

Characterization of the thermophysical properties of molten polymers and liquids using the flash technique

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Presented at the 17th European Conference on Thermophysical Properties, Bratislava, Slovakia,
5–8 September 2005

Abstract. Characterization of liquids, pastes, and melts is nowadays becoming increasingly important for industrial applications. The thermal conductivity of a heat-transfer paste is, for example, one of the crucial parameters for the application of the material, and characterization of polymers in the liquid range is important for the analysis and optimization of the production processes.

A new container system has been developed allowing flash measurements to be carried out on liquids, pastes, and molten polymers. Technical details of the container and the data on processing techniques are presented. Reliability tests (on water) have also been carried out and the results are compared with literature values. Various application examples for liquids, pastes, and polymers, through the melt stage are reported.

1 Introduction

For decades, the laser flash method (Parker et al 1961) has been widely used for measuring the thermal diffusivity of solid materials. In a laser flash test, a short laser pulse heats the front side of a plane-parallel sample disc. The resulting temperature rise of the rear side of the sample is measured as a function of time with an infrared detector. Fast measurement times, easy sample preparation, and high accuracy are only some of the advantages of this contactless nondestructive measurement technique. Furthermore, the method can be easily adapted to the measurement of multilayer samples.

We have developed a new container for the measurement of the thermal diffusivity of liquids and pastes (figure 1). The sample holder system was made either of aluminium (for applications up to 500 °C) or from a platinum–rhodium alloy (for applications up to 1600 °C). The system consists of a crucible and a lid with fixed dimensions. For sample preparation, the material (~50 µl) is loaded into the crucible. The lid presses the liquid or paste into a layer with a well-defined thickness of around 0.5 mm. The entire setup is then placed in the standard sample holder of a laser flash apparatus (see figure 1). Prior to the test measurements, the bottom of the crucible and the central area of the lid are coated with graphite to ensure high emissivity, and thus good energy absorption by the surfaces irradiated by the light source (laser, flash lamp), and strong signal for the IR detector. Evaluation of the measured detector signals is done by a three-layer analysis routine based on the theory of Lee (1975). The specific heat capacity required for the analysis was measured with a differential scanning calorimeter (Blumm and Kaisersberger 2001).

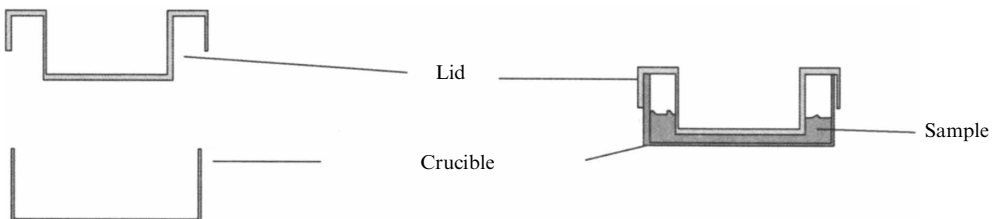


Figure 1. Sample holder system for liquids and pastes for flash measurements.

The temperature dependence of density is considered by using literature data for the thermal expansion. The flash tests were performed with two different flash systems, the NETZSCH models LFA 447 NanoFlash, and LFA 457 MicroFlash.

2 Results and discussion

Figure 2 shows the results of measurements on purified water. The tests were done between 25 and 50 °C with three different aluminium container systems. At each temperature, 5 individual tests were carried out to check the repeatability of the measurement results. Literature values (Incropera and DeWitt 1996) for the density and specific heat were used for the analysis. Additionally, literature values (grey area) for the thermal conductivity of water (Incropera and DeWitt 1996; Lax and Synowietz 1967) are shown in the plot. It can be clearly seen that the results for the thermal conductivity are in the typical range for water. Both thermal diffusivity and thermal conductivity increase slightly with temperature. The difference between the individual results and literature values for the thermal conductivity are generally less than $\pm 2\%$. These test results demonstrate the high level of reproducibility and low uncertainty that can be achieved with the new container system.

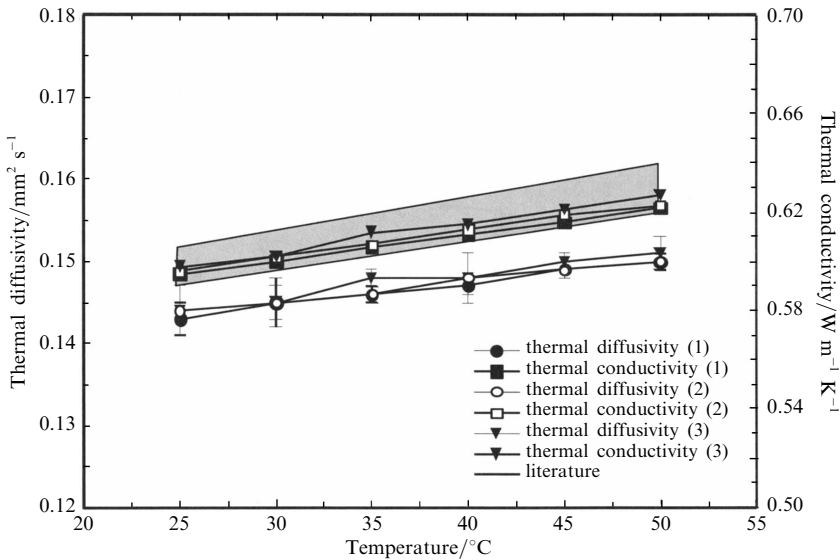


Figure 2. Thermal diffusivity and thermal conductivity of purified water measured with the new sample holder (three tests in different batch containers).

Figure 3 shows the thermophysical properties (thermal diffusivity, specific heat, and thermal conductivity) of a polycarbonate sample between room temperature and 300 °C. Polycarbonate is usually an amorphous solid at room temperature. Therefore, the material was first heated above the glass transition (up to 200 °C). At this temperature the material is soft or liquid. At 200 °C the lid was pressed on the crucible to make the sample adopt the required shape. The sample container was then cooled down to room temperature and the real test was started. This procedure ensured a plane-parallel disc between the aluminium walls of the container and good thermal contact between the container and the sample. As can be seen in figure 3, the thermal diffusivity shows a nearly linear decrease between room temperature and 130 °C. Between 130 and 150 °C, a drop to lower values was obtained. This effect is caused by the glass transition in the material. 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 with temperature. During the glass transition, the typical jump to higher values was obtained. The resulting thermal conductivity shows

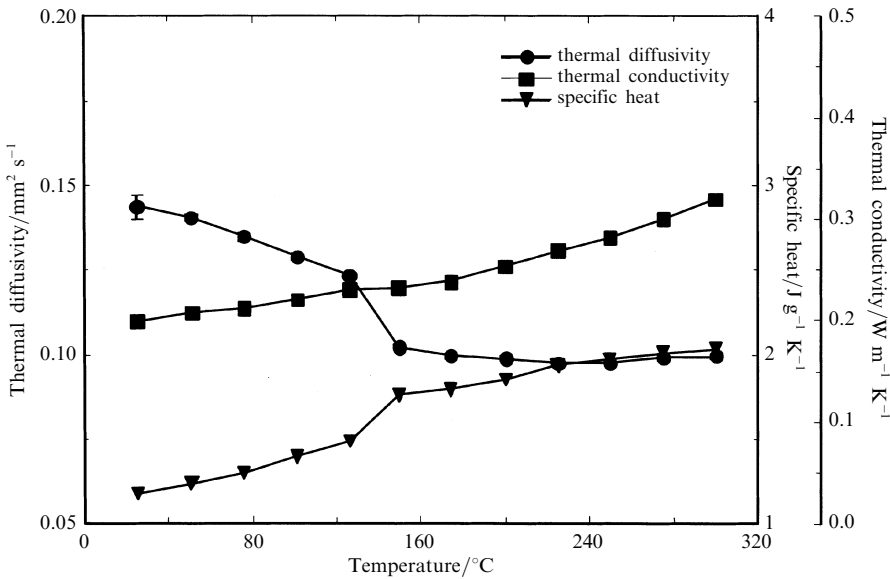


Figure 3. Thermal diffusivity, specific heat, and thermal conductivity of polycarbonate. Sample thickness 0.55 mm, width 11.00 mm.

a continuous increase with temperature. No significant influence of the glass transition was obtained.

Figure 4 shows the apparent specific heat (specific heat and the overlapping phase transition enthalpies) of a polypropylene sample between 40 and 300 °C measured with a differential scanning calorimeter. The specific heat shows a continuous increase with temperature. Between ~ 120 and 210 °C, the heat of fusion overlaps the specific heat. The crystalline material melts in this temperature range. The enthalpy change caused by the melting process was evaluated at 77.5 J g^{-1} . For the analysis of the thermal diffusivity and thermal conductivity, a linear interpolation was carried out to remove the additional enthalpy change. This is indicated as a straight line in the plot.

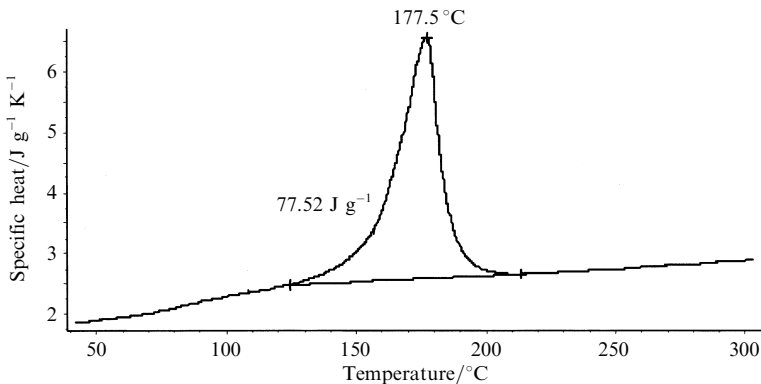


Figure 4. Apparent specific heat of a partially crystalline polypropylene sample.

Figure 5 shows the obtained values of thermal diffusivity, specific heat (after interpolation), and thermal conductivity of the polypropylene material between room temperature and 300 °C. As can be seen, the thermal diffusivity shows a decrease up to 120 °C, and a slight increase above this temperature. The specific heat shows an increase over the entire temperature range, but the rate of increase was higher in the solid region. The resulting thermal conductivity shows a nearly linear increase with temperature, typical for this kind

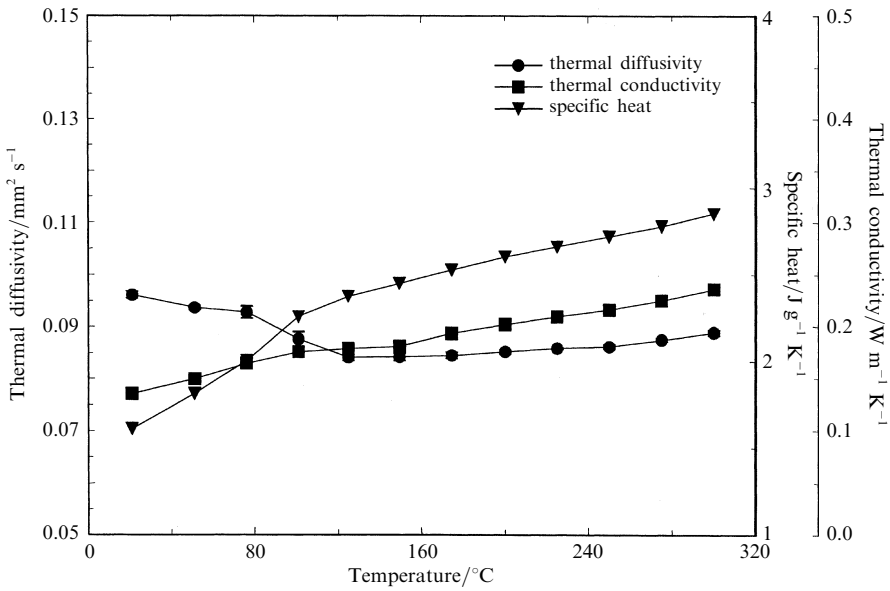


Figure 5. Thermal diffusivity, specific heat, and thermal conductivity of polypropylene. Sample thickness 0.55 mm, width 11.00 mm.

of semicrystalline thermoplastic material. During melting a slight drop to lower values was obtained.

Figure 6 shows the thermal diffusivity and specific heat of a paraffin mixture between -30 and 50 °C. These tests were carried out in the platinum–rhodium container system. This material shows a broad melting range between 0 and 40 °C. 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 interpolation process in this temperature range. The measured apparent thermal diffusivity shows a decrease between -30 and 25 °C, then the values increase up to 35 °C; above 35 °C, the apparent thermal diffusivity is nearly constant.

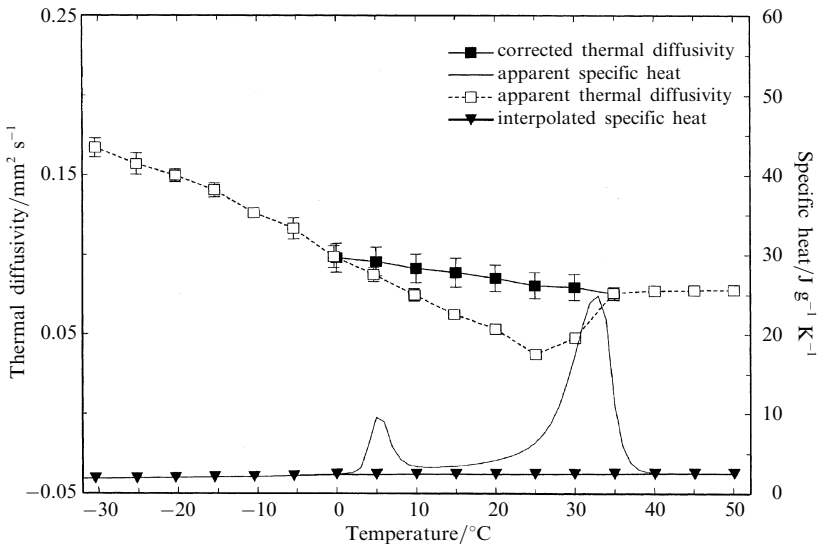


Figure 6. Apparent thermal diffusivity and apparent specific heat of a paraffin mixture. Sample thickness 0.506 mm, density at 35 °C 0.757 g cm⁻³.

However, one has to consider that measurements in the phase-change region, such as during an ongoing melting process, might be critical. The reason for this is that the transient heat transfer equation generally used for the analysis of the results of a flash experiment is no longer valid. It must be extended by an additional term taking account of the influence of the enthalpy changes during melting/solidification. This melting/solidification generally occurs during heating by the flash source and on reducing the sample temperature to the initial temperature. This effect can be taken into account by using an advanced numerical solution of the transient heat transfer equation. Considering the three-layer arrangement used for the tests, such a solution might be extremely complex. Another solution, used in this work, is to carry out flash tests at different well-defined pulse energies and therefore with different temperature rises inside the sample. Extrapolating the results to zero pulse energy allows the calculation of thermal diffusivity without the influence of melting/solidification.

The results of such extrapolation processes for the test results at 0 and 25 °C are presented in figure 7. It can be clearly seen that there is a nearly linear dependence of the apparent thermal diffusivity. The dependence between the apparent thermal diffusivity and the flash energy is large in the temperature range where there are large enthalpy changes during melting (at 25 °C) and relatively weak in the ranges of small enthalpy changes (at 0 °C). Also shown in the plot are the results of a nonlinear regression of the test results using a first-order polynomial. It can be seen that the measured data fit this linear approximation within the scatter of the measured data. Similar approximations were carried out for all results in the phase-change region.

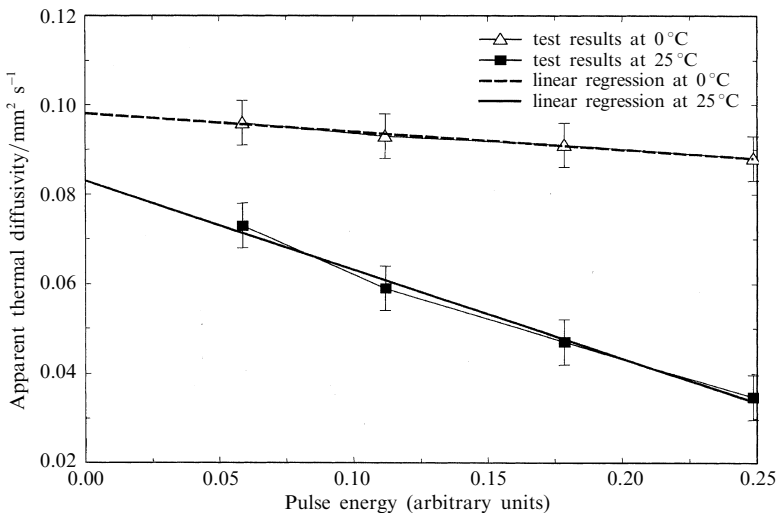


Figure 7. Apparent thermal diffusivity of the paraffin mixture as a function of pulse energy for temperatures of 0 and 25 °C. Also shown are the results of linear approximation of the measured test results.

The results for thermal diffusivity after extrapolation to zero pulse energy are also shown in figure 6 as corrected thermal diffusivity. It can be seen that, after the correction for the pulse energy influence, the thermal diffusivity shows a nearly linear decrease with temperature in the melting range.

Using the corrected thermal diffusivity and the specific heat (without the overlapping enthalpy change during melting), we calculated the thermal conductivity. The density change during melting was also considered. The results for the thermal conductivity are presented in figure 8. As can be seen, the thermal conductivity decreases in the

temperature range -30 to 35 °C. The rate of decrease gets weaker in the phase-change region. In the fully molten region, nearly constant values were obtained for the thermal conductivity.

3 Conclusion

New container systems were developed for flash devices for measurements on liquids, pastes, and polymers extending into the molten region. The new container systems together with advanced analysis routines allow detailed insight into material behaviour even in the phase-change region. Tests conducted on various types of liquids and pastes demonstrate the capability of the new container systems.

References

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