Thermal Conductivity of Polymers by Hot-Wire Method

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SYNOPSIS

The hot-wire standard technique, mostly used for ceramic materials, was adapted to determine the thermal conductivity of nylon 6,6, polypropylene, poly(vinyl chloride), and poly(methyl methacrylate). The results obtained showed that the hot-wire standard technique can be used with accuracy and reproducibility to measure the thermal conductivity of polymers. In the second stage, to verify the effect of the use of a lignin (a "macromonomer") in the thermal conductivity of phenolic resins, this technique was applied to phenol–formaldehyde and phenol–lignin–formaldehyde resins. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

By considering the results presented in the literature,[1] one may notice that the experimental determination of the thermal conductivity presents some difficulties and requires high precision in determining the necessary parameters for its calculation.[2] In this work, the hot-wire method[3,4] was proposed for the determination of the thermal conductivity of polymeric materials. It is an absolute, non-steady-state, and direct method, and therefore it makes the use of standards unnecessary. This methodology has been successfully utilized with ceramic materials.[5]

The hot-wire method was first used by Van der Held and Van Drunen[6] in 1949. However, it was Haupin[7] who in 1960 first used it to determine the thermal conductivity of ceramic materials and established the basis for all the current variations of the method. It is nowadays a method used worldwide to measure thermal conductivity up to 25 W/m K.[8]

METHODOLOGY[2]

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. Applying an electric current throughout the wire, a constant amount of heat, per unit time and per 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 temperature, which is logarithmically dependent on time. In practice, the theoretical linear source is approached by a thin electric resistance and the infinite solid is replaced by a finite sample.[9]

The difference between the experimental and theoretical curves in its initial section is due to the contact resistance between the hot wire and the sample, whereas the difference seen in the final section derives from the finite size of the sample. The intermediate zone, where both curves exhibit the same behavior, defines the time limits that must be considered when measuring the thermal conductivity through the hot-wire technique. Thus, the maximum measurement time decreases as the conductivity of the material increases. This limits the use of this method with metallic materials because their high thermal conductivity would greatly reduce the maximum time of measurement. Furthermore, it is not possible to use this method for electrical conductor materials, unless some process of electric isolation between the hot wire and the sample is developed.

In the case of polymeric materials, these restrictions do not exist. Nevertheless, the use of this method in the measurement of thermal conductivity of polymers has not been documented as yet.

Four variations of the hot-wire method are known:

- Standard technique (cross technique)
- Hot-wire resistance technique
- Two-thermocouple technique
- Hot-wire parallel technique

The theoretical model is the same, and the basic difference among these variations lies in the temperature measurement procedure. Consequently, the final equation obtained for the calculation of the thermal conductivity is different for each one of these variations.

EXPERIMENTAL

Although two test pieces (230 × 115 × 65 mm) are necessary in all variations for ceramic materials, for polymeric materials it was possible to reduce their dimensions to 200 × 50 × 25 mm. Both the parallel hot-wire technique and the cross technique were tried.

To measure the thermal conductivity using the hot-wire parallel technique, a constant electric current is applied throughout the wire. The temperature increase inside the material, at a distance **r** from the hot wire, is then recorded. It was observed that for polymeric materials this is a limiting factor since a high electric current generates excessive heat in the wire and can change the properties of the polymer. On the other hand, reduced electrical currents generate such a low thermal gradient that it is not possible to obtain accurate temperature measurements, and, consequently, unsatisfactory results are obtained. Therefore, the cross technique was chosen in this work. In this technique, developed by Mittenbüler,[10] a thermocouple junction is welded at the middle of the hot wire. The temperature variation can be more easily detected in this way than in the technique described above, i.e., the parallel hot-wire technique, especially because of the low thermal conductivity of polymers and the requirement of using lower electric currents than those used for ceramic materials.[11]

The measurements, in this case, were carried out at room temperature. The temperature increase as a function of time was recorded by using an x-t ECB graphic recorder Model RB 102 series 252.

When positioning the electric resistance and the thermocouple, two orthogonal grooves were forged on one of the faces of one of the pieces, passing through its center, in order to receive the measurement cross. The depth of these grooves should correspond approximately to the diameter of the wires to be embedded. The measurement cross consists of the hot wire and the thermocouple, which has one of its junctions welded perpendicularly to the wire. The other junction of the thermocouple is maintained at a constant reference temperature. Once the wires are correctly positioned, the thermal contact is guaranteed by pressing the two pieces one against the other by means of grips, in the center and at the borders. This technique was standardized in 1976[12] by DIN51046 standard-Part 1. The thermal conductivity is calculated by using eq. (1):

$$k = \frac{q'}{4\pi} \times \frac{\ln\left(\frac{t_2}{t_1}\right)}{T_2 - T_1} \qquad (1)$$

where k = thermal conductivity of the material, q' = linear power density, t_1 and t_2 = elapsed times after the beginning of heat release, and T_1 and T_2 = temperature increase at time t_1 and t_2, respectively.

RESULTS

Six measurements were carried out for each sample: three (L_1, L_2, and L_3) in one direction of current and three (L_4, L_5, and L_6) by reversing the polarity of the dc voltage (Table I). Such a procedure is necessary when using dc, because of the asymmetrical arrangement of both thermocouple legs on the hot wire.[4] Table II shows (column A) the average values obtained for nylon 6,6, polypropylene (PP), poly(vinyl chloride) (PVC), and poly(methyl methacrylate) (PMMA), including the corresponding values found in the literature (column B).[13]

Once the reproducibility and reliability of the method was proved by using samples of commercial polymers, the thermal conductivity of the laboratory-synthesized phenolic[14] and phenol–lignin resins (30% of phenol was substituted by lignin, w/w) was measured. The results are showed in Table III.

Table I Measurements of the Thermal Conductivity of Nylon 6,6, PP, PVC, and PMMA

	L_1	L_2	L_3	k_{i+}	Δ	L_4	L_5	L_6	k_{i-}	Δ	$\langle k \rangle$
Nylon	0.317	0.294	0.280	0.297	±5%	0.309	0.298	0.299	0.302	±2%	0.300
PP	0.247	0.243	0.248	0.246	±1%	0.246	0.240	0.244	0.243	±1%	0.245
PVC	0.184	0.185	0.192	0.187	±2%	0.198	0.200	0.219	0.210	±5%	0.200
PMMA	0.241	0.231	0.218	0.230	±5%	0.226	0.222	0.229	0.226	±2%	0.228

Δ, standard deviation; $\langle k \rangle$, average value.

DISCUSSION

The results obtained with the hot-wire parallel technique were not satisfactory. This is attributed to the fact that it is necessary to use a low electric current in order not to change the properties of sample, for instance, by melting or degradation. Consequently, the increase of temperature registered by the thermocouple at 16 mm from the hot wire is very small and leads to inaccurate results for the thermal conductivity of the material, as confirmed in all measurements using the hot-wire parallel technique.

When the cross technique is employed, the temperature increase is measured on the wire itself. Then, higher values are obtained and the source of errors associated to the low-temperature measurements is eliminated.

Once the appropriate technique was established, the size of the samples was gradually decreased. This was possible because the thermal conductivity of polymers is usually lower than is the thermal conductivity of ceramic materials.[11] A smaller sample is desirable when the samples are prepared in laboratory scale.

As the dimensions of the sample were being decreased to 200 × 50 × 25 mm, some experimental procedures were adopted:

- The electric current intensity was kept constant for all sample sizes.

Table II Thermal Conductivity of Polymers (k) in W/m K

Polymer	Column A	Column B
Nylon	0.300	0.245
PP	0.245	0.120
PVC	0.200	0.130–0.290
PMMA	0.230	0.210

- The calculations of the thermal conductivity were carried out by using the same time interval, i.e., from 360 to 600 s.
- The temperature at the interface sample/environment was recorded during the measurement interval, with the purpose to ensure that there was no heat exchange during the data acquisition time interval.

The reliability of the results obtained for the commercial samples—nylon 6,6, PP, PVC, and PMMA—may be demonstrated by the correlation coefficient (R), when temperature vs. ln time data are fitted by a linear regression analysis procedure, as proposed by eq. (1).

In Figure 1 is shown the curve obtained for PMMA sample, and in Table IV, the data for the other polymers are indicated. The reproducibility was also confirmed since the scattering in the experimental measurements for each polymer was smaller than 5%.

By analyzing the results obtained, one may assert that they have the same magnitude of those found in the literature.[13] The difference observed between the data of thermal conductivity of PP (columns A and B, Table II) can be associated to different degrees of crystallinity of the two samples. It is not possible to get a conclusion now, because these data were not provided for the sample mentioned in column B, Table II.[15]

Phenolic Resins

The present work was part of a study where it was intended to verify the changes observed in the

Table III Thermal Conductivity of Phenolic Resins

Percentage of Lignin	k (W/m K)
0	0.265 ± 3%
30	0.285 ± 4%

properties of phenolic resins, when lignin partially replaces phenol in their formulation. Lignin can be recovered from renewable sources, like wood or sugar cane bagasse. The extracted material has a complex structure, with phenolic rings in its composition.[16]

In the stage described here, it was intended to analyze the effect on the thermal conductivity of the obtained resin when lignin is introduced in the network. The values determined as the thermal conductivity of the two samples, here considered, are within the range of amorphous polymers,[17] which can be taken as another indication that the method is suitable for the measurement of thermal conductivity of polymers.

It was verified, in a similar synthesis procedure in a previous work,[18] that lignin is really introduced in the network, acting as an extender chain, and not as a filler. From the results obtained for the thermal conductivity of the two samples, it can be inferred that both have the same behavior, i.e., the presence of lignin does not affect this property.

CONCLUSION

Different methods are mentioned[19-27] in the literature for the measurement of the thermal conductivity of polymers, but results derived from the use of the methodology presented here have not been pub-
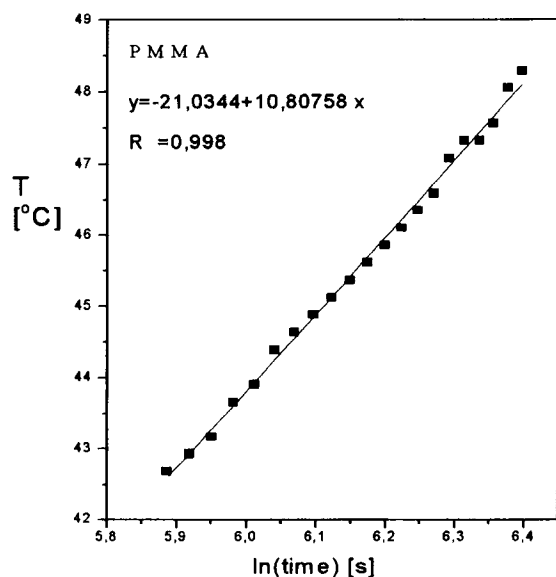
Table IV   Data Experimental for Polymers

Polymer	Equation	R
Nylon	$y = 15.4455 + 9.8234x$	0.999
PP	$y = 23.2029 + 9.2955x$	0.998
PVC	$y = 9.4537 + 11.8355x$	0.999

lished yet. The experimental results obtained allow us to assume that the hot-wire method used for ceramic materials is also an adequate experimental technique for polymeric materials, when the standard (cross) technique is employed.

With this technique, it is possible to measure the conductivity of polymers, whose values are in the range of 0.10–0.80 W/m K. The measurements that are in course at the present time led to a prognostic that it will be also possible to use this technique for foams used in thermal insulation, which have thermal conductivity in the range of 0.015–0.040 W/m K.

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P M M A

$y=-21,0344+10,80758 x$

$R =0,998$

Figure 1   Temperature (°C) vs. ln t(s) for PMMA sample.

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