theoretical model. In this case, these two thermal properties, thermal conductivity and specific heat, are simultaneously determined from the same experimental transient. So, with knowledge of the density, thermal diffusivity is then calculated using eq. (1). Therefore, by using the same apparatus, it is possible to determine these three thermal properties in the same experiment.

The schematic diagram of the apparatus used in this work, as shown in Figure 2, is fully automatic, and the transient of the temperature de-

tected by the thermocouple is recorded and processed by a computer via an analog-to-digital converter using a software specially written for this purpose.

SAMPLE PREPARATION

In this work, specimens of commercial polymers in the shape of a rectangular parallelepiped with dimensions $230 \times 80 \times 30$ mm were cut from large polymer plates. The parallel ground grooves were made with the aid of the hot wire itself by applying a suitable electric current, melting the polymer and providing a perfect contact between the wire and the sample. The measuring point M_p was kept between 15 and 16 mm in all samples. The sample arrangement is shown in Figure 3. With the purpose to minimize electronic noise and eliminate fluctuations of the amplifier caused by very low input voltages, the reference joint was kept at 0°C . This procedure is recommended, since low linear power density is applied through the wire to avoid any meltdown regions and degradation inside the sample, having in mind the low melting point of polymers when compared with ceramic materials. To ensure good contact between the samples, they were pressed one against the other with the use of stainless-steel rings.

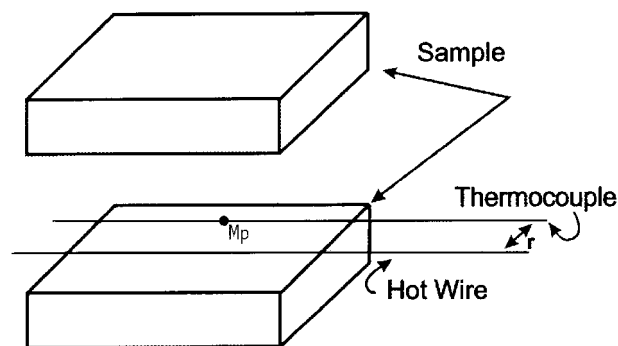


Figure 3 Parallel hot-wire technique. Experimental set-up.

Five different samples were prepared using different classes of polymers. Details of the samples are given in Table I.

RESULTS AND DISCUSSION

Measurements were carried out from room temperature to approximately the maximum service temperature. A typical temperature transient registered is shown in Figure 4 (sample PMMA–25°C). The thermal conductivity and specific heat were obtained from the temperature transient for the corresponding sample using a nonlinear least-squares fitting method, and the thermal diffusivity was derived with the aid of eq. (1).

Experimental results obtained are compared with those ones found in the literature,^{1,13–16} and they are shown in Table II(a, b). By analyzing the results shown in Table II(a), it is possible to assert that the hot-wire parallel technique is a suitable method for measuring the thermal properties of polymers, even any deviations that can be found when the results are checked against the

Table I Sample Details

Polymer	ρ (kg/m ³)	T_g (°C)	T_m (°C)	T_s (°C)
Nylon 66	1151 ^a	55 (ref. ¹)	265 ^b	110 ^b
PP	906 ^a	–10 (ref. ¹)	170 ^b	90 ^b
PMMA	1186 ^a	105 (ref. ¹)	—	70 ^b
PVC rigid	1368 ^a	80 (ref. ¹)	—	70 ^b
PU foam	32 ^a	—	—	35 ^b

ρ , density; T_g , glass transition temperature; T_m , melting point temperature; T_s , maximum service temperature.

^a Specimen density obtained by using the relation mass/volume.

^b Data furnished by individual manufacturers.

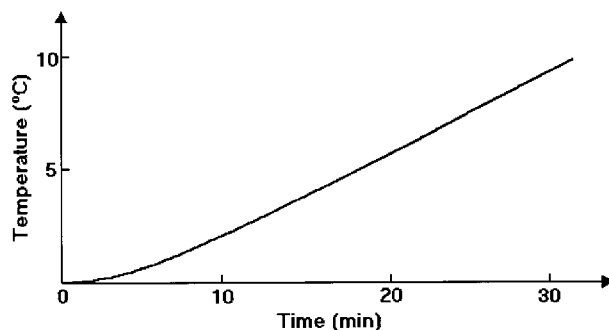


Figure 4 Time–temperature transient for sample PMMA–25°C.

values found in the literature. These discrepancies perhaps may be associated to the degree of crystallinity or the thermal history of the sample, since these factors can affect the thermal properties of polymers. Table II(b) shows that the experimental results obtained are in excellent agreement with the data found in the literature and obtained by the hot-wire standard technique, for the same materials, except for the PMMA. However, for this material, the experimental results obtained with the hot-wire parallel technique are in excellent agreement with the data found in the literature with deviations of only 2.30, 3.00, and 5.96% for the thermal conductivity, specific heat, and thermal diffusivity, respectively.

With the purpose to check once more the technique proposed against independent results of the thermal conductivity and thermal diffusivity, obtained by independent methods, the angström method¹⁷ was used to determine the thermal diffusivity, and the hot-plate/cold-plate calorimetric technique was chosen to measure the thermal conductivity of Nylon 66, the specimen selected for this comparison test. Measurements were carried out around 100°C, and the results are shown in Table III. A deviation of only 9% on the thermal conductivity and 10% on the thermal diffusivity was observed when three different techniques were employed. The results obtained are again in excellent agreement, showing the reliability of the technique proposed. The regression analysis procedure adopted in this work is a very useful mathematical tool with which the simultaneous determination of thermal conductivity, thermal diffusivity, and specific heat was possible. This is the great advantage of this technique. The quality of the fitting may be demonstrated by checking the correlation coefficient. All are greater than 0.998. For the perfect fitting, this coefficient should be equal to 1.

Table II Experimental Results and Comparisons and Hot-wire Parallel Technique Versus Hot-wire Standard Technique⁷

(a) Experiment Results and Comparisons							
Polymer	Temperature (°C)	Hot Wire			Literature		
		k (W m ⁻¹ K ⁻¹)	C_p (J kg ⁻¹ K ⁻¹)	α (× 10 ⁻⁷ m ² /s)	k (W m ⁻¹ K ⁻¹)	C_p (J kg ⁻¹ K ⁻¹)	α (× 10 ⁻⁷ m ² /s)
Nylon 66	25	0.3022	1783.66	1.4730	0.2400 (ref. ¹³)	1700.00 (ref. ¹³)	1.01 (ref. ¹³)
	63	0.3065	1689.73	1.5770	0.3000 (ref. ¹⁴)	1674.40 (ref. ¹⁵)	1.30 (ref. ¹⁶)
	107	0.3191	2261.54	1.2270	0.2400 (ref. ¹⁵)	—	—
PP	25	0.2321	1812.98	1.4550	0.2400 (ref. ¹³)	1925.56 (ref. ¹³)	0.6500 (ref. ¹³)
						1925.56 (ref. ¹⁵)	0.9000 (ref. ¹⁶)
PMMA	100	0.2395	1910.34	1.3840	—	2100.00 (ref. ¹)	—
	25	0.1955	1422.41	1.1550	0.2000 (ref. ¹³)	1465.10 (ref. ¹³)	1.09 (ref. ¹³)
					0.2100 (ref. ¹⁵)	1465.10 (ref. ¹⁵)	—
PVC rigid	68	0.2010	1553.51	1.0870	0.2000 (ref. ¹)	1450.00 (ref. ¹)	—
	25	0.1858	997.70	1.3590	—	—	—
					0.1600 (ref. ¹³)	1004.64 (ref. ¹³)	1.16 (ref. ¹³)
PU foam	69	0.1861	1378.15	0.9854	0.1300	837.20	—
	25	0.0305	1447.79	6.5740	to	to	—
					0.2900 (ref. ¹⁵)	1172.08 (ref. ¹⁵)	—
				0.2100 (ref. ¹)	1100.00 (ref. ¹)	1.10 (ref. ¹⁶)	

(b) Hot-wire Parallel Technique Versus Hot-wire Standard Technique ⁷			
Polymer	Hot-wire Parallel Technique k_p (W m ⁻¹ K ⁻¹)	Hot-wire Standard Technique k_s (W m ⁻¹ K ⁻¹)	Deviation (%)
Nylon 66	0.3022	0.3000	0.73
PP	0.2321	0.2450	5.56
PMMA	0.1955	0.2300	17.65
PVC rigid	0.1858	0.2000	7.64

Influence of the Heat Flux

The thermal properties should not depend on the linear power density applied on the hot wire. If this phenomenon occurs, it can only be attributed to disturbances in the method. Tables IV(a–c)

show the results obtained for PMMA and PP when using three different values of the linear power density.

According to these results, it is possible to conclude that those properties, as expected, are not

Table III Hot-wire Technique Versus Angstrom and Calorimetric Methods for Nylon 66

	k (W m ⁻¹ K ⁻¹)	C_p (J kg ⁻¹ K ⁻¹)	α (× 10 ⁻⁷ m ² /s)
Hot wire	0.32	2261.54	1.227
Angstrom	—	—	1.353
Calorimetric	0.35	—	—

Table IV Influence of the Heat Flux on the Thermal Conductivity, on the Specific Heat, and on the Thermal Diffusivity

(a) Influence of the Heat Flux on the Thermal Conductivity ^a				
Polymer	Linear Power Density (W/m)	k (W m ⁻¹ K ⁻¹)	Correlation Coefficient	δ (%)
PMMA	25.91	0.1955	0.99988	1.46
	40.30	0.1973	0.99933	0.55
	59.94	0.1984	0.99992	0.00
PP	25.78	0.2391	0.99897	1.92
	40.30	0.2346	0.99982	0.00
	58.25	0.2395	0.99948	2.09
(b) Influence of the Heat Flux on the Specific Heat ^b				
Polymer	Linear Power Density (W/m)	C_p (J kg ⁻¹ K ⁻¹)	Correlation Coefficient	δ (%)
PMMA	25.91	1422.41	0.99988	1.17
	40.30	1405.65	0.99933	0.03
	59.94	1406.01	0.99992	0.00
PP	25.78	1812.98	0.99897	2.72
	40.30	1863.60	0.99982	0.00
	58.25	1917.39	0.99948	2.89
(c) Influence of the Heat Flux on the Thermal Diffusivity ^c				
Polymer	Linear Power Density (W/m)	α ($\times 10^{-7}$ m ² /s)	Correlation Coefficient	δ (%)
PMMA	25.91	1.1550	0.99988	2.61
	40.30	1.1790	0.99933	0.59
	59.94	1.1860	0.99992	0.00
PP	25.78	1.4550	0.99897	4.75
	40.30	1.3890	0.99982	0.00
	58.25	1.3790	0.99948	0.72

^a $\delta = \text{abs}(k_{\text{ref}} - k)/k_{\text{ref}} \times 100$, where k_{ref} is the k value for the highest correlation coefficient and abs means absolute value.

^b $\delta = \text{abs}(C_{p_{\text{ref}}} - C_p)/C_{p_{\text{ref}}} \times 100$, where $C_{p_{\text{ref}}}$ is the C_p value for the highest correlation coefficient and abs means absolute value.

^c $\delta = \text{abs}(\alpha_{\text{ref}} - \alpha)/\alpha_{\text{ref}} \times 100$, where α_{ref} is the α value for the highest correlation coefficient and abs means absolute value.

affected by the heat flux throughout the material. However, it was observed that as a lower linear power density is applied the noise level detected in the thermal transient recorded is higher. So, it is not convenient to work with a very low linear power density.

Reproducibility

The reproducibility is very good since the aspects concerning the theoretical model need to be followed carefully. With respect to the thermal conductivity, the reproducibility is still very good even with a defective experimental arrangement with respect to

the theoretical model. However, deviations from the theoretical model greatly influence the specific heat values. With an intentional defective experimental arrangement, concerning hot wire and thermocouple embedding, a deviation of only 0.5% on the thermal conductivity and 32% on the specific heat was observed, when compared with the correct experimental arrangement.

Measuring Time

The measuring time depends on the sample size and its thermal diffusivity. Considering that a minimum time interval [t_{min} , t_{max}] is required for

the exact determination of the thermal conductivity and specific heat, as the thermal diffusivity decreases, the minimum required sample thickness also decreases, since t_{\max} depends on the thermal diffusivity and sample thickness. Smaller samples are always desirable, mainly when they are prepared in the laboratory scale. In this work, the sample size described previously was kept the same in all experiments and the time intervals considered in the calculations were always from 480 to 1500 s. During the data acquisition time interval, the temperature at the surface of the sample was recorded with the purpose to ensure that no heat exchange to the surroundings occurred during the measuring time. This should be a recommended procedure when it is not possible to have any idea concerning the materials thermal diffusivity.

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