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New direct measurement techniques for thermal conductivity, thermal diffusivity, and specific heat of advanced materials [a]

Kay Henry and Karl G. Coumou
Holometrix, Inc., Bedford, MA 01730 (USA)

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Abstract

Thermal conductivity, specific heat and thermal diffusivity are all essential properties of engineered plastics, ceramics, composites and other materials, whether for end-use products or processing applications. The paper presents new fully automated instrumentation for direct measurement of these properties on a wide variety of materials. Thermal conductivity can be measured in a solid or molten state up to 300 °C. Thermal diffusivity measurements can be performed to 2000 °C, with optional software for specific heat calculation. Finally, a large-sample calorimeter provides specific heat measurements on composites and other inhomogeneous materials which cannot be tested accurately using conventional (differential scanning calorimeter) instrumentation.

INTRODUCTION

Thermal conductivity is defined as the rate of heat flow through a substance under steady-state conditions. Specific heat is a measure of the quantity of heat absorbed or released by a material as it is heated or cooled. Finally, thermal diffusivity is a derived material property that determines how long it takes to heat or cool a material to some required temperature level. The importance of these properties for development of materials ranges from determining safe operating temperatures, to predicting the rate of heat dissipation from electronic components, to controlling the injection molding process for polymers.

The three properties are related mathematically by the following formula

$$D = \frac{\lambda}{wC} \tag{1}$$

where D = thermal diffusivity; λ = thermal conductivity; w = density; C = specific heat. This relationship allows researchers to measure any two properties and (if material density is known) to derive the third.

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Typical instruments for measuring these properties in the polymer industry include differential scanning calorimeters (DSCs) for specific heat and various ASTM-approved apparatus for measuring thermal conductivity, with thermal diffusivity normally being the derived property. Recent technological advances, however, now permit convenient and highly accurate measurement of all three parameters. The methods presented in this paper are the guarded heat-flow meter method for measuring thermal conductivity, quantitative adiabatic calorimetry for measuring specific heat, and the laser-flash method for measuring thermal diffusivity. All three instruments discussed herein have been developed and are manufactured by Holometrix Inc., Bedford, MA.

THE GUARDED HEAT-FLOW METER METHOD FOR MEASURING THERMAL CONDUCTIVITY

The commercial instrument which measures thermal conductivity by the guarded heat-flow meter method (ASTM F433) is capable of testing solid materials, thin films and materials that melt during the test, over a temperature range of 30–300 °C. The measurement is carried out under steady heat flow conditions through the sample. Solid and thin film materials in the range 0.1 to 10 W mK^{-1} can be tested with an estimated accuracy of $\pm 5\%$. Samples that melt during the test are measured using a special cell that limits the upper range to 1 W mK^{-1}. Accuracy estimates are based on results obtained when testing materials of known thermal conductivity. Only a few materials of intermediate thermal conductivity are available for reference purposes. Two of these are Pyrex Brand 7740 and Pyroceram 9606, which have been tested extensively by various methods. [1].

The guarded heat-flow meter method can also be used for testing thin samples of non-rigid materials (e.g. polymer films and paper products, starting at 0.1 mm). The technique involves measuring successive increases in the thermal resistance of a stack of thin samples as new samples are added. The estimated accuracy is $\pm 10\%$, based on comparisons with published data on similar materials.

A cross section of the test cell is shown in Fig. 1. A test sample is placed between two heated surfaces controlled at different temperatures, resulting in a steady heat flow from the hotter to the colder plate (in this case, from the top to the bottom). The amount of heat passing through the sample is measured with a thin heat flow transducer located underneath the lower plate. The entire cell is surrounded with a cylindrical guard heater to minimize lateral heat transfer. The heat flow transducer consists of a multi-junction thermopile embedded in a polyimide matrix. The output of the thermopile is proportional to the heat flux through the transducer. Because the relationship is temperature dependent, the transducer must be calibrated over the temperature range of the instrument.

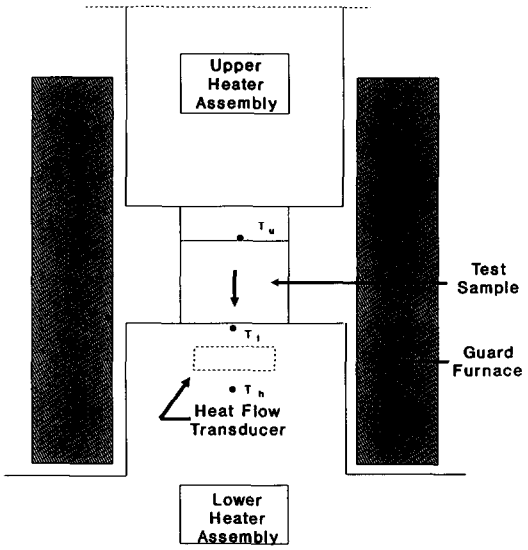


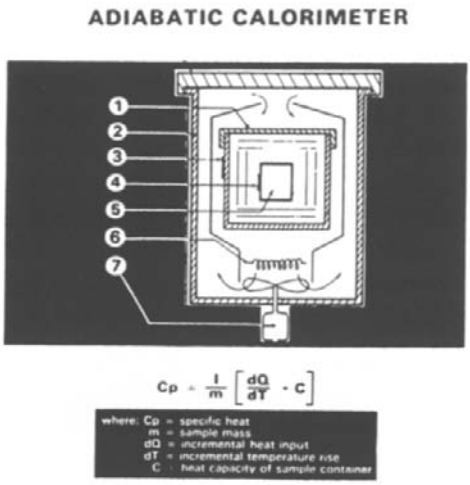
Fig. 1. Schematic of model TCA test section.

The overall temperature difference between the two surfaces in contact with the sample is measured with built-in temperature sensors (T_u and T_l), eliminating the need for direct connection of instrumentation to the sample. Thermal resistance of the interfaces between the sample and adjacent surfaces is minimized by applying a coupling agent, usually silicone oil or a heat sink compound. Interface resistance, provided it is reproducible, is accounted for in the data analysis. A reproducible contact pressure on the test stack is assured with pneumatic controls.

ADIABATIC CALORIMETRY MEASUREMENTS OF ENTHALPY AND SPECIFIC HEAT OF LARGE SAMPLES

When characterizing composite materials, problems often arise due to the small sample size required by most calorimeters including DSCs. Testing a small sample of an inhomogeneous material usually yields results which are not representative of the bulk material. A new fully automated calorimeter measures specific heat and enthalpy change on both homogeneous and inhomogeneous materials, solid or non-solid, in a single run on samples up to 100 ml. Test temperatures range from -50–$300\,^{\circ}C$ (for testing below $40\,^{\circ}C$ the test chamber must be cooled with liquid nitrogen). Estimated accuracy is better than $\pm 3\%$ when comparing test results with published data for pure copper (electrolytic or $> 99.9\%$ pure) [2a] and distilled water and ice [2b].

The test cell (Fig. 2) shows a removable sample container with a heating element at its center. The container is placed in a closed, uniformly heated



1 Adiabatic Guard
2 Test Chamber
3 Guard Heater
4 Sample Heater
5 Test Sample Inside Removable Container
6 Air Heater
7 Fan

Fig. 2. Schematic of QTA test section.

guard furnace controlled throughout the test to the same temperature (within 0.1° C) as the sample container. This creates an adiabatic environment with all the supplied heat being used to raise the temperature of the container and its contents. The air temperature in the space between the guard furnace and the outer wall of the test chamber is maintained a few degrees below that of the guard, to facilitate precise guard control.

Heat input to the sample is provided in brief (1–2 min) pulses calculated to raise the container temperature by approximately 5° C, an interval which can be varied at the operator's discretion. Following each pulse, the system is allowed to come to thermal equilibrium before another heat pulse is applied to the sample. (During phase changes of the sample material, the heat pulse may not raise the temperature at all until the transformation is complete.)

USE OF THE LASER FLASH SYSTEM TO PROVIDE DIRECT THERMAL DIFFUSIVITY MEASUREMENTS

Although it is possible to derive thermal diffusivity from specific heat and thermal conductivity data using the equation specified in the introduction, there also exist fast, accurate methods to measure this important property directly on solid materials. A recently developed, fully automated, compact system uses the laser flash method to measure thermal diffusivity of solids, including polymers and composites. Direct measurement of thermal conduc-

tivity is sometimes unreliable or not feasible, e.g. when testing thin sections of high thermal conductivity material or when testing at temperatures above 1000 °C. In those cases, thermal diffusivity can be measured and, if needed, thermal conductivity can be derived from eqn. (1).

The test section shown in Fig. 3 indicates the position of a 10 mm diameter sample which is inserted into a cylindrical container and then lowered into a tantalum furnace. The sample is supported coaxially at the midplane of the furnace, with its flat faces horizontal. This configuration takes advantage of the force of gravity and provides for simpler sample support than a vertical orientation. As with the other two instruments, there is no need for direct instrumentation of the sample at temperatures above ambient. A small thermocouple is attached to the sample surface for measurements below room temperature.

Once a sample is inserted, menu-driven software prompts the operator to input sample dimensions and temperature range. Again, the system operates unattended after this initial set-up with the microprocessor controlling vacuum, temperature and laser pulse. During a test, the sample is heated to the desired temperature (between −170 °C, with cryogenic attachment, and 2000 °C) and then irradiated on one face by a short pulse from a fully enclosed, high energy laser beam. Temperature response on the opposite face is recorded using an IR detector and high-speed scanner, and diffusivity is calculated from the length of time required to reach one-half of the total temperature rise (typically in microseconds). A diffusivity test takes less than 15 min per data point, compared with 60 min per data point when measuring thermal conductivity directly.

Accuracy of thermal diffusivity measurements when testing several available reference materials (electrolytic iron, tungsten, copper and graphite) is ±5% over the temperature range 100–2000 °C (3).

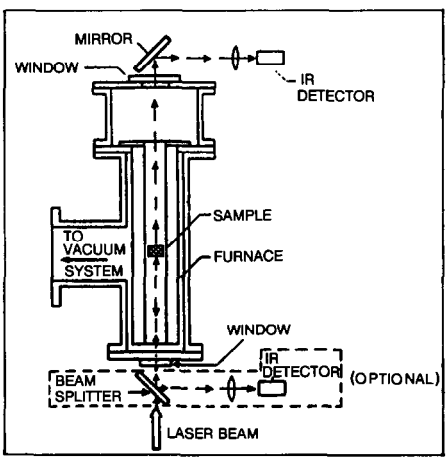


Fig. 3. Schematic of laser flash test section.

SUMMARY

Thermophysical properties of many new materials, from engineered plastics to composites and ceramics, that are being developed for special applications can now be measured conveniently, accurately and reliably using equipment that combines proven test methods with advanced measurement technology. These bulk material properties, which relate to the way a material transfers or stores heat, must be included in the engineering data base for applications ranging from electronics to polymer processing.

REFERENCES

1 L.C. Hulstrom and R.P. Tye, Round-robin testing of thermal conductivity reference materials, in D.W. Yarbrough (Ed.), Thermal Conductivity, Vol. 19, Plenum Press, New York, 1988.
2 (a) Specific Heat, Metallic Elements and Alloys, Vol. 4 of TPRC Data Series: Thermophysical Properties of Matter, Plenum Press, New York, 1970.
(b) Handbook of Chemistry and Physics.
3 Thermal Diffusivity, Vol. 10 of TPRC Data Series: Thermophysical Properties of Matter, Plenum Press, New York, 1973.