Thermochimica Acta, 126 (1988) 93–100
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

A METHOD FOR THE DETERMINATION OF THERMAL CONDUCTIVITY OF SHEET MATERIALS BY DIFFERENTIAL SCANNING CALORIMETRY (DSC)

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(Received 16 June 1987)

ABSTRACT

The differential scanning calorimeter was adapted to perform the measurement of thermal conductivity of polymeric and other sheet materials. Conditions for maintaining stable and reproducible heat flow were developed, reproducible and recyclible sensor materials were fabricated, and the use of a thermal lubricant at the solid–solid interfaces tested. The technique was applied to poly(methylmethacrylate) and poly(tetrafluoroethylene) sheets of varied thicknesses over the temperature range 45–175 °C. Values for thermal conductivity were somewhat lower than those quoted in the literature. Further improvements and calibration methods are discussed.

INTRODUCTION

There are many techniques for determining the thermal conductivity of polymeric and other materials, for example various ASTM methods [1]. Some of these techniques involve the use of differential scanning calorimetry [2,3]. However, all of them require thick specimens so that none are comparable to the technique developed in this paper. This method measures the thermal conductivities of thin sheets and has the potential to measure changes in thermal conductivity as a function of time or distance from a reacting gaseous interface, such as oxygen, at elevated temperatures. However, the method was developed in its simplest form so as to test the ability of the theoretical assumptions used herein to determine correct values for thermal conductivities without previous calibration with standards of known thermal conductivity.

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(This research was funded by The Center for Fire Research, National Bureau of Standards, Gaithersburg, Maryland 20899, U.S.A., NBS Grant 60 NANB4D0040 entitled "Thermal and Material Transport and the Solubility of Oxygen and Other Gases in Oxidizing Polymers.)

0040-6031/88/$03.50

Thermal conductance and thermal resistance are important for assessing and modeling heat flow in polymeric materials. The thermal resistance multiplied by the heat capacity equals the thermal time constant for a material which can, especially in materials with low thermal conductivity (such as foams and chars), be the rate limiting factor for smoldering, combustion and other processes.

THEORETICAL DEVELOPMENT

The theory of differential scanning calorimetry has been developed in detail [4–6]. The method used here utilizes the measurement of rate of heat flow into a sensor material during its first order transition to obtain the thermal resistance of a material placed between the sensor material and the heater in the DSC.

If, at constant heating rate, a sensor material (such as indium at its melting point) goes through a "sharp" transition where the temperature over which the transition occurs is much smaller than the temperature change of the heating calorimeter during the interval in which heat must flow into the material to match the transition enthalpy, the net heat flux from the calorimeter into the specimen will increase linearly, according to Newton's law, until the transition is completed. Therefore, the steady slope of the leading edge of the transition peak of the sensor material will be given by eqn. (1)

$$\text{slope (sensor)} = B/R \tag{1}$$

where B is the heating rate, and R is the thermal resistance between the heater in the calorimeter and the sensor specimen. The DSC curve for this case is illustrated by curve (a) in Fig. 1. If a sheet material is placed between the sensor specimen and the calorimeter, as shown in case (b) in Fig. 1, then the heat must flow through this increased resistance and the steady slope of the leading edge of the transition peak will be

$$\text{slope (sensor + sheet)} = B/R' \tag{2}$$

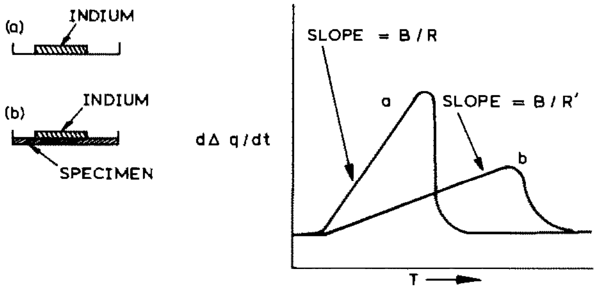

Fig. 1. DSC curves for melting of indium: (a), indium; (b), indium + specimen sheet.

where R' is the new thermal resistance between the heater and the sensor specimen which now also includes the resistance to heat flow of the sheet material.

Obviously, the thermal resistance of the sheet R_s can be obtained from

$$R_s = R' - R \tag{3}$$

If the enthalpic calibration constant of the instrument is in units of J cm^{-2}, the chart speed in cm s^{-1}, the heating rate in K s^{-1} and the slope in cm cm^{-1}, the thermal resistance will be in units of K s J^{-1}. The thermal conductivity of the sheet k is obtained from

$$k = L/A(R' - R) \tag{4}$$

where L is the thickness of the specimen sheet, and A is the contact area between the sensor material and the sheet. If R and R' are in K s J^{-1}, L in cm and A in cm^2, then the thermal conductivity of the sheet k will be in units of J cm cm^{-2} K^{-1} s^{-1}.

The heat flow model, as described above, combines all the thermal steps into a single interface and does not take into account the additional interface resulting from the introduction of the specimen and variations in thermal resistance resulting from differing degrees of contact when the sensors and sheets are changed or even disturbed. The inadequacies of the model will be discussed in the final section when the values for thermal conductivities obtained in this study are compared with values from the literature. Sources of variability in experimental measurements and efforts to minimize this variability are discussed in the section on the development of the technique.

There are several factors which affect the reproducible measurement of thermal resistance of a specimen by this technique. (1) Sensor materials must have sharp melting points which are reproducible upon recycling. (2) The contact area between the sensor material and the specimen sheet must be known and remain constant. (3) The stability of the baseline of the instrument must be maintained among the experiments. (4) Variation in the thermal resistances at each of the solid–solid interfaces must be minimized and kept as constant as possible. These interfaces are (a) between the sensor material and the specimen sheet and between the specimen sheet and the calorimeter cup, or (b) between the sensor material and the calorimeter cup when no specimen is present.

DEVELOPMENT OF TECHNIQUE

As each experiment covers a narrow temperature range, a slight baseline curvature can be tolerated. Also high enthalpic sensitivity is not necessary. Therefore, a readily available, albeit archaic, Perkin–Elmer DSC-1B dif-

TABLE 1

Sensor materials tested

Sensor material	Melting point (°C)
Benzophenone	48 [a]
1,2-Diphenylethane	52
o-Terphenyl	58 [a]
1,2-diphenylpropene-1	72
Naphthalene	80.5 [b]
m-Terphenyl	89 [a]
Benzoic acid	122
Indium	156.6

[a] Formed glass on cooling. [b] Slope of transition proved to be dependent on heat flow through the naphthalene rather than heat flow through the polymer sheet.

ferential scanning calorimeter was used in these experiments. It was connected to a two-pen recorder, and dried nitrogen purge gas circulated through it at 30 ml min^{-1} during operation. A heating rate of five degrees Kelvin per min was employed in almost all of the experiments.

The enthalpic constant for the instrument was calculated from the heat of fusion of indium to be 0.09886 mJ s^{-1} cm. Isothermal temperature calibration from melting point standards was accomplished using the method suggested by Flynn [7]. Thermal time lag was determined as a function of heating rate for the melting of indium.

The sheet materials used as specimens in these first studies were poly(methylmethacrylate) (thicknesses 0.246, 0.287, 0.427, 0.437 and 0.820 mm) and poly(tetrafluoroethylene) (thicknesses 0.130, 0.264, 0.889, 1.067, 1.295 and 1.600 mm). The sensor materials tested during this phase of research and their melting points are listed in Table 1.

The ideal experimental procedure would be for the sensor materials of standard surface area to be in close contact with the surface of the specimen sheets. However, even for metallic sensors such as indium, their geometrical integrity could not be maintained upon recycling through a melting transition. Also such sensors could not be used with porous substrates such as foams and chars. Therefore the sensors were encapsulated in aluminum sample pans. Use of these pans required further assumptions for the model, viz. that there was no thermal resistance between the specimen and the aluminum pan and that the pan maintained the temperature of the sensor during the transition, i.e. the effective heat capacity of the sensor included that of the pan.

If the aluminum sample pan came in contact with the side of the calorimeter cup, the heat path was considerably altered, and the steady state slope of the melting peak affected. This could happen during an experiment as a result of vibrations, purge gas flow, etc. This problem was remedied by using the smaller diameter "volatile liquid" aluminum sample pans with their wide crimped lips sheared off by a defective crimping tool. Care still had to be taken to check whether the pans had migrated to make contact with the sides of the calorimeter cup since insulating spacers around the pans proved to be impractical.

The positions of the lids of the calorimeter cups were found to affect the heat flow from experiment to experiment. In fact, minor vibrations would cause them to shift sufficiently for measurable base line shifts to result. It was found that removal of the lid did not appreciably affect the sensitivity or stability of the DSC measurement so later investigations were performed without lids on the sample and reference calorimeter cups.

The flow of heat from the calorimeter heater to the sensor material passes through three important interfaces, (a) between the calorimeter cup and the specimen, (b) between the specimen and the aluminum sample pan and (c) between the aluminum sample pan and the melting point sensor. The last interfacial resistance (c) remains constant for a specific melting point specimen after the first melting. However, it may vary from specimen to specimen and will vary considerably from one sensor to another. Ideally, the thermal resistances of all three interfaces should be kept as constant as possible and also should be kept as small as possible with respect to the thermal resistance of the specimen of interest. The interfacial resistance is lowered by flattening the specimen and pan surfaces and by inserting a "thermal lubricant" into the interface. Both of these procedures were attempted.

In general, if these resistances can be kept constant or negligible for two experiments for which the only difference is in the thickness of specimens of the same material, then the differences between the resistances obtained for the two experiments should be that for a thickness of polymer equal to the difference in thickness between the two specimens, i.e.

$$R(\text{specimen of thickness, } L2 - L1) = R(L2) - R(L1) \qquad (4)$$

Therefore eqn. (4) was also utilized in the thermal conductivity calculations. Many experiments were performed to achieve a degree of optimization of the above factors. The circular bottoms of the rimless cells were flattened. These bottoms have a surface area of 0.5648 cm^{-2} and since the heat flow to the sensor material is through this surface, this area was used to calculate the thermal conductivity. Efforts were made to flatten the polymer sheets used as specimens in order to improve surface contact between them, the calorimeter cup and the base of the encapsulated sensor material. Wood's metal was the first material investigated as a thermal lubricant to lower and standardize interfacial thermal resistance. Although it did decrease the resistance, it proved to be unsatisfactory as it did not wet surfaces well and froze into discrete clumps when the temperature was lowered. A high viscosity silicone oil was more successful. Silicone oil in the interface reduced the total thermal resistance between the calorimeter heater and an encapsulated indium specimen from 1.254 to 0.522 s K mJ^{-1}. Therefore it had the dual effect of making the resistance more reproducible and making it a smaller factor in the measurement of the total resistance.

Much of the experimental effort thus far has been expended in seeking solutions to the problems discussed above. However, some results obtained during the development of the technique are given in the next section.

RESULTS

Some typical results for calculated thermal conductivities of poly(methylmethacrylate) using 1,2-diphenylethane, 1,2-diphenyl propene-1 and benzoic acid sensor materials and of poly(tetrafluoroethylene) using an indium sensor are given in Table 2.

The values for thermal conductivity in Table 2 are uniformly lower than those found in the literature. For example, the thermal conductivity of poly(tetrafluoroethylene) was found to be 10.7×10^{-4} J cm cm^{-2} K^{-1} s^{-1} at 25°C and 9.07×10^{-4} J cm cm^{-2} K^{-1} s^{-1} at 160°C [8]. Literature values for poly(methylmethacrylate) include 10.7, 13.4, and $17–25 \times 10^{-4}$ J cm cm^{-2} K^{-1} s^{-1} in refs. 9–11.

TABLE 2

Polymer	Temperature (°C)	Thickness (cm)	Thermal conductivity calculated from eqn. (4) ($10^4 \times$ J cm s^{-1} K^{-1} cm^{-2})
Poly(methylmethacrylate)	46	0.0246	3.93
	46	0.0427	3.97
	46	0.0437	4.86
	48 [a]	0.0820	5.23
	75	0.0246	4.93
	77 [a]	0.0427	4.31
	78 [a]	0.0437	2.68
	85 [a]	0.0820	2.63
	122	0.0246	3.72
	124 [a]	0.0437	6.02
	125 [a]	0.0427	3.89
	136 [a]	0.0820	8.82
	160 [b]	–	–
Poly(tetrafluoroethylene)	160	0.033	3.76
	161 [a]	0.089	5.23
	167 [a]	0.107	5.94
	175 [a]	0.160	4.85
			6.98
			5.94

[a] Average temperatures of thick specimens are higher due to thermal lag.

[b] Polymer softened below indium transition temperature (156°C).

DISCUSSION

Ignoring, for the moment, the wide scatter of the values for thermal conductivity in Table 2, it can be seen that they are consistently about one-half those quoted in the literature. This correspondence is encouraging rather than discouraging when the simplistic theoretical treatment used in their calculation is taken into account. It gives confidence that the method is actually measuring thermal conductivity of the specimens rather than some other rate-limiting heat flow process. The theoretical model combines all thermal steps into sharp interfaces. When specimens of low thermal conductivity such as these polymers are used, heat flow through the specimen must become at least partially rate limiting so that the effective interface appears to move into the specimen [5]. This might account for the low thermal conductivity values obtained above. However, the simplest and most probable explanation for the low thermal conductivity values is that the contact surface area of the sensor material is less than the assumed value of the total area of the bottom of its aluminum pan and thus conductivities calculated from eqn. (4) would be too low. In any event, it appears that, at worse, the method may require calibration with substances of known thermal conductivity.

The experimental thermal conductivity values in Table 2 show a scatter of as much as ± 50%. It is probable that the greatest source of variation results from changes in the degree of contact between the base of the aluminum sensor container and the specimen sheet. This problem is more severe for polymeric sheets which often tend to warp and buckle upon heating than for more rigid isotropic materials. The obvious way to lessen this effect is to apply force from above on the sensor container to maintain more reproducible contact between it and the specimen. This could be achieved either with a loaded spring or a metallic weight massive enough to act as a heat sink.

Also, use of more recently developed DSC apparatus of greater sophistication may further reduce experimental variability. The testing of more specimens with independently known thermal conductivities should allow assessment of whether the low values obtained in these preliminary studies are inherent to the technique or artifacts of instrumentation or analysis.

An important aspect of this method is that it is nondestructive so that the temperature may be cycled back and forth over the transition temperature of the sensor to measure the change in thermal conductivity with time during a chemical reaction such as polymer oxidation. Therefore the technique may be used as a thermoanalytical method to measure changes in thermal conductivity as a function of programmed temperature and gaseous atmosphere. For example, films of differing thicknesses and multiple sandwiches of films and sensor materials can be employed to obtain thermal conductivities at various distances from a surface exposed to oxygen. Several sensor materials may be used for the same specimen to obtain the thermal conductivity at the transition temperature of each sensor.

Many interesting systems could be investigated by this technique. Many polymers such as poly(vinyl chloride) and poly(vinyl alcohol) first degrade by stripping off side groups to form conjugated polyene chains similar to the super(electrically)-conducting polyacetylenes. It should be of special interest to monitor the changes in thermal conductivity in this type of polymer as it degrades and approaches the polyacetylenic structure. A very large number of polymeric materials form chars as a result of thermal or oxidative degradation. Char is composed largely of graphite, and the thermal conductivity of graphite is much greater than the thermal conductivities of polymers. Therefore large changes in thermal conductivity may be expected for these char-forming polymers as they degrade. Thermal conductivity, along with radiation, convection and endothermic reaction, is a process by which heat is removed from the smoldering region of a material. Therefore changes in thermal conductivity as a function of time or distance from a reacting oxygen interface are important factors in modelling these systems undergoing smoldering combustion.

Once the problems of maintaining constant sensor surface area and flatness of specimen sheets have been overcome, this simple method should find wide application in these and other thermoanalytical investigations.

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