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Round-Robin Test of Paraffin Phase-Change Material

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Abstract A round-robin test between three institutes was performed on a paraffin phase-change material (PCM) in the context of the German quality association for phase-change materials. The aim of the quality association is to define quality and test specifications for PCMs and to award certificates for successfully tested materials. To ensure the reproducibility and comparability of the measurements performed at different institutes using different measuring methods, a round-robin test was performed. The sample was unknown. The four methods used by the three participating institutes in the round-robin test were differential scanning calorimetry, Calvet calorimetry and three-layer calorimetry. Additionally, T-history measurements were made. The aim of the measurements was the determination of the enthalpy as a function of temperature. The results achieved following defined test specifications are in excellent agreement.

Keywords PCM · Phase-change material · DSC · Calorimetry · Enthalpy

1 Introduction

Latent heat storage with materials undergoing a solid–liquid phase change is gaining increasing interest due to its potential for applications in energy systems [1–3]. The high storage density in a small temperature range promises many advantages,

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especially in solar applications such as solar power plants, solar process heat, and many applications regarding the heating and cooling of buildings. The demand for optimized storage materials has led to an intensification of materials research in recent years. In this respect, as well as for the quality control of existing commercial phase-change materials (PCMs), an accurate determination of the thermophysical properties is necessary. To characterize the heat storage capability, the enthalpy as a function of temperature, or the enthalpy change in temperature intervals, is used.

In recent years a quality mark for PCMs was introduced by the RAL Quality Association based in Germany [4]. The quality mark is given to suitable PCM materials after successful testing following the requirements imposed by the quality association PCM for the assessment of PCM materials. The association determines suitable measuring methods, details on measurement performance as well as requirements for a written report.

For the determination of the specific enthalpy change, three requirements are to be met by the material and the method.

1. Three specimen of one sample are to be measured.
2. Each specimen is to be measured three times up and down through the melting region, meaning from a temperature below the phase-change region to a temperature above and back again.
3. The heating rate or temperature steps are to be halved until:
   a. The difference between two heating curves or the difference between two cooling curves is less than 0.2 K or
   b. The difference between the heating curve and the cooling curve is less than 0.5 K.

While 1 and 2 are common requirements, requirement 3 is specifically applied to ensure measurement at thermal equilibrium in the sample. This is especially important due to the high enthalpy change during a phase change. For example, measurements using different heating or cooling rates will lead to broadening of the melting/solidifying peak with higher rates as the thermal equilibrium will not be given for higher rates (Fig. 1) [5].

Should the above requirements be met, then the results may be used for a certification of the material. In this round-robin test, measurements were done on a paraffin, RT8 HC, supplied by Rubitherm. Calibration was not specified and was up to the participating institutes.

2 Measuring Methods

The three institutes participating in the round-robin test, FHG ISE, ZAE Bayern, and w&a, employed different measurement methods for the determination of the enthalpy change. The round-robin test was thus also a test of the comparability of different measuring methods. The used methods were Calvet calorimetry at FHG ISE, differential scanning calorimetry at ZAE Bayern, three-layer calorimetry at w&a, and T-history again at ZAE Bayern. Though the basic measuring principle is similar, all have a heat flux in/out of the sample measured via a calibrated resistance, the specific details differ strongly, most obviously in the masses of the measured samples.

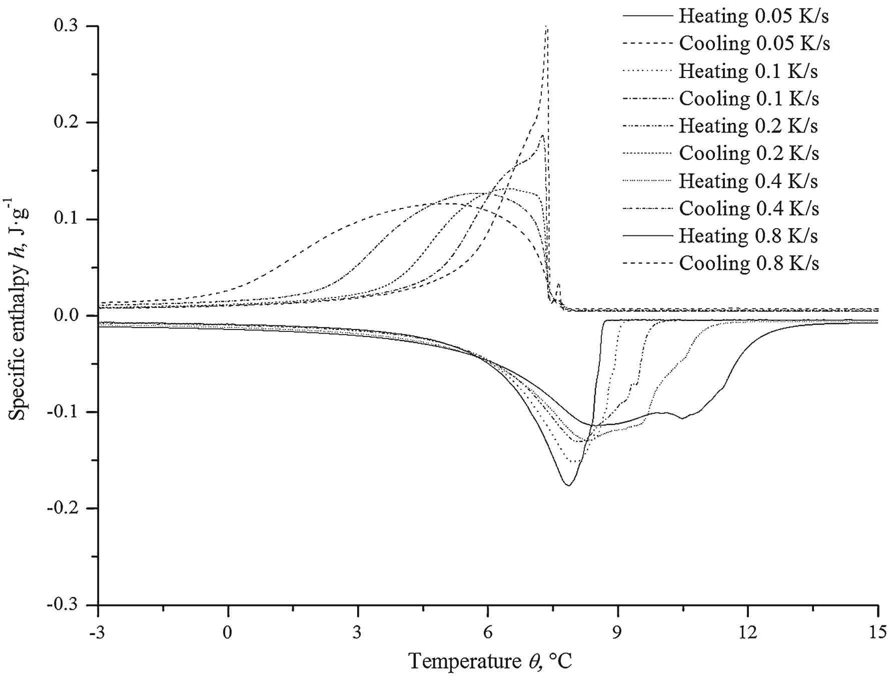

Fig. 1 Specific enthalpy change in the phase-change range for different heating and cooling rates

The Calvet calorimeter uses cylindrical samples of roughly 100 μL. The samples are heated via thermoelements, and the heat is fed through a defined path. The heat flux through an area surrounding the whole sample is measured.

The DSC uses the smallest samples, being around 10 μL. It uses an oven to heat or cool the samples in a defined way and determines the heat flux into the sample by measuring the temperature difference between an empty pan and the pan with the sample over time. The temperature difference is usually measured below the pan.

The three-layer calorimeter employs the largest samples with about 100 mL. The samples are exposed to a temperature change implied by a climate chamber, and the heat flux is again determined by comparing the temperature over time curves of the sample and a reference material. The temperatures are measured inside the sample and reference material.

The T-history uses around 10 mL of sample material which is exposed to a temperature jump together with a reference material. Comparison of the temperature over time curves of both leads to the heat flux into the sample. The temperatures are measured at different positions on the surface of the sample holder. The T-history measurements were not an official part of the round-robin test but are added for this paper.

3 Results

Figures 2 and 3 show the specific enthalpy change of the material for temperature steps of one kelvin at a given temperature. This special representation was chosen

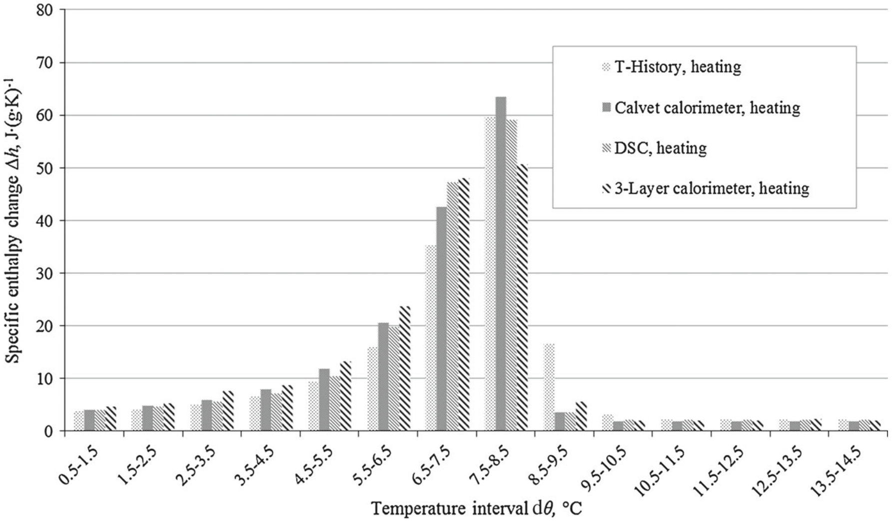

Fig. 2 Specific enthalpy change for 1 K temperature steps at different temperatures while heating

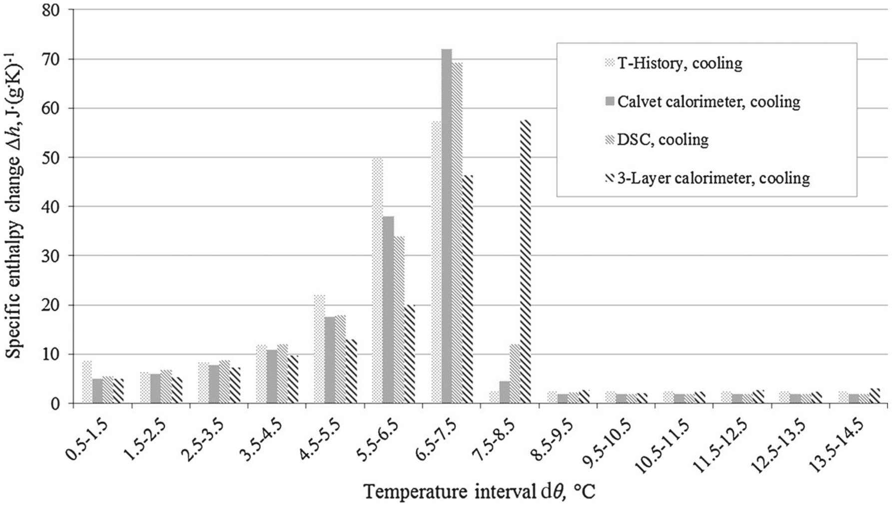

Fig. 3 Specific enthalpy change for 1 K temperature steps at different temperatures while cooling

by the PCM quality association because it was thought that it would be a suitable representation, keeping in mind that the people who will be using the results mostly work in more applied fields, namely, architects, engineers, etc. It allows a person to easily calculate the storage capability of a material in a temperature interval given by an application. Out of the enthalpy curves the enthalpy change over the entire melting range was calculated, and the peak temperatures detected (Table 1). The peak temperature value of the 3-layer calorimeter is shown in brackets as only the stepwise results of Figs. 2 and 3 were available, which made a more exact determination of

Table 1 Measured specific enthalpy change in the temperature range from −0.5 °C to 14.5 °C and temperature of the enthalpy peak

	Calvet	DSC	3-Layer	T-history
Specific enthalpy change, $\Delta h(-0.5\,^\circ\mathrm{C}$ to $14.5\,^\circ\mathrm{C})$, heating ($\mathrm{J \cdot g^{-1}}$)	178	176	183	169
T(peak), heating (°C)	7.89	7.85	(7.67)	8.00
Specific enthalpy change, $\Delta h(-0.5\,^\circ\mathrm{C}$ to $14.5\,^\circ\mathrm{C})$, cooling ($\mathrm{J \cdot g^{-1}}$)	177	183	184	181
T (peak), cooling (°C)	7.46	7.44	(8.00)	6.70

the peak temperature impossible. It is easily visible that all the measurements of the specific enthalpy change over the melting range are in excellent agreement. This is remarkable in view of the stepwise results, which show differences clearly over 10 % in the enthalpy peak height and differences in the temperature of the enthalpy peak of over 0.5 K, and is a sign of the difficulties arising through different measuring methods, different sample sizes, different heating rates, etc. It also shows that the value for the whole temperature range, which is the value of importance for later applications, can be measured with good agreement using different methods.

4 Conclusions

The results show that the measuring requirements specified by a RAL quality association lead to a very high measuring reproducibility even when using different measuring methods. This is especially due to the third requirement which guarantees that the samples are in thermal equilibrium during the measurement.

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