Thermal Properties of Rigid Polymers. I. Measurement of Thermal Conductivity and Questions Concerning Contact Resistance*

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Synopsis

Several studies of the influence of contact resistance on the measurement of thermal conductivity of polystyrene using a steady-state device are presented. In each case it is seen that, although this influence can perhaps be minimized, it cannot be eliminated as an experimental complication. A novel technique is then described which does eliminate entirely contact resistance as a variable, and this technique is shown to yield an unequivocal value of thermal conductivity.

INTRODUCTION

The importance of the measurement and understanding of the thermal properties of polymeric systems has been well recognized in recent years. In particular, the thermal conductivity of a material determines the time-independent or steady-state conditions of heat flow rates and temperature distributions which are important during heating or processing. On the other hand, the thermal diffusivity determines time-dependent heat flow rates and temperature distributions through a material during transient, cyclical, or other unsteady-state situations. Clearly, precise information concerning both thermal conductivity and thermal diffusivity must be available for the analysis of polymer processing operations or heat flow situations in general where transient energy phenomena are of concern.

However, it has also been recognized that the measurement of any thermal property of polymers, either thermal conductivity or diffusivity, or heat capacity or volumetric coefficient of expansion, is a difficult and often time-consuming experimental procedure.[‡] These difficulties have led to confusion in the literature over the detailed nature of many thermal properties. For example, it is instructive to compare reported values of thermal conductivity of a common polymer such as polystyrene, where one finds not only large discrepancies at any given temperature but also widely varying dependencies on temperature. (Although instructive, we will not make such a comparison here as it is not our intention to critically examine literature data.) Certainly some of this wide variability is due to varying polymer characteristics, such as

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[‡] For a general review of experimental procedures, see, for example, Ref. 1.

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molecular weight or molecular weight distribution perhaps, but experimental uncertaincies and error must also play a prominent role.

During the source of our investigations of polymer thermal properties, we have built and rigorously tested devices for measuring thermal conductivity and thermal diffusivity. The design of the thermal conductivity device is fairly conventional and will be described in the next section; the design of the thermal diffusivity device is novel and will be described in detail in a future paper. During the course of the construction and testing of these devices, we studied many phenomena associated with their performance and accuracy, and with the fabrication of test specimens. One of the most important questions which emerged concerned the contact between test specimen and various parts of a device, and the resultant contact resistance which results when this contact is imperfect. The purpose of this report is to describe several studies we made concerning contact resistance, and then discuss a procedure which eliminates contact resistance as a variable.

EXPERIMENTAL

Thermal Conductivity Apparatus

The thermal conductivity apparatus used to obtain the data reported here is based on a design consisting of a stacked series of elements of circular symmetry in the following order: upper mold assembly/sample/copper diffusing plate/thermofoil heater (No. HK5116-A-21.6, Minco Inc., Minneapolis, MN)/copper diffusion plate/sample/lower mold assembly. This device is symmetrical with respect to both the radial and the perpendicular directions, and by properly adjusting the thicknesses of the various elements the need for guard heaters can be eliminated. Provision is made for measuring temperatures using thermocouples fashioned from 3 mil, Teflon-coated iron and constantan wire (Omega Engineering, Stamford, CT) near the copper plate/sample and sample/mold assembly interfaces at three points each. The outer mold assemblies can be shimmed with respect to the samples and other inner elements, and the entire cell bolted to maintain a constant sample thickness. The apparatus can also be used in an unbolted condition, thus allowing the sample to expand freely. Details of this device are shown schematically in Figure 1.

The two elements referred to above as simply "upper mold" and "lower mold assembly" are in fact rather massive heat sinks with long, thin fins attached at the ends to aid heat conduction. Further, almost the entire lateral surface of the mold assembly/sample/copper plate sandwich is insulated with a calcium silicate material (Dresser Industries, Brunswick, GA). These features are shown schematically in Figure 2. The heat sinks and insulators were carefully designed to reduce radial heat flow, and thus eliminate the need for guard heaters on the lateral surface. Direct measurement using thermocouples of temperatures in the radial direction and across the lateral surface indicated radial heat losses to be negligible for most specimens, and no greater than 0.75% for the thickest specimens.

Once assembled, the thermal conductivity device is placed on a stand in a forced draft oven. The ambient temperature of the oven, which in turn
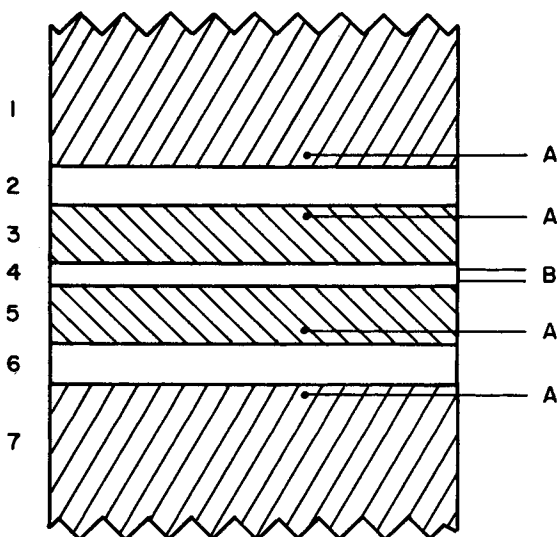
Fig. 1.   Diagram of inner core of stacked series of elements of thermal conductivity device. Numbered elements with approximate thicknesses correspond to: (1) upper copper mold assembly (1.5 in.); (2) sample (0.005–0.100 in.); (3) upper copper diffusing plate (0.125 in.); (4) thermofoil heater (0.007 in.); (5) lower copper diffusing plate; (6) sample; and (7) lower copper mold assembly; (A) thermocouples (four of 12 shown); (B) leads from thermofoil heater.

determines the steady-state temperatures across the polymer sample, is controlled by a rheostat and has a range of room temperature to 300°C. At steady-state the oven temperature is constant to about ±0.2°C, and the average temperature drifts by no more than 0.1°C/h. If a perturbation of 20–50°C is made in the ambient oven temperature, a period of 60 min is required to reestablish steady-state conditions within the polymer samples. This feature is somewhat unfortunate as it results in rather long testing times,
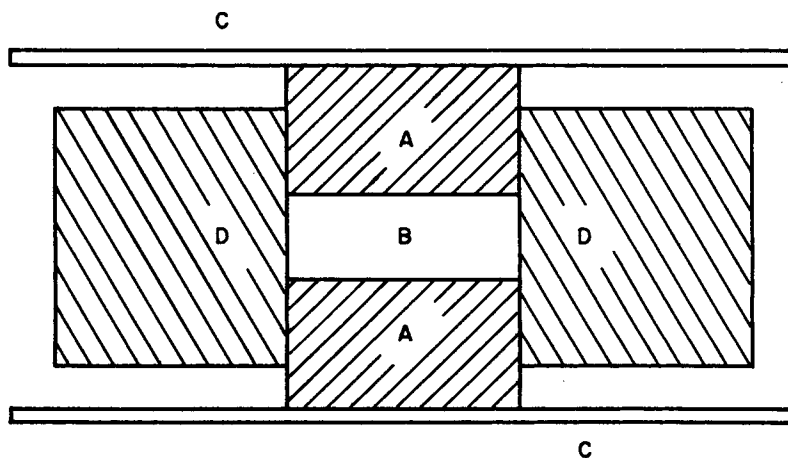

Fig. 2.   Diagram of outer elements of thermal conductivity device: (A) upper and lower copper mold assemblies (1.5 in. thick, 2.55 in. diameter); (B) inner core (see Fig. 1); (c) upper and lower copper fins (0.020 in. thick, 9 in. diameter); (D) insulation (3 in. thick and 8 in. diameter).

and this may be inconvenient at higher temperatures if the polymer being tested is sensitive to thermal decomposition.

The voltage and current to the thermofoil heater and the voltages from the thermocouples are measured with a microvolt digital multimeter (No. 177-1788, Kiethley Instrument Co., Cleveland, OH). Typical values for the heater are a voltage of 15 V and current of 0.5 A, and a typical temperature drop across a polymer sample is 5°C. These data, along with the measured thickness of the sample (typically 5–100 mils), allow thermal conductivity to be calculated directly from an integrated form of Fourier's law of steady-state heat conduction.

It was estimated that heat flow by radiation is less than 0.5% of the total heat flow, and hence is not an appreciable factor. However, a correction was made for this effect.

SAMPLE PREPARATION

All of the results reported here were obtained using samples fabricated from a commercial grade of polystyrene (Lustrex HH-101, Monsanto Chemical Co., Springfield, MA). This polystyrene is reported[2] to have a glass-transition temperature of 106°C, a number-average molecular weight of 110,000 and a weight-average molecular weight of 270,000. Physically the polymer is in the form of small cylindrical pellets, and was used as received.

Test specimens were prepared by compression molding polymer pellets in a homemade, stainless steel mold using a laboratory hydraulic press (Model M, Carver Inc., Menomonee Falls, WI). A typical pressing sequence included: (1) a warmup period of 10 min to 150°C; (2) a breathing period of 1 min under 500 psi applied pressure; (3) a compression period of 4 min at 150°C under full applied pressure of 1600 psi; (4) a heat treatment period of about 5 min at 180°C with no load; and (5) a slow cooldown period to room temperature. A typical specimen had a 2.5 in. diameter, and was between 5 and 100 mils in thickness.

Because of the extensive contact (roughly 5 in.[2] per face) between the specimen faces and mating metallic parts of the test cell, the question of smoothness and parallelness is of particular significance. Consequently, mold surfaces were surface-ground to a flatness of 0.2 mil and a 0.05 mil finish. The resulting molded specimens had excellent optical properties and no apparent surface imperfections. Because of some unevenness of the hydraulic press platens, individual samples tended to show thickness variations of 1–3 mils, usually in the form of a gradual slope across a diameter of the disk. Although only the best specimens were chosen for testing; nevertheless, we could find no evidence that thickness variations in this range caused distortion of the axial heat flow pattern in the heat sinks.

CONTACT RESISTANCE

In spite of our efforts to achieve smooth sample and metal plate surfaces, experimental evidence suggested the existence of an additional resistance at these interfaces, which we have denoted "contact resistance." In principle, thermal conductivity should be independent of sample thickness, other things being equal. However, we observed thermal conductivity to increase with
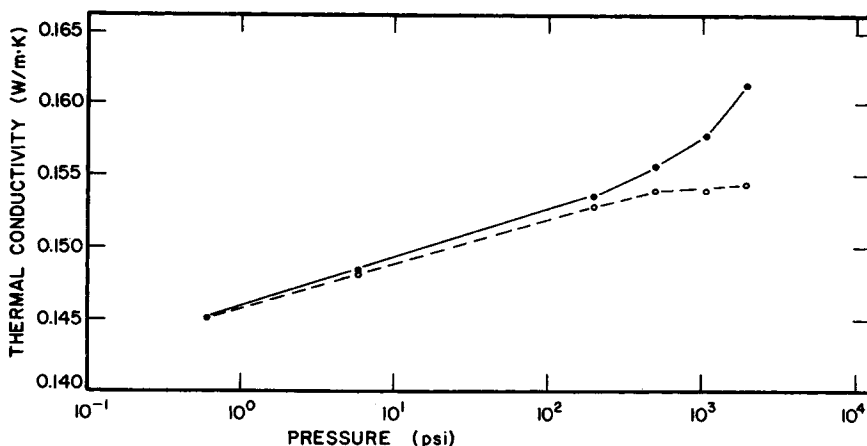
Fig. 3. Thermal conductivity vs. pressure applied to measurement stack: (●) as measured; (○) correction applied for sample dimension change with pressure.

increasing sample thickness. This behavior suggests an interface-related contact resistance, essentially independent of sample thickness and hence of diminishing importance as sample thickness increases. It should be noted in this and the following discussion that we assume the highest measured value of thermal conductivity to most nearly approximate the true value, being least influenced by contact resistance.

Clearly it is necessary to eliminate or reduce to a very small relative percent the influence of contact resistance in the measurement of any thermal property such as thermal conductivity. To this end, we investigated three possible techniques, pressure, grease application, and high temperature pretreatment, which will be described in the first three subsections which follow. In the final subsection we will discuss the simultaneous application of the latter two of these techniques.

Pressure

Application of pressure to the sample/plate sandwich presumably tends to squeeze out air gaps at the interfaces and force the polymer samples to better conform to the plate surfaces. A series of thermal conductivity measurements was made over an applied pressure range of 0.6 psi (corresponding to the pressure produced by the upper sink plate under normal operating conditions) to 2000 psi. These measurements were performed at 60°C using the same pair of samples of 35.2 mil thickness throughout.

The results of these measurements are shown in Figure 3. Also shown are values of thermal conductivity corrected for the decrease in sample thickness with increasing pressure using a compressibility factor of 2.23×10^{-5} psi^{-1}.[3] It is seen that the application of relatively little pressure significantly increases the measured value of thermal conductivity. However, this technique is complicated by two factors. First, the correction for compressibility is seen to be quite large at higher pressures, introducing an uncertainty into the corrected value. Second, and perhaps more importantly, several investigators have shown that the thermal conductivity of polymer solids[4,5] and melts[6-8] is
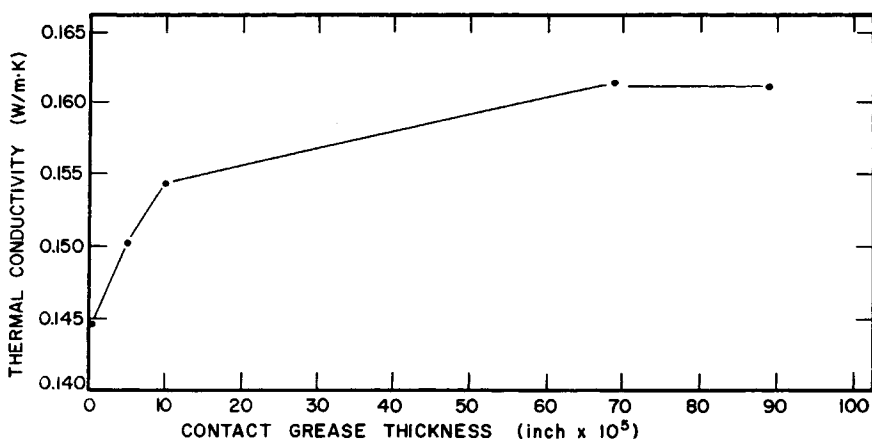
Fig. 4.   Thermal conductivity vs. thickness of contact grease layer.

itself pressure-dependent, increasing with increasing pressure. For these reasons, and because of containment problems of a melt under high pressure, we abandoned this technique as a practical solution to contact resistance.

Contact Grease

Contact grease is often used in an attempt to fill in any void pockets or other minor imperfections at interfaces and thus give better thermal contact. For this purpose we used an electrical heat sink compound (Type Z-9, GC Electronics, Inc., Rockford, IL) consisting of metallic oxides suspended in a silicone grease. This material is reported to have a useful temperature range of -65–$400°F$, and a density and thermal conductivity at $20°C$ of 2.7 g/cm^3 and 0.52 W/(m K), respectively.

Results of thermal conductivity measurements at $60°C$ for several different thicknesses of contact grease are shown in Figure 4. Contact grease thickness was estimated from the known weight of grease applied, this grease being carefully and evenly spread across the surfaces of an interface. Considerable improvement in thermal conductivity values is observed for grease thicknesses above 0.7 mil, and probably thicknesses in the 1.0 mil range would be optimal. However, as we were concerned about the possible influence of the temperature dependence of a grease layer of thickness as great as 1.0 mil, we elected to use a thickness of 0.4 mil for routine testing work.

High Temperature Pretreatment

Above its glass-transition temperature, an amorphous polymer such as polystyrene becomes reasonably plastic, and this fact suggests high temperature pretreatment as a technique to achieve better sample/plate contact. The result of such a premeasurement cycle to $175°C$, that is, about $70°C$ above the sample glass-transition temperature, is shown in Figure 5. The value of thermal conductivity at $60°C$, which for comparison is the temperature at which the studies of pressure and contact grease were conducted, is considerably improved after a single heating and cooling cycle. Subsequent cycles had
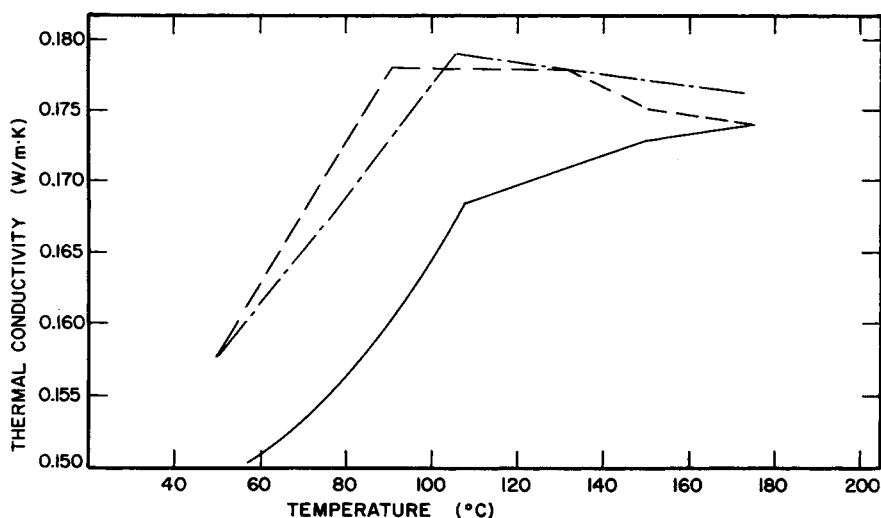
Fig. 5. Thermal conductivity vs. temperature showing effects of high temperature pretreatment: (–), first heating to 170°C; (—·—) first cooling from 170°C; (---) second heating to 170°C.

little further effect, suggesting that the polymer sample did indeed flow slightly and conform during the period of time above the glass-transition temperature.

Summary of Contact Resistance Studies

The results of the application of the three techniques discussed above are summarized in Table I. Also listed is an indication of the relative increase in thermal conductivity obtained using each technique. It is seen that very significant increases in thermal conductivity result in each case.

For routine testing it appeared to us that a combination of the latter two techniques, contact grease and high temperature pretreatment, offered the most promising possibility. Results of thermal conductivity measurements at 60°C using a 0.4 mil contact grease thickness and single high temperature pretreatment cycle to 175°C are shown in Figure 6. Also shown for comparison are results where no precautions were taken to reduce contact resistance.

TABLE I
Summary of the Effect on Thermal Conductivity of Several Techniques
Used to Reduce Contact Resistance

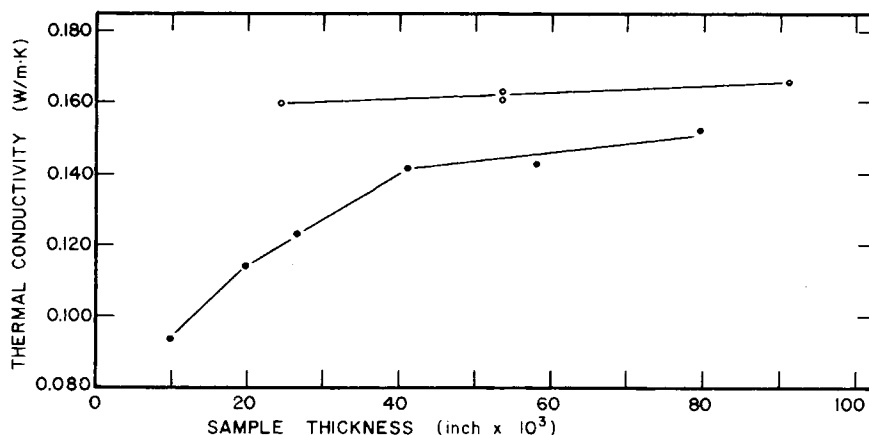| Technique	Thermal conductivity [W/(m K)]		
	Without technique	With technique	Percentage increase
Pressure	0.145	0.155	6.5
Grease	0.145	0.161	9.9
Pretreatment	0.145	0.163	11.0
Grease and pretreatment	0.145	0.165	12.1

Fig. 6. Thermal conductivity vs. sample thickness: (●) no special precautions taken; (○) 0.4 mil contact grease layer and single high temperature pretreatment to 175°C.

Again very significant increases in thermal conductivity result, and as shown in Table I, a maximal value of 0.165 W/(m K) is obtained.

The results of efforts to reduce contact resistance seen in Figure 6 are very encouraging. Nevertheless, closer inspection of the data where every precaution has been taken reveals a slight, but significant, upward slope, thermal conductivity values rising from 0.160 to 0.165 W/(m K). This suggests that contact resistance, although greatly reduced, has not been entirely eliminated as a complication. In an effort to obtain unequivocal values of thermal conductivity, we investigated a new measurement technique and this will be described in the next section.

PROPOSED MEASUREMENT TECHNIQUE

Consider the total resistance across the sample to be comprised of two parts, sample resistance and contact resistance, that is,

$$\text{total resistance} = \text{sample resistance} + \text{contact resistance} \qquad (1)$$

Since the total resistance is the observed temperature drop ΔT divided by the total heat flow Q (where Q is the product of the measured current and voltage), and the sample resistance is given by $\Delta x/kA$ (where Δx, k, and A are the sample thickness, thermal conductivity, and surface area, respectively), we can write

$$\frac{\Delta T}{Q} = \frac{\Delta x}{kA} + \text{contact resistance} \qquad (2)$$

Now if the contact resistance is assumed to be independent of sample thickness, an assumption which the experimental results reported in the previous section appear to support, then eq. (2) implies a plot of $\Delta T/Q$ vs. Δx should yield a straight line with slope $1/kA$ and intercept equal to contact resistance.
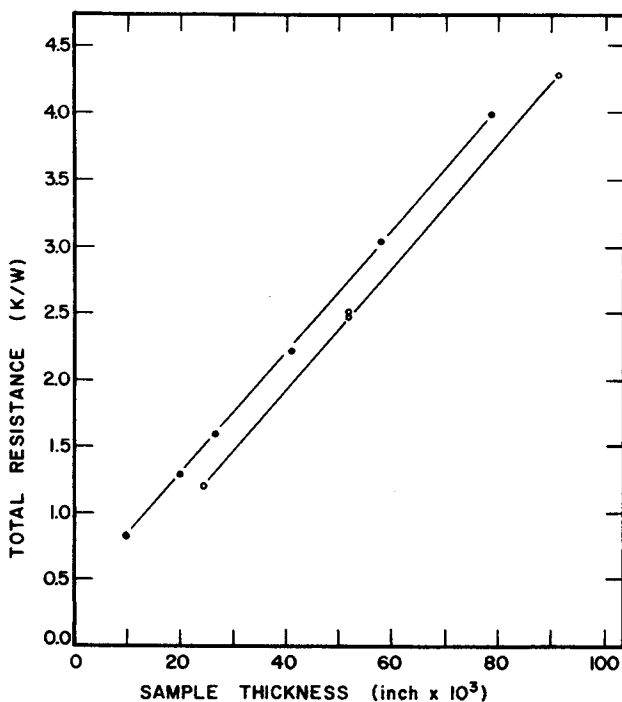
Fig. 7.   Total resistance vs. sample thickness: (●) no special precautions taken; (○) 0.4 mil contact grease layer and single high temperature pretreatment to 170°C.

The analysis presented above suggests a measurement technique for determining thermal conductivity which is independent of the presence or absence of contact resistance. To test this procedure the data shown in Figure 6 are replotted in the form of total resistance vs. sample thickness and shown in Figure 7. Both sets of data, that is, set (1) for which no special precautions were taken to minimize contact resistance and set (2) for which both contact grease and high temperature pretreatment were employed, do indeed yield linear plots. As expected, set (1) has a much greater contact resistance (intercept); however, as suggested in the previous section, contact resistance has not been entirely eliminated in set (2) as evidenced by the small, but nonzero, intercept. Perhaps most importantly, the slopes of sets (1) and (2) are virtually identical, and yield a value of thermal conductivity of 0.168 W/(m K). Comparing this value with those already examined in Table I, the present value is seen to be the highest, again as expected if the proposed method has merit. We emphasize again that this result was obtained regardless of whether precautionary measures concerning contact resistance were observed or not. This seems an important feature of the proposed measurement method, and a confirmation of the analysis presented in the first part of this section. Also, it is interesting to note that if radial heat losses were present, the proposed method would lead to a lower value of thermal conductivity (since the slope of the total resistance vs. thickness curve would be smaller) than the true value, whereas in conventional calculations one would obtain an erroneously high value.
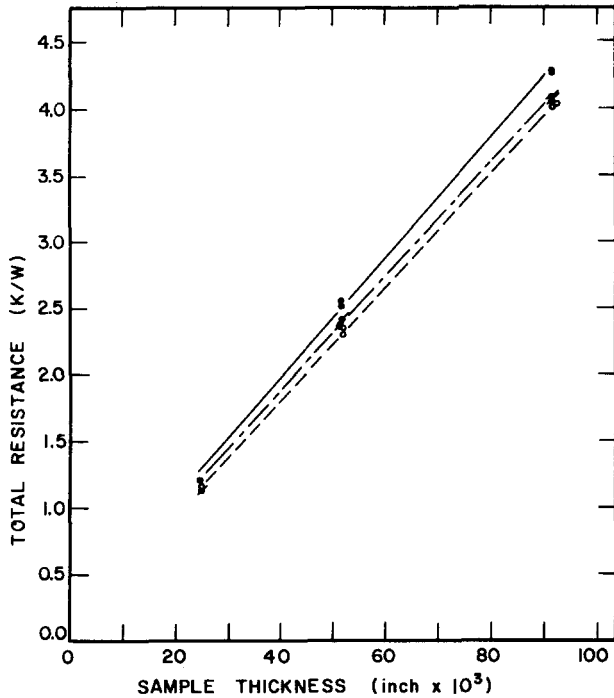
Fig. 8. Total resistance vs. sample thickness for three temperatures: (●) 60°C; (○) 110°C; (◐) 170°C.

TABLE II
Determination of Thermal Conductivity and Estimation of Relative Importance
of Contact Resistance at Three Temperatures

Temp (°C)	Thermal conductivity [W/(m K)]	Contact resistance (K/W)	Percent contact resistance		
			25 mil	50 mil	90 mil
60	0.168	0.0876	7.6	3.8	2.1
110	0.1777	0.0631	5.8	2.9	1.66
170	0.176	0.0755	6.8	3.4	1.9

In the course of this experimental evolution two further sets of data were obtained; at 110 and 170°C, and otherwise identical to set (2) above. These data are shown in Figure 8, and summarized in Table II where an indication is given of the relative importance of contact resistance at each thickness and temperature. It is interesting to note that this relative importance is essentially independent of temperature.

CONCLUSIONS

Contact resistance is seen to be an important influence in the measurement of thermal conductivity, and presumably any thermal property where there is appreciable surface contact between test specimen and surfaces of the test

device. Even when elaborate precautions are exercised, this influence cannot be entirely eliminated.

A new measurement technique is proposed, and is seen to yield an unequivocal value of thermal conductivity, independent of whether precautions to reduce contact resistance are taken or not. This feature is clearly the outstanding virtue of the proposed method. A distinct disadvantage is the fact that a series of three or more sample thicknesses must be tested, adding greatly to the time and cost of sample preparation and measurement. Nevertheless, in situations where the highest accuracy is required, the proposed method is to be preferred.

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