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Thermal characterization of liquids and pastes using the flash technique

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Abstract

For decades, flash methods [W.J. Parker, R.J. Jenkins, C.P. Butler, G.L. Abbott, J. Appl. Phys. 32 (1961) 1679–1684] have been well-known for characterizing the thermophysical properties such as the thermal diffusivity of solid materials. Fast measurement times, easy sample preparation and high accuracy are only some of the advantages of this non-contact, non-destructive measurement technique. Furthermore, the method can easily be adapted to the analysis of multi-layer samples as long as appropriate mathematical models are employed for the analysis of the detector curves. Nowadays, characterization of liquids, pastes and melts is becoming increasingly important for industrial applications. Presented in this work are principle details regarding newly developed sample holders for such applications. Furthermore, reliability tests (on water and ethylene glycol) are presented and compared to literature values. Additionally, some application examples on pastes and polymer melts are shown.

Keywords: Laser flash; Liquids; Pastes; Thermal conductivity; Thermal diffusivity

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1. Introduction

Flash methods [1] are generally employed for the measurement of single-layer solid materials. The method can be used for the analysis of highly conducting materials such as metals or ceramics as well as low-conducting materials such as polymers. In a laser flash test, the front side of a plan-parallel sample disk is heated by a short laser pulse. The heat diffuses through the sample and leads to a temperature rise on the rear side of the sample. By measuring this temperature rise versus time, the thermal diffusivity of the sample can be determined. Using a comparative technique, the specific heat can be determined. By multiplying the room temperature bulk density and the measured thermal diffusivity and specific heat determination of the thermal conductivity is possible. Fast measurement times, easy sample preparation, and high accuracy are only some of the advantages of this non-contact, non-destructive measurement technique. In the past view years the analysis of liquids and pastes is becoming more and more interesting. For example, to optimize the design of heat exchanger systems, the thermophysical properties of the liquids used in the system must be known. Another example can be found in the electronics industry. The thermal conductivity of a heat transfer paste is one of the crucial parameters for the later application of the material. Furthermore, characterization of polymers in the liquid range is important for the analysis and optimization of the production process.

2. Experimental

New container systems were developed allowing flash measurements to be carried out on liquids, pastes and molten polymers. Depending on the temperature range of interest and the thermal conductivity range of the liquids, specific materials and designs were developed, optimized and finally tested. For measurement of liquids and pastes, a new container was developed. Presented in Fig. 1 is the principle design of this new container system. The sample holder system was designed either in aluminum (for applications up to 500 °C) or in platinum–rhodium (for applications up to 1600 °C). The system consists of a crucible and a lid with well-defined dimensions. For low-conductivity liquids, an additional stainless steel ring (not shown in the figure) is employed between the crucible and lid to avoid the heat flow via the container system. During sample preparation, the material (approximately 50 μl) is filled into the crucible. The lid presses the liquid or paste into a layer with a well-defined thickness of approximately 0.5 mm. The entire setup is then placed into the standard sample holder of a flash device. Prior to the test measurements, the bottom of the crucible and central area of the lid are coated with graphite to ensure a good absorption and emissivity of the surfaces irradiated by the light source (laser, flash lamp) and visible by the infrared

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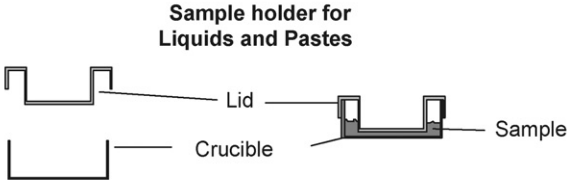

Fig. 1. Sample holder system for liquids and pastes for flash instruments.

detector. Evaluation of the measured detector signals is made using a three-layer analysis routine based on the theory of Lee [2]. The specific heat data required for the analysis were measured using a differential scanning calorimeter [3] or taken from literature. The temperature dependence was considered employing literature data for the thermal expansion. The flash tests were performed in two different flash systems, the NETZSCH models LFA 447 *NanoFlash* and LFA 457 *MicroFlash*.

3. Results and discussion

Presented in Fig. 2 are the results measured on three separately prepared purified water samples. The tests were done between 25 and 50 °C. At each temperature, five individual tests were carried out to check the repeatability of the measurement results. Literature values [4] for the density and specific heat were employed for the evaluations. Additionally, literature values (grey area) for the thermal conductivity of water [4,5] are shown in the plot. It can clearly be seen that the results for the thermal conductivity are in the typical range for water. Both the thermal diffusivity and thermal conductivity slightly increase with temperature. The differences between the individual results and literature values for the thermal conductivity are generally less than ±2%.

Presented in Fig. 3 are the results measured on ethylene glycol sample. The results are intercompared with literature values [6] for the thermal conductivity. The uncertainty of the literature values was assumed to be 3% and is depicted as error bars in the figure. For the calculations, literature values [6] for the density and specific heat were employed. It can be seen that the deviations between the literature values and the measurement results are by far within the uncertainty of the test method (approximately 5%) and the accuracy of the literature values. An increasing thermal conductivity versus temperature was obtained. Similar to the water tests, the thermal diffusivity decreases versus temperature. However, the temperature dependencies of both properties are weak.

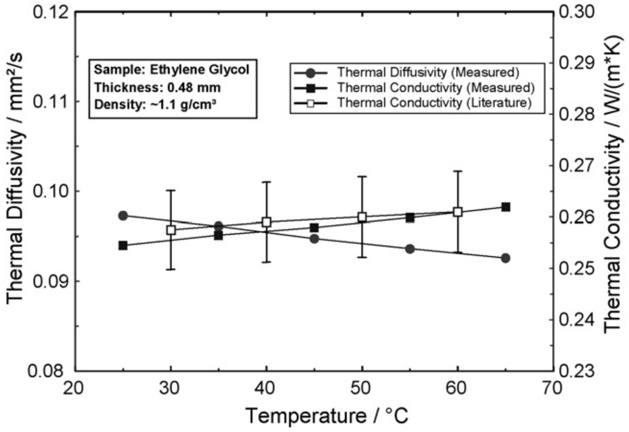

Fig. 3. Thermal diffusivity and thermal conductivity of ethylene glycol measured with the new sample holder for liquids and pastes.

The test results for the water and ethylene glycol samples proves the high level of reproducibility and accuracy which can be achieved with the new container systems on liquid materials. Further tests were carried on an amorphous polymer to check the reliability of the method on a material undergoing a phase change (glass transition) during thermal treatment. Presented in Fig. 4 are the thermophysical properties (thermal diffusivity, specific heat and thermal conductivity) of a polycarbonate sample between room temperature and 300 °C. The material was first heated above the glass transition (up to 200 °C). At 200 °C, the lid was pressed on the crucible and the polymer melt was pressed into the required shape. The sample container was then cooled down to room temperature and the actual test was started. This procedure ensured a plane-parallel disk between the aluminum walls of the container and a good thermal contact between the container and the sample. As can be seen in Fig. 4,

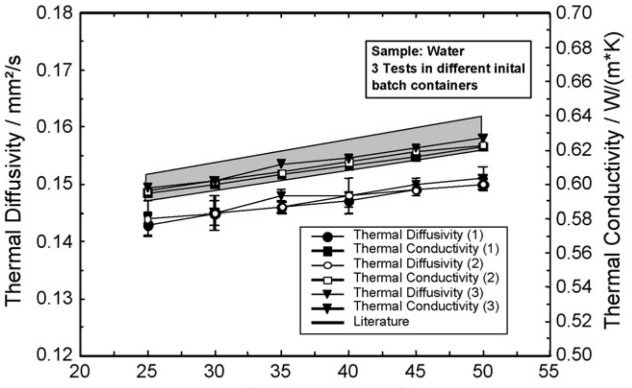

Fig. 2. Thermal diffusivity and thermal conductivity of water measured with the new sample holder for liquids and pastes.

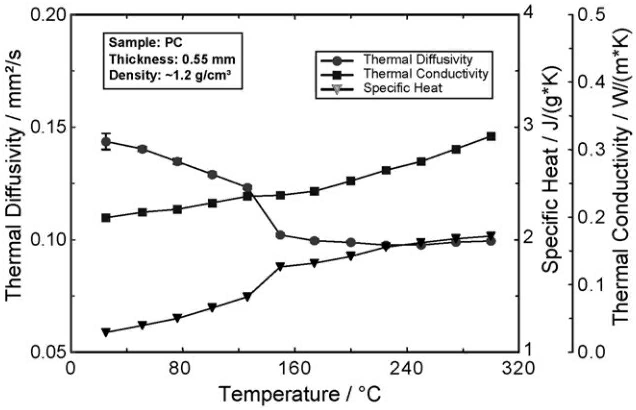

Fig. 4. Thermal diffusivity, specific heat and thermal conductivity of polycarbonate (PC).

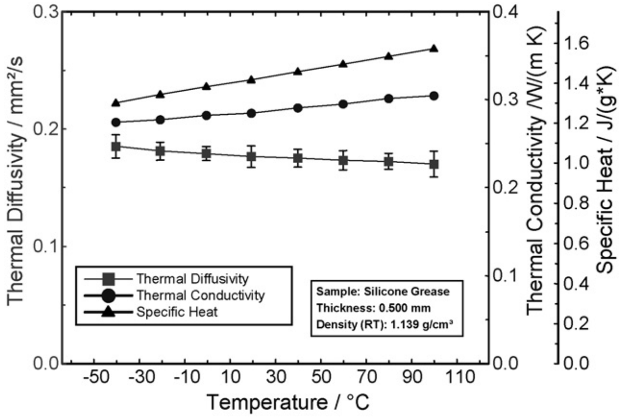

Fig. 5. Thermal diffusivity, specific heat and thermal conductivity of a silicon grease.

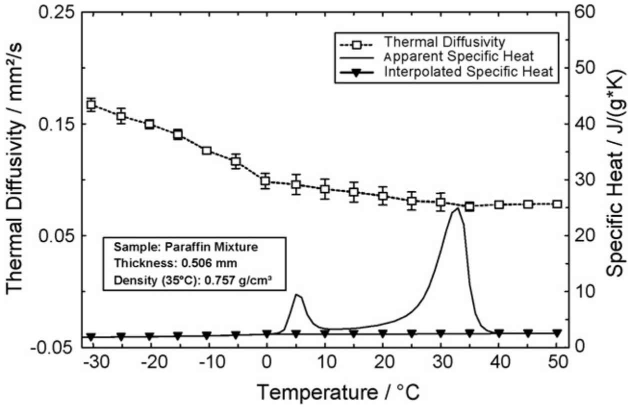

Fig. 6. Apparent thermal diffusivity and apparent specific heat of a paraffin mixture.

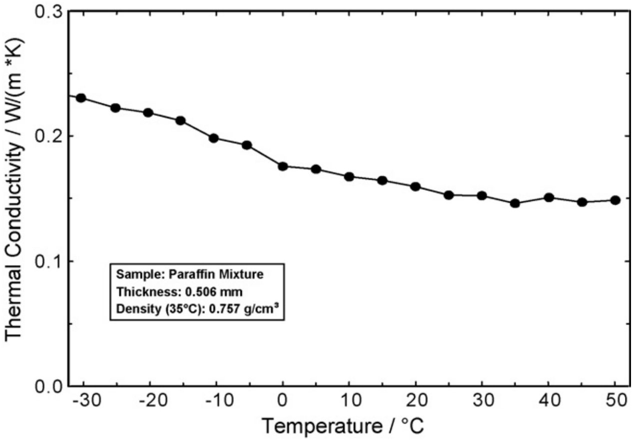

Fig. 7. Thermal conductivity of the paraffin mixture between −30 and 50 °C.

the thermal diffusivity decreases from room temperature up to 130 °C. Between 130 and 150 °C, the glass transition occurs and a step is visible in the thermal diffusivity. Above the glass transition, only a slight temperature dependence was detected in the thermal diffusivity. The specific heat (measured by differential scanning calorimetry) shows a nearly linear increase versus temperature with an overlapping step in the glass transition region. The resulting thermal conductivity continuously increases versus temperature which is a typical behaviour of amorphous materials and liquids.

Presented in Fig. 5 are the thermal diffusivity, specific heat and thermal conductivity of a silicone grease. The measurements were performed between −40 and 100 °C. Silicone greases are often used for vacuum applications and for the preparation of thermal conductivity pastes. In the later application, generally a lot of inorganic powder is added to the silicon grease. In the actual case, only a small amount of inorganic materials was added to the grease. This additive is the reason that the density is slightly above the typical range of silicone greases (0.8–1 g/cm^3). A density of 1.136 g/cm^3 was measured on the paste at room temperature (24 °C). The measured thermal diffusivity decreases versus temperature while the specific heat increases. The resulting thermal conductivity increases nearly linearly over the entire temperature range.

Depicted in Fig. 6 are the thermal diffusivity and specific heat of a paraffin mixture between −30 and 50 °C. These tests were carried out in the platinum container system. This material shows a broad melting range between 0 and 30 °C (mushy or phase change region). In the measured apparent specific heat, the melting process is visible as an overlapping endothermal effect (solid straight line). The specific heat without the influence of the heat of fusion was determined by an interpolation process (The values in the phase change region are determined by a linear interpolation of the results in the fully solid and fully liquid regions.) Therefore, the enthalpy change caused by the phase transition (melting process) can be separated from the specific heat contribution. The measured thermal diffusivity decreases between −30 and 35 °C. Above 35 °C, the values for the thermal diffusivity are nearly constant. In the melting region, the measured thermal diffusivity was corrected for the influence of the ongoing melting process. The correction is based on tests at different well-defined pulse energies at each temperature. Extrapolating the results to pulse energies of 0 allows calculation of a thermal diffusivity without the influence of melting/solidification.

Using the thermal diffusivity and the specific heat (without the overlapped enthalpy change during melting), the thermal conductivity was calculated. The density change during melting was also considered. The results of the thermal conductivity are presented in Fig. 7. As can be seen, the thermal conductivity decreases from −30 to 35 °C. The decrease gets weaker in the region of the phase change. In the fully molten region, nearly constant values were obtained for the thermal conductivity.

4. Conclusion

New container systems for flash devices for the measurement of liquids, pastes and polymers into the molten region were developed and checked on various well-defined liquids and polymer melts. Furthermore, tests were carried out on industrially relevant pastes and mixtures. The tests have proven the capability of the new container systems for the determination of the thermophysical properties of liquids and pastes and therefore, extend the capability of flash devices.

References

[1] W.J. Parker, R.J. Jenkins, C.P. Butler, G.L. Abbott, J. Appl. Phys. 32 (1961) 1679–1684.

[2] H.J. Lee, PhD Thesis, Purdue University, 1975.

[3] J. Blumm, E. Kaisersberger, J. Therm. Anal. 64 (2001) 385–391.

[4] F.P. Incropera, D.P. DeWitt, Introduction to Heat Transfer, John Wiley & Sons, Inc., 1996.

[5] E. Lax, C. Synowietz, Taschenbuch für Chemiker und Physiker Band 1, Springer Verlag, Berlin, 1967.

[6] Technical Data Sheet, Ethylene Glycol, INEOS Oxide, http://www.ineosoxide.com/pdf/eg.pdf.