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Intercomparison of Measurements of the Thermophysical Properties of Polymethyl Methacrylate[1]

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Results of an intercomparison of measurements of thermal conductivity, thermal diffusivity, specific heat capacity, and density of polymethyl methacrylate (PMMA) in the temperature range between −70°C and +80°C are presented. The purpose of this comparison is to investigate the variability of the results among guarded hot-plate (GHP) and guarded heat-flow meter (GHF) techniques on the one hand and among GHP/GHF and other measuring instruments on the other. The primary objectives are to characterize the material properties mentioned and to quantify the effects of thermal contact resistances and temperature measurements. With regard to future use of PMMA as a reference material, reference data for the thermal conductivity are derived.

KEY WORDS: polymethyl methacrylate (PMMA); specific heat capacity; thermal conductivity; thermal diffusivity.

1. INTRODUCTION

For thermal conductivity measurements, different methods are in use. In most cases, a specific method or measuring instrument can be used only

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Table I. Participants of the Intercomparison

Participant	Country
Austrian Research Centers (Seibersdorf)	Austria
BASF AG (Ludwigshafen)	Germany
Brandenburgische Technische Universität (Cottbus)	Germany
Eidgenössische Materialprüfungs- und Forschungsanstalt (Dübendorf)	Switzerland
Forschungsinstitut für Wärmeschutz e.V. (München)	Germany
Fraunhofer Institut für Bauphysik (Stuttgart)	Germany
Institut für Begutachtung und Überwachung von Baustoffen GmbH (Herzogenrath)	Germany
Institut für Fenstertechnik e.V. (Rosenheim)	Germany
Laboratoire de Technologies Industrielles Henri Tudor	Luxembourg
Materialforschungs- und Prüfanstalt Weimar	Germany
Materialprüfungsamt NRW (Dortmund)	Germany
Materialforschungs- und Versuchsanstalt (Neuwied)	Germany
National Physical Laboratory (Teddington)	United Kingdom
Physikalisch-Technische Bundesanstalt (Braunschweig)	Germany
Saint-Gobain Isover G + H AG (Ladenburg)	Germany
Taurus Instruments GmbH (Weimar)	Germany
Universität Erlangen	Germany

in a limited temperature and thermal conductivity range. But often the range of application for an instrument or measurement method and the resulting measurement uncertainty are not sufficiently specified. Furthermore, improper sample preparation can result in large systematic measurement errors.

This is a problem in legal metrology where, e.g., the thermal conductivity or the thermal resistance of an insulation material must be validated and checked at regular intervals. Though certified reference materials of very low thermal conductivities (e.g., IRMM 440 or NIST 1450c) are available, there is a lack of reference materials for the upper range of insulation materials (e.g., porous brick, polymer materials). Another field of interest involves the calibration and verification of so-called multi-property instruments for different thermophysical properties like thermal conductivity, thermal diffusivity, and the product of density and specific heat capacity.

The objectives of this intercomparison which was initiated by PTB were to compare different measurement techniques for the determination of the thermal conductivity and reference data of the thermophysical properties and to get a realistic idea of the measurement uncertainties realized by 17 European laboratories from the field of product characterization and monitoring (Table I).

2. MEASUREMENTS

2.1. Material Characterization

PMMA is an amorphous, colorless thermoplastic material of excellent optical transparency and a luminous transmittance of about 92%. It has good abrasion resistance and dimensional stability but is brittle and notch sensitive. Its water absorptivity is very low in comparison with other polymer materials. In the past PMMA has been successfully used at different institutes as a transfer standard for thermal conductivity.

The PMMA (Plexiglas®, type GS) investigated in this intercomparison was produced by casting and supplied by Degussa Röhm Plexiglas GmbH. Hydrostatic weighing at 20°C was carried out for density determination and to examine the homogeneity of the PMMA. The result of the density measurements at PTB was $\rho_{\text{mean}} = 1185.0\,\text{kg}\cdot\text{m}^{-3}$ with an expanded measurement uncertainty ($k = 2$) of $U\,(\rho_{\text{mean}}) = 2.0\,\text{kg}\cdot\text{m}^{-3}$.

The material IR transmittance determines whether or not a radiative contribution to the heat transfer has to be considered. The analysis of FTIR transmittance spectra at PTB (Fig. 1) on a sample 10 mm in thickness showed that the material is opaque at wave numbers less than about $4500\,\text{cm}^{-1}$. Indications for significant radiation heat transfer in the investigated temperature range were not found.

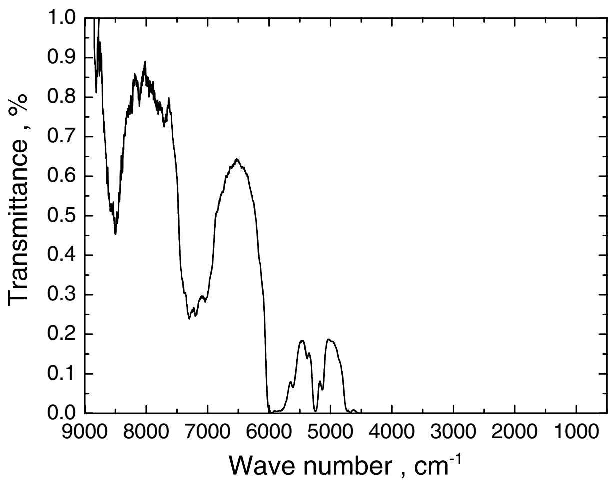

Fig. 1. FTIR transmittance spectrum of a 10 mm thick polymethyl methacrylate window.

2.2. Measurement Techniques

Different experimental methods, both steady-state and transient, were applied in this intercomparison. For steady-state thermal conductivity measurements, the guarded hot-plate (GHP) and the guarded heat-flow meter methods (GHF) were used. Transient measurements were carried out by means of the transient hot-strip (THS) and the transient plane-source techniques (TPS/Hot Disk) as well as the needle-probe technique. The specific heat capacity was measured by power compensated differential scanning calorimetry (DSC). From the results for the thermal conductivity, specific heat capacity and density values for the thermal diffusivity were derived.

All measurement uncertainties of the PTB were determined in accordance with the "Guide to the Expression of Uncertainty in Measurement (ISO-GUM)" [1]. The assigned uncertainties are expanded ones, i.e., the standard coverage factor $k = 2$ was used which corresponds to a coverage probability of approximately 95%. The majority of the participants declared measurement uncertainties based on ISO-GUM, EN12664, EN1946-2, or standard deviations.

3. RESULTS

The specific heat capacity of the material was measured at PTB with a relative measurement uncertainty of 1.5% [2]. The results (Fig. 2) are in very good agreement with literature data evaluated and summarized in the ATHAS database by Oak Ridge National Laboratory and the University of Tennessee.

Figure 3 shows the results of the thermal conductivity measurements of the participants in the intercomparison. Two of the partners found a decrease in the thermal conductivity as a function of temperature, which is in contradiction to the expected behavior and to the results of most participants. One of the two partners used the GHP method and the other one the GHF method. It was also observed that two other participants found a more significant increase in the thermal conductivity as a function of temperature than the other ones, but again they used different methods. When comparing all results, no method-dependent deviations were found. The observed spread of the data was between $\pm 8\%$ at $20^{\circ}C$ and $\pm 12.8\%$ at $50^{\circ}C$. These values are three times higher than the uncertainty declared by most of the partners. The explanation for this fact is that the influence of the thermal contact resistances between the temperature sensors and the sample surfaces were underestimated. A similar behavior was reported for the certification of a Pyrex glass as a BCR reference material [3].

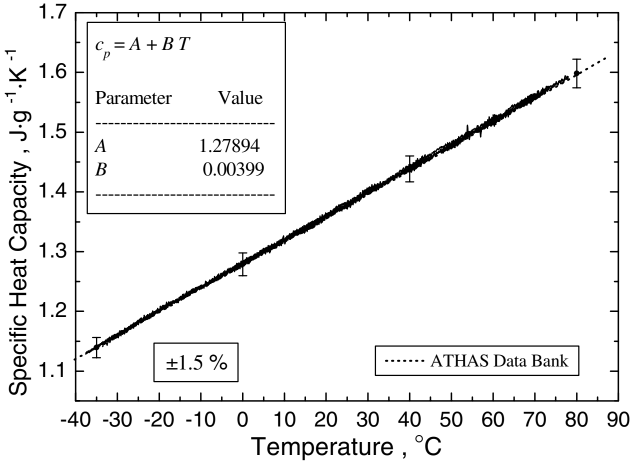

Fig. 2. Specific heat capacity results of polymethyl methacrylate as a function of temperature T measured by differential scanning calorimetry.

To independently prove that the thermal contact resistance is adequately taken into account, measurements were carried out at PTB by two different methods (GHP, THS) [4, 5]. The results for the two methods

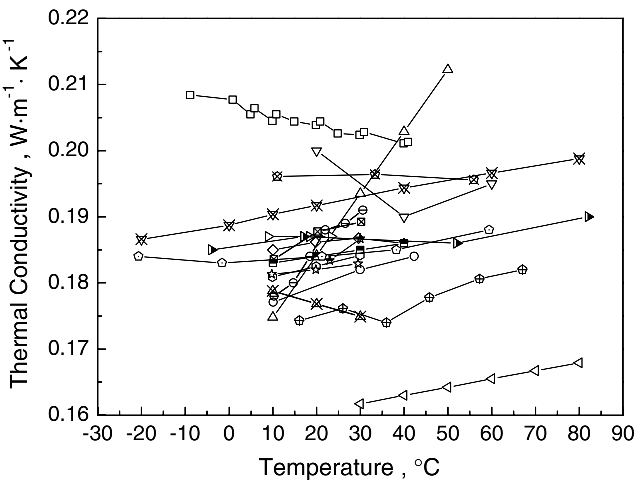

Fig. 3. Thermal conductivity results measured by different steady-state and transient techniques. —⊠—, —★—, —⊠—, —⊖—, —▶— GHF technique; —▽— TPS technique; —⬠— Needle-probe technique; All other symbols:GHP technique.

(Fig. 4) are in very good agreement. Furthermore, good agreement was found with the results of NPL measurements on Perspex (PR44.06) (Salmon, Private commun.).

From the results of PTB measurements for the thermal conductivity λ, specific heat capacity, c_p, and density, ρ, values of the thermal diffusivity a were calculated (Fig. 5) according to $a = \lambda/\left(\rho c_p\right)$. The relative expanded ($k = 2$) uncertainty of the thermal diffusivity is 4.4% at temperatures below −30°C and 3.0% at temperatures higher than or equal to −30°C. Table II shows the results of PTB measurements for the thermophysical properties of PMMA.

4. CONCLUSIONS

The unexpectedly large spread of the results of the thermal conductivity measurements raises some questions. There are different certified reference materials with very low thermal conductivities of about $0.04\,\mathrm{W \cdot m^{-1} \cdot K^{-1}}$ and relative uncertainties lower than 1.5%. At higher thermal conductivities, a BCR Pyrex glass with a value of about $1.14\mathrm{W \cdot m^{-1} \cdot K^{-1}}$ and a relative uncertainty of 1.7% can be used for the calibration of instruments or testing of uncertainty budgets. One would expect that the uncertainty budget for a measurement of a material like PMMA with a thermal conductivity of about $0.19\,\mathrm{W \cdot m^{-1} \cdot K^{-1}}$ has been checked by these two types of reference materials.

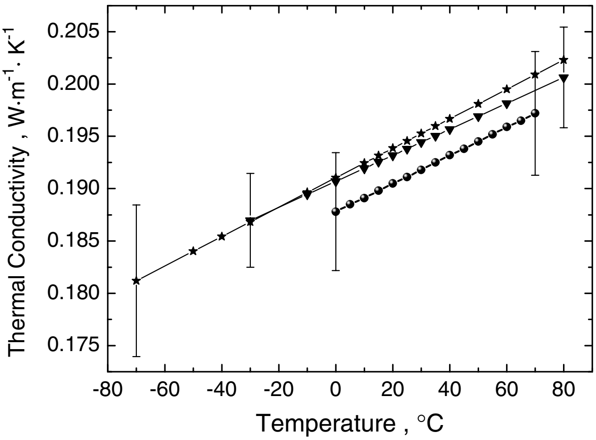

Fig. 4. Comparison of the results of the PTB measurements of the thermal conductivity (star(THS); down triangle(GHP)) with the NPL reference material Perspex (PR44.06, circle).

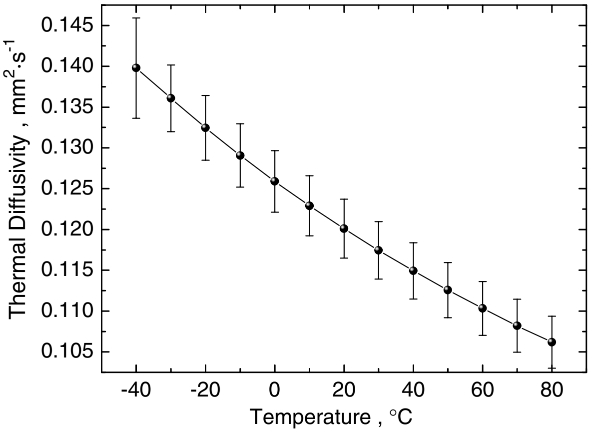

Fig. 5. Thermal diffusivity results calculated from the PTB measurements of the thermal conductivity, specific heat capacity, and density.

From this point of view the large discrepancy between the stated uncertainties and the observed scatter means that there is some need for action. Obviously most of the participants overestimated the accuracy of their measurements.

Table II. Summary of PTB Measurement Results of the Thermophysical Properties of Polymethyl Methacrylate

T(°C)	c_p $(\mathrm{J \cdot g^{-1} \cdot K^{-1}})$	λ $(\mathrm{W \cdot m^{-1} \cdot K^{-1}})$	a $(\mathrm{mm^2 \cdot s^{-1}})$
−70		0.1812	
−60		0.1826	
−50		0.1840	
−40	1.119	0.1854	0.140
−30	1.159	0.1869	0.136
−20	1.199	0.1882	0.133
−10	1.239	0.1895	0.129
0	1.279	0.1908	0.126
10	1.319	0.1921	0.123
20	1.359	0.1934	0.120
30	1.399	0.1947	0.117
40	1.439	0.1959	0.115
50	1.478	0.1972	0.113
60	1.518	0.1985	0.110
70	1.558	0.1998	0.108
80	1.598	0.2011	0.106

Therefore, a certification of PMMA as a reference material based on a weighted mean as a function of temperature and using the squares of the associated standard uncertainties of the weights would be most questionable.

Another question is the relation between steady-state and transient measurement methods. One can understand that the results of measurements by means of, e.g., a GHP apparatus optimized for investigations of insulation materials, show systematic deviations due to the thermal contact resistance between the sample and the surfaces of the apparatus. This problem should not occur with instruments specified to cover a much broader range of thermal conductivities.

As a conclusion, the results emphasize the need for a suitable reference material and the importance of intercomparison measurements. In the next step only selected partners with evaluated methods and uncertainty budgets will participate in the certification of this material.

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