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Thermal Properties of Multiphase Polymeric Materials and Dynamic Methods for their Characterization

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Summary: The thermal conductivity, diffusivity and specific heat of multi phase polymeric materials such as polystyrene and polymethylmethacrylate are reported. With emphasis on the thermal properties of such materials, a variety of implementation and classification regarding heat conduction will be highlighted. These properties were measured using dynamic methods namely; the transient plane source named also Gustafsson probe (TPS), the dynamic plane source (DPS) and the pulse transient technique (PTT), for measurements of thermal effusivity, thermal conductivity, thermal diffusivity and specific heat of solids One of the advantages considering these techniques is the possibility to extract all thermophysical parameters, the thermal conductivity, thermal diffusivity and specific heat from one single transient recording. Dynamic methods use a probe that is technically a "resistive element", as the heat source. The first two TPS and DPS employ this probe as both heat source and temperature sensor. The later method PTT, for temperature sensing, uses a thermocouple placed apart of the heat source. A description of the main features and the principles on which these methods are based will be highlighted.

Introduction

The thermal properties of multiphase polymeric materials are of practical importance because they govern the temperature-rise magnitude, the anisotropy [1-2] of heat flow and the thermo-mechanical reliability in the thermal designs for modern manufacturing of such materials.

In addition, computer simulation of polymer flow dynamics [3-4] during the filling and post-filling stages in manufacturing require the knowledge of thermal properties. In this work, we will deal with all thermophysical properties that are directly related to heat

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conduction such as thermal conductivity λ, thermal diffusivity κ, and specific heat C_p. Behavior of thermophysical properties of any kind of materials can be correlated to their mechanical and structural changes. The relatively small change in structure can be correlated with reasonable change in the value of the specific heat. The other two parameters, thermal conductivity and thermal diffusivity, are transport parameters related to the ability of material to transport heat. In general, the thermal properties of amorphous polymers depends on many factors, such as chemical constituents, structure, type and strength of defects or structure faults, strength of bonding, molecular weight distribution, molecular weight of side groups, processing conditions and temperature. Depending on temperature, different polymers undergo different structural changes leading to changes in their phases. According to Jäckel and Scheibner5), the low temperature thermal behavior is strongly influenced by the anisotropy nature of the bonding forces; the phonon vibration spectrum is governed by three-dimensional interchain oscillations at low temperature and the molecular motions inside the polymer chains dominate at elevated temperatures. Data about such materials at different thermodynamic stages (phases), within different temperature ranges, usually are not available; therefore, a direct measurement of thermal properties of these materials is highly demanded for the use in specific applications.

The reliability of a specific method to measure thermophysical properties is given by several factors, such as the speed of operation, the required accuracy and performance under various environmental conditions, the physical nature of material, and the geometry of the available sample. However, in most methods the main concern is to obtain a controlled heat flow in a prescribed direction so that the actual boundary conditions in the experiment correspond with those assumed in the theory.

The transient dynamic methods are a class of methods for measurements of thermal properties of materials. The principle of these methods is simple. The sample is initially kept at thermal equilibrium, and then a small disturbance is applied on the sample in a form of a short heating pulse. The change in temperature is monitored at one or more points during the time of measurement. The thermal diffusivity is then evaluated by correlating the experimental temperature measurements with the theoretical relationship obtained from the solution of the differential heat equation. Carslaw and Jaeger (1959)6) give solutions for different experimental arrangements at various initial and boundary conditions.

The simplest transient methods, the hot-wire or the hot-strip each uses a line heat source (wire or strip) that is embedded in the specimen initially kept at uniform temperature. With these methods, it is possible to measure both the heat input and the temperature changes, and then the thermal conductivity or both (only in hot strip case) conductivity and diffusivity are simultaneously determined.

The transient plane-source (TPS) method is originally based on hot strip method and characterized by the transient temperature rise of a probe "resistive element" at constant energy input. The probe is a plane double spiral, Fig 1., used as both constant heat source and temperature sensor. The probe (TPS-sensor) is made of a Ni strip 10 μm thick covered from both sides with thin insulating layer made of Kapton, different sizes of sensors were used in this work. The duration of the current pulse (time of measurement) is usually in the order of few seconds. Measurement is simply performed by recording the voltage (resistance/temperature) variations across the sensor that is supplied with pulsed electrical current[7-8)].

In the dynamic plane source (DPS) method[9-10)] we have used the TPS-sensor as a plane source placed inside a medium in such a way that its experimental arrangement resembles a one-dimensional heat flow, as shown in Fig. 2.

In the pulse transient technique (PTT) another but heat plane source is used [21)]. The sample set consists of three parts representing an infinite medium (Fig. 3). The temperature is recorded by thermometer that is usually a thermocouple placed apart of the heat source. From the parameters of the transient record all thermophysical parameters can be calculated.

In this work, we are using these methods to measure the thermal conductivity, diffusivity, and specific heat of multiphase polymeric materials.

Experiment

I. TPS method

The experiment is simply performed by recording the voltage variations over the TPS-sensor while its temperature is slightly raised by a constant electrical current pulse. The sensor is clamped between two identical cylinders or square-shaped pieces to insure a good thermal contact between the sensor and the sample pieces, see Fig. 1. The duration of the current pulse (time of measurements) ranges from several seconds to several minutes. The short measuring time is an advantage that can significantly reduce the risk of thermal degradation, which is a common characteristic of polymer materials. Furthermore, during this short period, care is taken not to increase the temperature in the samples more than by few degrees, since a small temperature increase (small gradient) will reduce errors that may mask some phase transition which occur within narrow temperature regions during measurements.

The theory related to the method is based on a three-dimensional heat flow inside the sample, which can be considered as an infinite medium, if the time of the transient recording is ended before the thermal wave reaches the boundaries of the sample. The time dependent resistance of the TPS-sensor during the transient recording can be expressed as

$$R(t) = R_0[1 + \alpha\Delta T(t)] \qquad (1)$$

where R_0 ($\approx 4\ \Omega$ at room temperature) is the resistance of the TPS element before the transient recording has been initiated, α is the temperature coefficient of resistance (TCR), for the TPS sensor ($\alpha \approx 4.0 \times 10^{-3}\ K^{-1}$ at room temperature) and $\Delta T(t)$ is the time dependent temperature increase of the TPS sensor. Depending on the temperature range of interest, the TCR values for the TPS-sensor are determined within that particular temperature-range from separate calibration procedures by means of different thermometers such as a Pt-thermometer.

The assessment of $\Delta T(t)$ in the heater depends on the power output in the TPS sensor, the design parameters of the sensor and the thermal transport properties of the surrounding sample. For the disk-shaped sensor $\Delta T(t)$ is given by the following equation, from which the thermal conductivity and diffusivity can be obtained

$$\Delta T(\tau) = P_0(\pi^{2/3}a\lambda)^{-1}D(\tau) \qquad (2)$$

where, P_0 is the total output power, λ is the thermal conductivity of the sample, and a is the radius of the sensor. $D(\tau)$ is the theoretical expression of the time dependent temperature increase, which describes the conducting pattern of the disk shaped sensor, assuming that the disk consists of a number m of concentric ring sources[7,8)], see Fig. 1. For convenience the mean temperature change of the sensor is defined in terms of the non-dimensional variable τ, where $\tau = [\kappa t/a^2]^{1/2}$ or $\tau = (t/\Theta)^{1/2}$, t is the time measured from the start of the transient heating, $\tau = a^2/\kappa$ is the characteristic time, and κ is the thermal diffusivity of the sample. The specific heat is related to these parameters through the density ρ via the relation $\rho\, C_p = \lambda/\kappa$.

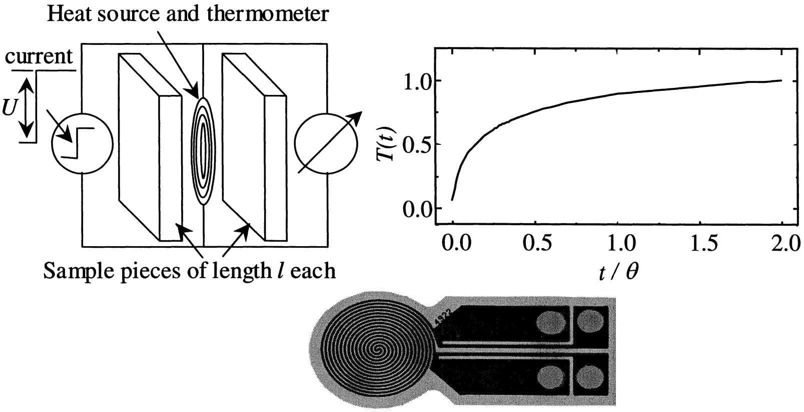

Figure 1. Experimental arrangement of TPS method; temperature response and TPS sensor.

II. DPS method

The main features distinguishing DPS from the TPS can be summarized as:

(i) DPS is arranged for a one-dimensional heat flow into a finite sample, which is in a contact with very good heat conducting material (heat sink) such as copper[10)].

(ii) DPS also works in the time region where the sample is treated as a finite medium and is not restricted only to the time region where the sample is regarded as infinite medium.

(iii) DPS has the potential to give λ, κ, and ρC_p from a single measurement even if the experimental arrangement resembles a one-dimensional heat flow.

The temperature increase in the plane $x = 0$, $(0< x < l)$, as a function of time will be given by

$$\Delta T(t) = \frac{q\ell}{\lambda\sqrt{\pi}} F(\Theta,t) \tag{3}$$

where q is the total output power per unit area dissipated by the heater, 2ℓ is the length of the sample (see Fig. 2) and $\Theta = \ell^2/\kappa$ is the characteristic time depending on the material properties and geometry of the sample. $F(\Theta,t)$ is a theoretical expression of the time dependent temperature increase[9)], whose value depends on the measuring time and the sample characteristics as follows:

For times $0 < t < 0.3\Theta$, $F(\Theta,t) = (t/\Theta)^{1/2}$ from which the value of effusivity $\xi = \lambda/\sqrt{\kappa}$ is obtained, then for times $t \geq 2\Theta$, $\Delta T(t)$ will approach the value $q\ell/2\lambda$ and λ can be readily obtained.

For times $t \geq 0.5\Theta$, the natural logarithm of the derivative of $\Delta T(t)$ can be expressed[10)] as:

$$\ln\frac{d\Delta T(t)}{dt} = \ln\frac{q}{\rho C_p \ell} - \frac{\pi^2 t}{4\Theta} \tag{4}$$

Then ρC_p can be obtained from the intercept of the graph between $\ln[d\Delta(t)/dt]$ and t. Finally, a further check for the obtained value of ρC_p can be verified via the data consistency relation $\rho C_p = \lambda/\kappa$.

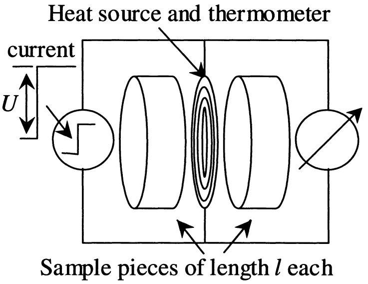

Figure 2. Schematic diagram shows the experimental set-up in the DPS method.

III. PT method

The principle of the Pulse Transient Method and specimen arrangement is shown in Figure 3. This method is fully automated and operates also in thermal analysis regime. The heat pulse is generated by the passing of the electrical current through the plane electrical resistor made of a nickel foil of 20 microns thick. The temperature response is measured by thermocouple. The thermophysical parameters are calculated from the parameters of the temperature response to the heat pulse. The temperature increase of transient record depends on the material, typical values of the total temperature increase are between 0.5 K and 4 K. The thermal diffusivity, specific heat and thermal conductivity is given by equations (5), (6), (7), respectively.

$$\kappa = h^2/2t_m \tag{5}$$

the specific heat,

$$c = \frac{Q}{\sqrt{2\pi e}\rho h T_m} \tag{6}$$

and the thermal conductivity

$$\lambda = \kappa \rho c \qquad (7)$$

where, $Q = RI^2 t_o$, R is the electrical resistance of the heat source, ρ is density and other parameters are given in Fig. 3.

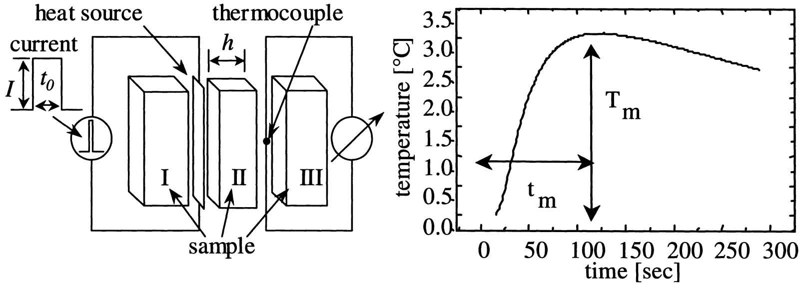

Figure 3. Principle of the Pulse Transient Method and a typical example of a transient record for the PMMA sample.

Results and Discussion

The TPS and DPS methods has been tested on four samples (shown in Table 1) with thermal conductivity ranging from 0.028 to 0.403 W/m K, These samples have been chosen because their thermal properties are within the range typical for polymeric materials. The data shown in the table are the average values of five independent measurements for the TPS technique and of six independent measurements for the DPS technique. The data differ by less than 5% from the published values [12-15]. Even though, these data where taken at ambient temperatures while the methods have the potential to test thermal properties during temperature variations and phase transition [16-17].

Fig. 4. shows the three thermophysical parameters of PMMA (PERSPEX) measured by PTT and TPS techniques. The data reliability was tested by using these two methods.

Table 1. Typical measured values of the thermal properties of four different samples.

Materials	λ (W/m-K)	κ (10^{-6} m^2/s)	$\xi = \lambda/\sqrt{\kappa}$ W s$^{1/2}$/m^2 K	ρCp (MJ/ m^3-K)
Polystyrene(PS)*	0.0273	0.666	------	0.0409
Acrylic-"Plexiglas" PMMA* (Polymethylmethacrylate)	0.19	0.11	-----	1.727
Adhesives and coatings (epoxy resin of density 1379 kg/m^3)	0.403	0.226	870	1.8
Polycarbonate(PC)*	0.245	0.171	590	1.4

*The first two samples measured using the TPS method and the rest using the DPS method.

Data were measured on commercial PERSPEX of 30 and 50 mm in diameter. For the TPS method we have used three probes of different sizes (Fig.1). Data were evaluated using standard evaluation analysis within the conclusions of the theory of sensitivity coefficients for given parameters and difference analysis [18)]. The PT method was tested for reproducibility under different experimental conditions like change in heat pulse power, reassembling specimen set, etc. All measurements by Pulse Transient Method were made at room temperature either in air or in vacuum of 10^{-3} Pa. Results and comparison of these analyses are given in Figs. 4 and 5.

The final difference of the averaged values for thermal conductivity and specific heat are less than 2% and for thermal diffusivity it is less than 4%. These data are in reasonable coincidence comparing to scattering of data that were collected from literature and were put to the data consistency relation $\lambda = \kappa \rho c$. Most of the literature data are obtained using steady state methods that are giving just one parameter. The scatter of the data from literature is usually larger than 10% for each parameter[11, 19)].

The effect of temperature change on thermal properties of multiphase polymeric materials is complex and it depends on several factors such as the type of polymer, degree of polymerization, the structure of the matrix etc. For example, with the temperature increase, the chain movements in low -conducting polymers could have two opposite folds: one that is related to the size and number of micro-voids created by these movements and the other is related to increasing the chain alignment and arrangement within the matrix. The former reduces the thermal conduction due to defects and the later enhances the conduction due to alignment and stacking of chains. Thus with this two-fold effect, thermally low - conducting polymers may show different conduction behavior and can be classified into two main groups. Polymers with large chain segments and long branches that will resist movements and as a result reduce

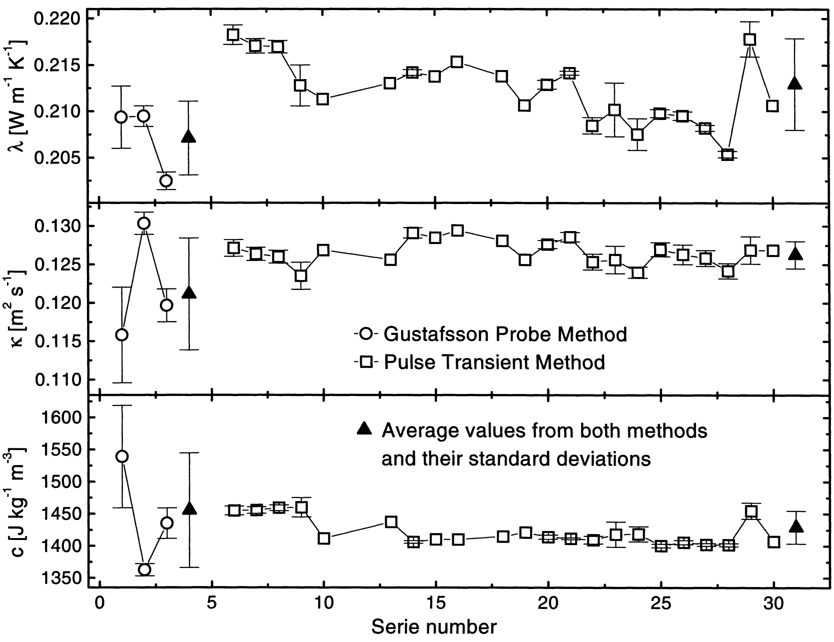

Figure 4. Thermophysical parameters of PMMA (PERSPEX) measured by Pulse Transient Method and Transient Plane Source Method. The first four points represent measurements on sensors of the different diameters - 6.6mm, 13mm and 20mm and their average values with marked standard deviations. Averaged data represent the measurements performed at the same experimental conditions. The total differences of the averaged values for both methods marked as up triangles are less than 2% for thermal conductivity and specific heat and for thermal diffusivity is less than 4%.

thermal conduction, and polymers with lighter chain segments and short branches that have high degree of polymerization which will enhance thermal conduction.

In addition, this type of polymers can be mixed with fillers to make polymer composites. Predicting the thermal behavior of such polymer composite will be a difficult task. In such composite material, thermal properties often vary from batch to batch (or from time to time), it could also vary under various environmental conditions, or during recycling processes. Therefore, developing a technique to measure thermal properties under various thermodynamic conditions within relatively short measuring time would significantly reduce the risk of thermal degradation and other rate dependent effects that tend to create significant spread in the measured values of thermal conductivity and diffusivity.

All three currently discussed methods have been developed to meet these demands. The methods have the potential to be utilized in research and development mapping applications where structural changes may be empirically correlated with the measured values of thermal conductivity, particularly, in cases where structural stability, structural control and/or the presence of defects are related to the thermal transport properties. These methods are non-destructive and relatively fast techniques that can be used as quality control assurance devices along the production line in manufacturing of components, especially, when information in production manufacturing processes with higher quality requirements is needed. In material research and developing, these methods can be used, when the knowledge of material behavior is required even during the steps of manufacturing.

Furthermore, multiphase polymeric materials including composites with inorganic fillers, the thermal diffusivity can reach the value of the same order as some metals20) and it is significantly related to the molecular and the super molecular structures in binary composites and polymer blends. Finally, multiphase polymers are promising materials for improving the physical and mechanical properties, which cannot be achieved by each particular polymer. Therefore, as described above, thermal properties are sensitively affected by change in the microstructure of materials and these measurements can be considered as probes to explore the change in microstructure of the blends, which do not require special physical or chemical modifications of the sample specimens.

Conclusions

The discussed Dynamic Transient Methods (TPS, DPS and PTT) are very sensitive techniques for measurements of thermophysical properties of solids within a wide temperature range and they have the potential to test these properties during structure relaxation and phase transformations. The main advantage is that the dynamic method can give all three thermophysical parameters, comparing to steady state methods.

These methods are non-destructive techniques due to the following reasons:

(i) During the experiment the temperature of the sample is practically unchanged ($\Delta T < 1$ K), thus, resulted parameters λ, κ and c_p could be used as a measure for the quality control even during manufacturing processes, as well as the stability in time.

(ii) The same sample can be used for next type of physical measurements (for example, electrical, or optical) which can be correlated to the thermal properties to deduce meaningful comparison and / or to develop a theoretical formalism correlating the structure and physical properties.

The thermophysical parameters, namely thermal conductivity, diffusivity and specific heat of polymeric materials are important parameters regarding safety issues for human (production against fire) or environmental issues during degradation of polymeric materials due temperature variations.

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