

Determination of the enthalpy of PCM as a function of temperature using a heat-flux DSC—A study of different measurement procedures and their accuracy

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SUMMARY

Thermal energy storage by latent heat allows storing high amounts of energy working in narrow margins of temperature. The use of phase change material (PCM) for the latent heat storage has been studied in different applications and it has been commercialized in containers to transport blood, products sensible to temperature, to decrease their energy demand. The use of PCM in cooling and refrigeration has been attracting a lot of interest lately, but for all applications, the properties of these materials need to be known with sufficient accuracy. Regarding heat storage, it is necessary to know the enthalpy as a function of temperature. The most widely used calorimeter is the heat-flux differential scanning calorimetry (hf-DSC). The objective of this study is to investigate different methods for hf-DSC analysis, namely the dynamic method and the step method, and to test their accuracy in the determination of enthalpy–temperature relationship of PCM. For the dynamic method, a strong influence of heating/cooling rate was observed. For the step method, the resulting enthalpy–temperature relationship is independent of heating/cooling rate. Commercial PCM RT27 was chosen as sample material to avoid subcooling and kinetic effects in the test measurements. The approach introduced in this study can be used to carry out similar investigations for other classes of PCM and/or other DSC instruments. Copyright © 2008 John Wiley & Sons, Ltd.

KEY WORDS: cooling thermal storage; phase change material (PCM); heat-flux DSC; dynamic method; step method; RT27; calorimetry; material property determination; thermal energy storage

1. INTRODUCTION

A phase change material (PCM) is a material that stores thermal energy as latent heat with a high

density (per unit volume or mass) at its melting/solidification temperature. Generally, it is possible to use the latent heat of solid–gas, solid–liquid and liquid–gas transformation. The advantage of the

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solid–liquid transformation is its low volume change and constant melting point independent of pressure [1]. The research done in recent years has increased the number of available PCM, and different applications are available on the market. Examples are applications for the heating and cooling of buildings within the human comfort (20–30°C), in transport boxes or in clothes [2–4].

The correct knowledge of the thermal properties of PCM is crucial for the correct design of commercial products. The most important property is the enthalpy–temperature relationship $h(T)$. When this relationship is determined using conventional differential scanning calorimetry (DSC) with standard methods and procedures, results for PCM are often wrong. The enthalpy values from heating/cooling are systematically shifted to higher/lower temperatures [5–7]. This temperature shift originates from a temperature gradient inside the PCM and depends on the heating/cooling rate and sample mass.

The objective of this study is to investigate different methods with the heat-flux DSC (hf-DSC), namely the dynamic method and the step method, regarding their accuracy.

2. DSC FOR THERMAL ANALYSIS

2.1. Measurement principle and source of measurement uncertainties

DSC is a standard method for thermal analysis [8]. An hf-DSC determines the amount of heat absorbed by a sample upon temperature change.

The temperature development of the sample in a furnace is compared with the temperature of a reference in a symmetric position; a temperature sensor is placed in the surface of the furnace. The design allows to measure the heat flow with accuracy, see Figure 1.

Thermal effects of the sample lead to a deviation in the sample temperature from the reference temperature. This temperature difference is detected and used to determine the heat flux between sample and furnace. A calibration of the heat flux is done using the melting enthalpies of standard materials ('heat calibration') or the sensible heat of a standard without phase change ('heat flow rate calibration').

From the heat flux, the specific heat as a function of temperature $c_p(T)$ can be obtained, and the enthalpy is determined by integration.

$$h(T) = \int_{T_0}^T c_p(\tau) d\tau$$

The start of the integration range T_0 can be chosen freely to normalize $h(T)$ curves.

When the enthalpy–temperature relationship of a PCM is determined using dynamic heating or cooling, the results are often wrong. The enthalpy values from heating/cooling are systematically shifted to higher/lower temperatures. The reason is that too high heating rates lead to a temperature gradient in the sample and the heat-flux signal therefore originates not from the sample at one temperature but from a temperature range. This effect is illustrated in Figure 2.

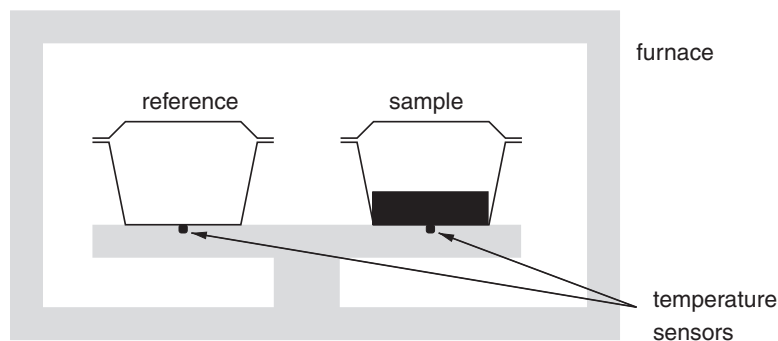


Figure 1. Sketch of the furnace of an hf-DSC.

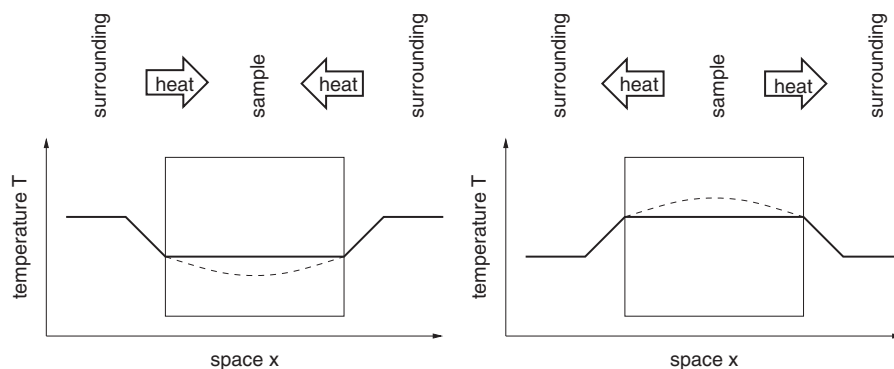


Figure 2. Sketch of the temperatures inside the sample during heating (left) and cooling (right). In the calculation of the thermal effect, the temperature of the material is assumed to be the same throughout the whole sample (solid lines). In reality, due to heat transfer limitations, the temperature is not uniform (dashed lines).

The measured temperature at the surface of the sample is higher than the average sample temperature for heating and lower than the average sample temperature for cooling runs. When doing both heating and cooling measurements, the real temperature of a thermal effect can be confined to a value between both extremes. If the thermal effect does not occur in thermal equilibrium, a further shift due to kinetic or dynamic reasons can increase the thermal shift. Because of this, and because the exact form of the gradient is not known, it cannot be assumed that the real value is indeed centered. Therefore, the distance between heating and cooling curves is a good indicator of the uncertainty of the measurement.

For heat transfer reasons, the temperature shift in heating/cooling data depends on the heating and cooling rate, the sample size, the thermal conductivity and the heat capacity of the sample. Measurement parameters as used for other materials often prove unsuitable when applied to PCM. This is because PCMs have a high heat capacity and a low thermal conductivity. As a consequence, the heat transfer problem increases significantly compared with most other samples.

Smaller sample size and lower heating and cooling rates reduce the temperature shift. However, both of them lead to a weaker signal and therefore to a decreased accuracy in enthalpy. In addition, using smaller samples increases the

risk to perform the measurement on a sample that is not representative of the bulk material. Choosing a heating/cooling rate and a sample mass is always a compromise between accuracy in enthalpy, accuracy in temperature and representativity. In our study, we want to find suitable parameters for a good accuracy of the $h(T)$ relationship.

There are different possibilities to use a DSC in thermal analysis of PCM [9–11]. In this work, we present measurement data using the *dynamic method* and the *step method*.

2.2. Dynamic method

The most widely used scanning mode consists of heating and cooling segments at constant rates ('dynamic method'). A typical temperature program and corresponding signal are shown in Figure 3.

The dynamic method is commonly used for the determination of melting enthalpies Δh_m . For heat storage applications, the interesting value is the sum of both latent and sensible heat h . In this case, good sensitivity also for small signals is necessary. This is achieved using the heat flow rate calibration. For the determination of h , a dynamic program is executed three times:

- First, with the empty crucible to generate the baseline.

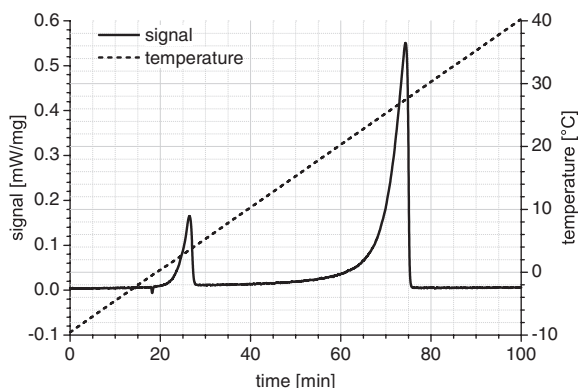


Figure 3. Typical heat flow and temperature evolution during a dynamic DSC measurement with constant heating rate. The peaks indicate strong thermal effects of the sample at the corresponding temperatures.

- Second, with a standard material (usually sapphire) in the same crucible to generate the standard line.
- Third, with the sample in the same crucible to generate the sample line.

From the heat flux, the specific heat as a function of temperature $c_p(T)$ can be obtained with the DSC software using the baseline, the sapphire and the sample heat-flux signal and the enthalpy $h(T)$ is determined by integration.

2.3. Step method

Another measurement routine is the step method. Here, the heating or cooling is not continuous, but small heating ramps are followed by periods in which the temperature is kept constant to allow the sample to reach thermal equilibrium. The resulting temperature program has small steps, and the signal created is a sequence of different peaks. A typical temperature program and resulting signal is shown in Figure 4.

The size of the steps should be long enough to ensure thermal equilibrium in the sample. Thermal equilibrium is reached when the signal goes back to the baseline. If the steps are too short, the signal will not fall back completely to the baseline and the thermal effect will be attributed to

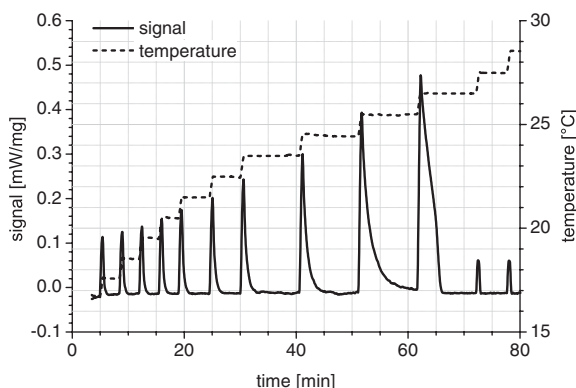


Figure 4. Typical heat flow and temperature evolution during a DSC measurement with the step method, here shown for heating. Different peaks indicate different amounts of heat transferred in the respective temperature interval.

the following temperature interval. However, if this happens, it can be detected directly by reading the signal.

In the steps method, the evaluation considers only peak areas and the exact shape of the baseline has no influence on the resulting $h(T)$ relationship. Therefore, we use the heat calibration for the evaluation of the data. The heat calibration is based on the comparison of measured peak areas of phase changes of standard materials to literature values of the phase change enthalpies. A sensitivity profile for the instrument is created and used to convert the directly measured thermovoltage signal into the heat-flux signal. This calibration only needs to be repeated from time to time, to assure the correct performance of the instrument.

From the sample heat-flux signal, the enthalpy $h(T)$ is determined by integration of every peak.

3. MATERIALS AND PROCEDURE

3.1. Sample material and measurement equipment

As a sample material, we used RT27 from Rubitherm GmbH [12], a paraffin based on a mixture of n-alkanes. RT27 was chosen as sample material to avoid additional problems due to subcooling, inhomogeneities or kinetic effects,

thus facilitating the interpretation of the data. The thermal properties of RT27 are shown in Table I.

The instrument used for thermal analysis was an hf-DSC, model Netzsch DSC 204 *Phoenix*, with a compression cooler and argon as a purge atmosphere. Our investigations were done with standard aluminum crucibles of 40 μl volume. For the heat flow rate calibration, sapphire samples as provided by Netzsch were used as standard material. The heat calibration of the instrument was done using water, potassium nitrate, indium, tin and bismuth.

For the determination of the sample mass, an analytic balance model Sartorius A210 with a precision of ± 0.1 mg was used.

3.2. Procedure

In order to examine the influence of sample mass and heating/cooling rates on the accuracy of the $h(T)$ data, measurements were carried out for varying sample mass and the temperature program. Three samples of the same bulk material were prepared, see Table II.

A variation of the sample mass is given with samples A and B. Sample C with approximately the same mass as sample B was prepared to test the reproducibility. On samples A and B, a DSC analysis was carried out using the dynamic method and the step method. On sample C, only the step method was applied. For both methods, heating and cooling measurements were done at six different rates in the range of 0.2–10 K min^{-1} .

As described in Section 2, the accuracy of an $h(T)$ curve can be evaluated by comparing results

Table II. Masses of the samples used in our investigations.

RT27	Weight (mg)
Sample A	9.0
Sample B	16.0
Sample C	16.3

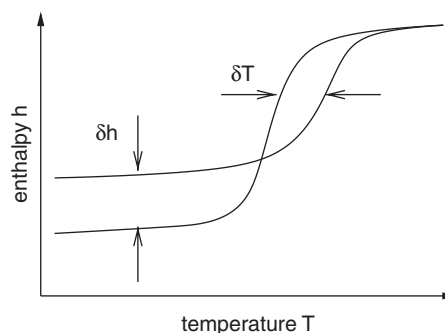


Figure 5. In order to satisfy design demands for the building sector, a high accuracy of the $h(T)$ curves is necessary. The technical goal for the accuracy is set to $\delta h < 10\% \Delta h$ and $\delta T < 0.5$ K.

from heating and cooling measurements. Particularly for applications in the building sector, where temperature changes of the PCM are often only a few degrees, accurate data is of crucial interest. For a successful design of PCM systems, the specific enthalpy should be known with an uncertainty δh smaller than 10% of h_m and δT smaller than 0.5 K [5], as shown in Figure 5.

4. RESULTS AND DISCUSSION

4.1. Dynamic method

Figure 6 shows the resulting $h(t)$ data for samples A and B, as determined by the dynamic method for different heating/cooling rates. All the enthalpies were normalized to 0 J g^{-1} at 30°C . For the large heating rates, the phase change was not completed at this temperature, so the curves were normalized such that they join the other curves in the liquid range. The temperature

Table I. Properties of RT27 as given by the manufacturer [10].

RT27	
Melting temperature	28°C
Density liquid, at 70°C	0.75 kg l^{-1}
Density solid, at 15°C	0.87 kg l^{-1}
Heat capacity liquid	$2.4 \text{ kJ (kgK)}^{-1}$
Heat capacity solid	$1.8 \text{ kJ (kgK)}^{-1}$
Phase change enthalpy $19\text{--}34^\circ\text{C}$	179 kJ kg^{-1}

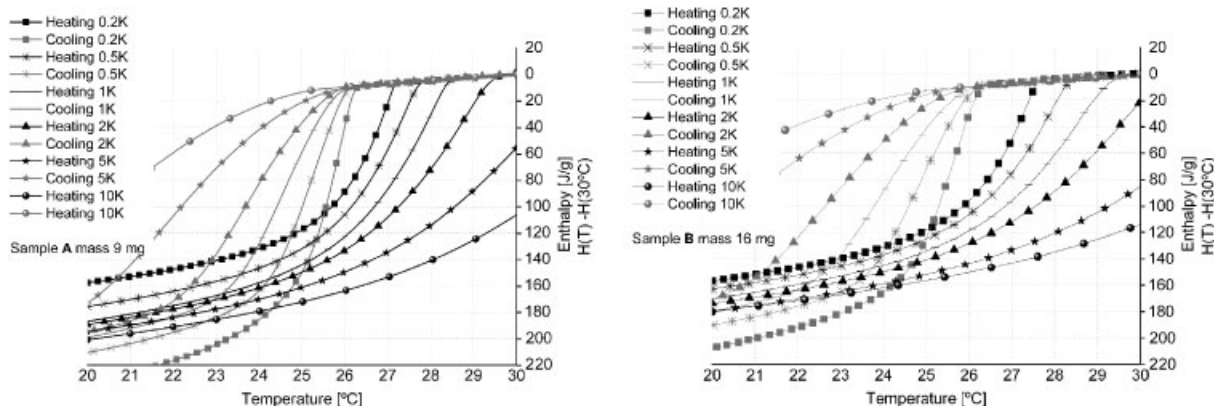


Figure 6. Results obtained with the dynamic method at different heating/cooling rates for sample A (left) and sample B (right).

interval to compare phase change enthalpies was set to 10 K.

The main findings are as follows:

- In both graphs, with heating/cooling rates $\leq 2 \text{ K min}^{-1}$, the $h(T=20^\circ\text{C})$ for the heating is lower than for the cooling, δh exceeding the allowed 10% deviation by far.
- In both graphs, for increasing heating/cooling rates the temperature shift δT increases. Even for the smallest rates, the difference between the heating and the cooling enthalpy curves is larger than 0.5 K.
- As to the influence of the sample mass, it can be seen that for the same heating rate, δT is larger for the larger sample B, but δh is smaller. For example, looking at the heating/cooling rate of $\pm 0.5 \text{ K}$, δT at $h = 80 \text{ J g}^{-1}$ for sample A is 1.5 K whereas it is 2 K for sample B. For those two measurements, the uncertainty in enthalpy δh at $T = 20^\circ\text{C}$ is 40 and 30 J g^{-1} , respectively.

It can be concluded that with increasing heating/cooling rates, the enthalpy determination is getting more accurate. But this is at the cost of a sharply increasing uncertainty in the temperature. Summarizing the findings of the dynamic method measurements, good results to fulfill the technical goal were not achieved with any of the tested heating/cooling rates.

4.2. Step method

Figure 7 shows the results of the enthalpy curves for samples A and B with the step method at all heating and cooling rates. Again, the results have been normalized to 0 J g^{-1} at 30°C .

The main findings are as follows:

- There is no significant difference in T visible between all curves. Owing to the step size of 1 K, the uncertainty δT can be considered $\pm 0.5 \text{ K}$.
- For all cooling and heating rates, the results are very similar. The maximum difference in $h(20^\circ\text{C})$ is 15 J g^{-1} for sample A and 10 J g^{-1} for sample B. In both cases, this is less than 10% of the phase change enthalpy Δh_m as required by the technical goal.
- However, there is some difference in Δh_m between the two samples: for sample A, $h(20^\circ\text{C})$ is 180 J g^{-1} whereas for sample B, $h(20^\circ\text{C})$ is 160 J g^{-1} .

It is suspected that the difference in Δh is due to a real difference in the material of samples A and B. Looking again at Figure 6, a similar difference in Δh between samples A and B is found for the large heating/cooling rates. As the instrument is designed for those large heating rates, and h from heating and cooling on one sample agree, we have good confidence in

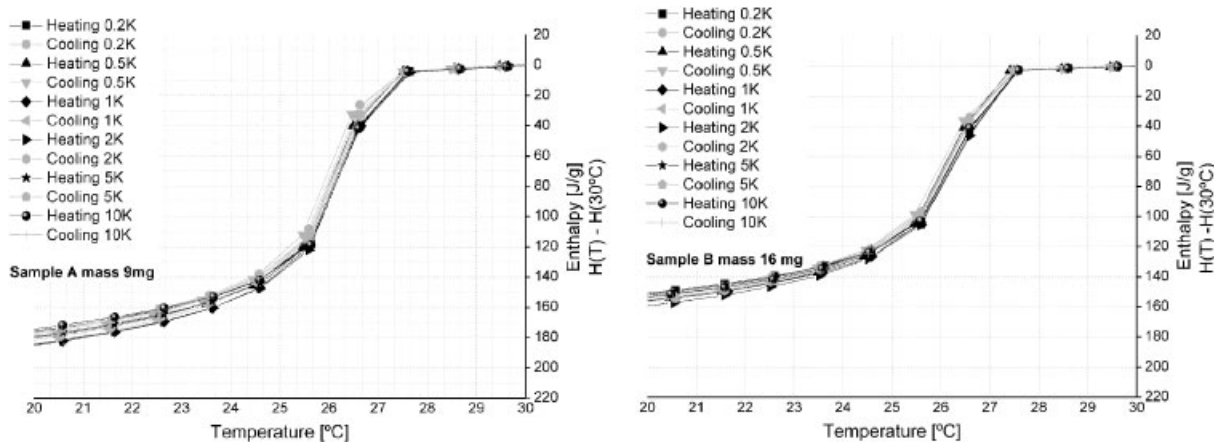


Figure 7. Results obtained with the step method at different heating/cooling rates for sample A (left) and sample B (right).

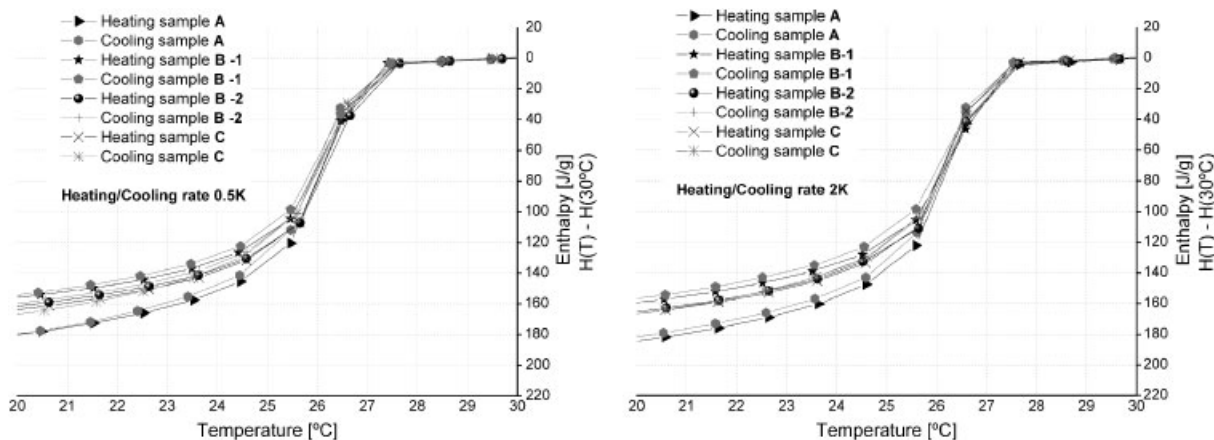


Figure 8. Results obtained with the step method comparing all measurements. Left: at 0.5 K min^{-1} ; Right: at 2 K min^{-1} .

this data. Therefore, it seems to be reasonable to assume that sample A is not of the same composition as sample B.

In order to check the reproducibility of the measurement and the sampling, some additional measurements were carried out. A second run was performed with sample B, to check the reproducibility without further variation of parameters. To test the influence of the sampling, a measurement was carried out on sample C that has very similar mass compared with sample B. In Figure 8, for two different heating/cooling rates,

the results of all four measurements (on samples A, B-1 and B-2, C) are compared.

For the 0.5 K min^{-1} tests, as well as for the 2 K min^{-1} tests, the enthalpy $h(20^\circ\text{C})$ is very similar for the larger samples. The difference between samples B and C does not exceed the difference between the two individual tests on sample B. There is no trend observed when comparing the different heating/cooling rates. Considering all measurements except for those of sample A, the uncertainty with regard to the enthalpy change Δh is about 8%.

Summarizing the findings of the step measurements, very little influence of the heating/cooling rate on the $h(T)$ data is observed. The accuracy of the results satisfies the requirements as described in Section 2. It is recommended to use a sufficiently large sample to avoid problems due to bad sampling.

5. CONCLUSION

In this study, we investigated different measurement procedures for differential scanning calorimetry (DSC) to determine enthalpy–temperature relationship of phase change materials (PCMs). Using the dynamic method, large uncertainties in the temperature usually observed can be reduced only at the cost of increasing uncertainty of the enthalpy. It is therefore not possible to obtain results with sufficient accuracy as required for the design of many applications. Using the step method, the accuracy can be increased to a satisfactory level. Additionally, the step method is far less sensitive to a variation in the measurement parameters.

This study was carried out using one particular paraffin sample. Our results quantify the uncertainties that have to be expected when performing similar measurements on unknown samples of the same material class. For other classes of PCM or other DSC instruments, the uncertainties to be expected and the best suitable parameters can be determined using the same approach.

This technology is very appropriate to evaluate the thermal properties of PCM used in cooling applications.

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