FULL PAPER
Standardization of PCM Characterization via DSC

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SUMMARY

Differential Scanning Calorimetry (DSC) is a widely used method for the characterization of phase change materials (PCM). Comparative measurements carried out at different laboratories revealed the need for a standardized methodology to reduce the deviations between these results and to determine representative and reliable PCM characteristics data.
Several comparative DSC measurements using different DSC devices have been carried out to develop a standard for the determination of the enthalpy curves for melting and solidification. Laboratory grade Octadecane (Parafol 18-97, Sasol) is used as PCM for these measurements. The first comparison showed large deviations in terms of transition temperature and enthalpy. Thereby, the need for a standardized measurement procedure and a specification of the calibration of DSC devices became apparent.
The developed procedure includes: I) the determination of the required heating and cooling rate, II) the calibration of the DSC device under consideration of the determined heating and cooling rate, III) the measurement itself, and IV) the data analysis and representation.

INTRODUCTION

An accurate material characterization of thermal energy storage materials is significant to develop an efficient thermal storage device or application. The most important temperature related characteristics of heat storage materials are heat capacity, thermal conductivity, density, and viscosity. All these parameters are needed to size thermal storages or to develop heat exchangers to charge and discharge them. Also the validity of simulation results are strongly influenced by the quality of the storage material data considered.
The heat capacity of PCM shows a very strong dependency on temperature. Thus, a good characterization is of particular importance. It seems to be not very challenging to determine the heat capacity of storage materials since there are many commercial DSC available, designed to measure heat flux into a material when the temperature is increased. A very common measurement method using DSC is to apply a constant heating or cooling rate to the material and to determine the heat flux into the material. Following this, the enthalpy curve is computed by integration of the heat flux signal. Figure 1 gives an example of enthalpy curves of octadecane measured by applying different heating rates. These enthalpy curves indicate a different dependency of the heat capacity on temperature. Even measuring the material twice with the same heating rate can lead to different results as indicated by the first and second cycle in the figure. These results are not only representing the measured PCM but also the DSC furnace geometry.
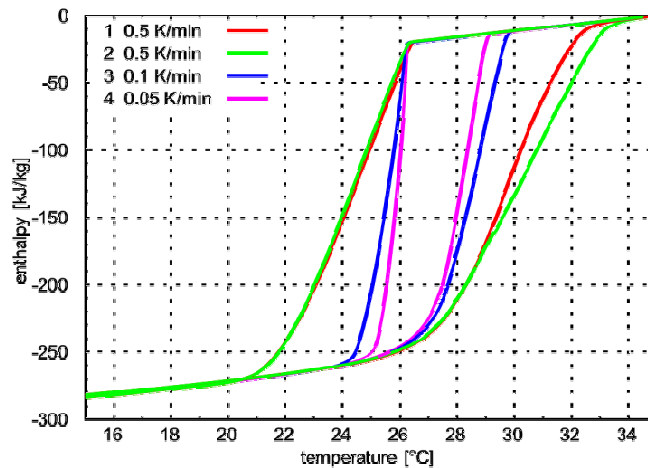
Figure 1. DSC measurement of octadecane applying different heating rates

Figure 2 shows a schematic drawing of a heat flux DSC furnace (left) and the temperature progression measured beneath the sample in different arrangements (right). The position of temperature sensors is outside the measurement crucibles. Due to this construction the measured temperature is not the real sample temperature. The difference of measured temperature and real sample temperature is depending on the quantity of sample in the crucible (sample mass), the thermal contact between sample and crucible and between crucible and temperature sensor, the sample´s thermal conductivity, and the applied heating rate. If the measured temperature should be close to the real sample temperature, slow heating and cooling rates are required to diminish the temperature gradient between sample and crucible. The heat capacity of the sample is computed by assuming that the thermal resistance of reference and sample crucible is the same. The thermal resistance is determined by a calibration using standard materials with well-known heat of fusion. The temperature sensors by the melting temperatures (onset temperatures) of these materials.
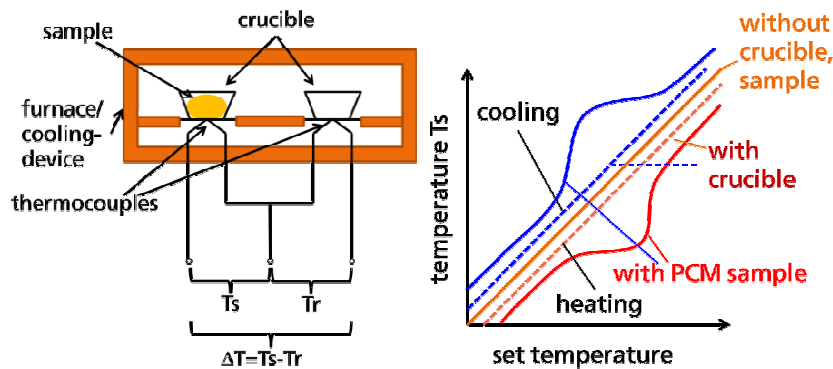

Figure 2. Schematic drawing of a DSC furnace (left) and temperature progression of a dynamic DSC measurement

Beyond the basic calibration of a DSC, the question is how comparable the results are if the same PCM is measured at different institutions by using DSCs from the same or different manufactures and how a procedure should look like to make these results comparable. To answer this question and to develop a procedure for the PCM measurement, a group of people working at different intuitions are cooperating in the framework of the IEA SHC Task 42 / ECES Annex 29. During this work, different round robin tests (RRT) have been carried out and two workshops have been arranged. This paper summarizes the work, the methods applied, and the results that have been achieved during the past six years.

METHODS

The paraffin Parafol 18-97 from Sasol Germany GmbH is used as sample for all the RRT. All samples send to the partners were taken out of the same batch. The chemical composition of the paraffin is given in Table 1. From its purity the material comes very close to pure Octadecane for which a melting temperature of 28.15 °C and a heat of fusion of 241.65 kJ/kg are reported by Domalski and Hearing (1996). The specific heat capacity in solid and liquid state is 1.91 kJ/kg K (Messerly et al. 1927) and 2.23 kJ/kg K (Höhne 1961), respectively.

Table 1. Chemical composition of the RRT paraffin Parafol 18-97

Component	Fraction [wt.-%]
C16	0.07
C18	98.11
iC18	0.4
Bromine	0.01

For the first RRT, all participants were asked to measure the paraffin as they are used to measure PCMs. There was no procedure given how to analyse or display the data.

The second RRT was carried out according to a DSC procedure defined in the German quality label PCM-RAL (PCM-RAL). This label defines how to determine the heating rate required in order to measure PCM. According to this procedure, several cycles - each consisting of a heating and cooling ramp - have to be applied to the sample. Thereby, the heating and cooling rate has to be reduced from cycle to cycle to the half value of its precursor. A suitable heating and cooling rate is reached when the peak temperature of the heat flow signals or inflection point of the computed enthalpy curves is not lower (heating ramp) or higher (cooling ramp) than 0.2 K of the one in the cycle before (criteria 1) or if the temperature difference between peak of cooling and peak heating signal is smaller than 0.5 K (criteria 2). Figure 3 illustrates the heating rate test and the conditions required by the PCM-RAL (criteria 1 left, criteria 2 right).
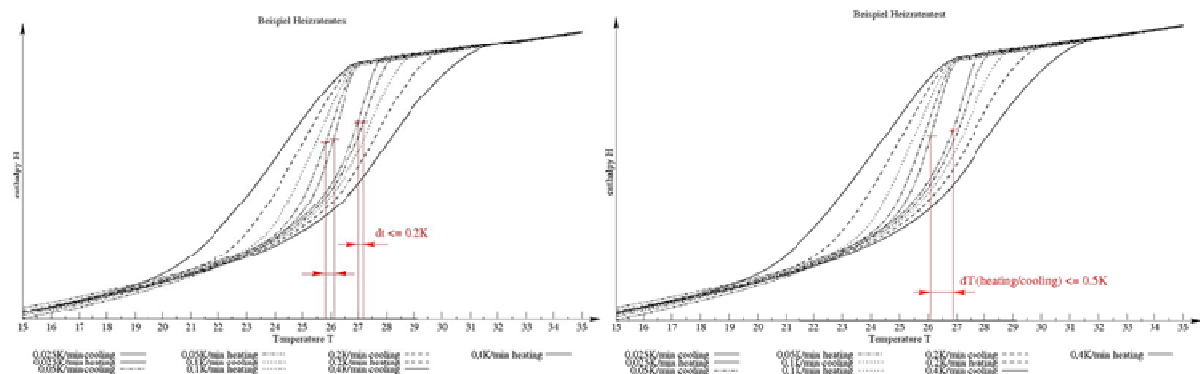

Figure 3. Conditions for the suitable heating rate according PCM-RAL

The third RRT was undertaken in a workshop held at Fraunhofer ISE in Freiburg, Germany. For this workshop DSCs from Netzsch, Perkin Elmer, Mettler Toledo, and TA Instruments were used to measure in parallel. A uniform calibration of all DSCs and applying the same sample mass (approx. 10 mg) yielded an excellent improvement in comparability of results for the heating process. The cooling curves showed still considerable devuations. This was reported by Lazaro et al. (2013).

A further improvement of results was obtained in terms of data analyses. Unstable baselines lead to a displacement of enthalpy curves like shown in Figure 4, right. This is caused by a

DSC baseline shift while measuring the sample or/and by an offset of the heat flow signal like shown in Figure 4, left. The method for baseline correction is published by Höhne, Hemminger and Flammersheim (2003). It moves the measured baseline to zero. The methods require isothermal sections before and after each heating and cooling ramp. It has to be ensured that thermal equilibrium is reached within these isothermal sections.
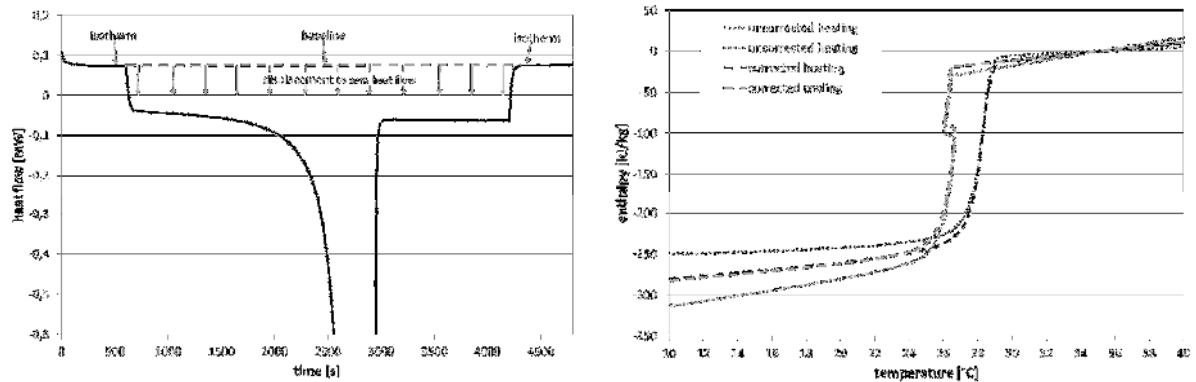

Figure 4. Left: schematic illustration of a baseline correction. Right: enthalpy curves before and after baseline correction.

The overall procedure developed for the DSC measurement of PCMs consists of five elements:

1. Heating and cooling rate test to determine suitable heating and cooling rates for the PCM to be measured. This is done by using the PCM to be characterized and applying heating and cooling rates starting from fast rates (e.g. 10 K/min) and slowing down the heating and cooling rates of consecutive cycles by halve the previous.
2. Calibration of the DSC by using 3 different calibration materials covering the desired temperature range (e.g. water, gallium and indium). The calibration has to be done with the determined heating rate.
3. Measurement of the empty crucible using the determined heating and cooling rates.
4. Sample measurements by applying the sample to the crucible (apply the same sample mass as for the heating rate test) using the determined heating rate.
   - four measurement cycles have to be applied
   - three samples have to be measured
5. Analysis of data
   - if necessary, baseline correction (displacement to zero heat flow)
   - subtraction of heat flow signal measured with empty crucible from sample measurement
   - data evaluation, computation of enthalpy curves

A more detailed procedure and a database to upload the results can be found on THERMAT (THERMAT).

RESULTS

Figure 5 shows the first RRT´s result with the reference temperature at 20 °C. They reveal a wide variation in melting and crystallization temperatures and enthalpy changes for fusion as well as for crystallization. This result is also confirmed by comparing the enthalpy curves which additionally show a wide variation in measured hysteresis behavior and melting ranges.
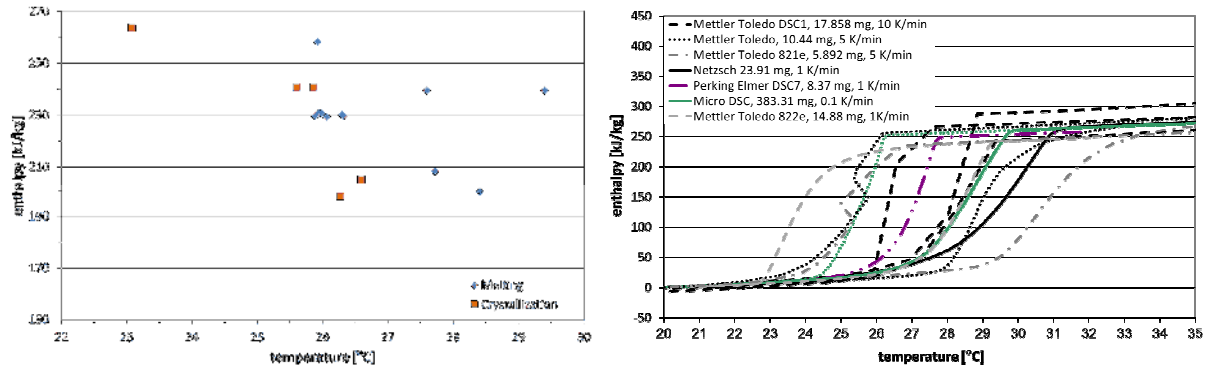

Figure 5. Results of the first RRT without any definition

Figure 6 depicts the enthalpy curves of the RRT in which the PCM-RAL heating rate test procedure is applied to determine a suitable heating rate. The reference temperature for the curves is 20 °C. Compared to the previous RRT the results are improved in terms of temperature variation and hysteresis. The variation of enthalpies is still on the level of the first RRT and show a deviation of 30 kJ/kg at 30 °C.

Figure 7 shows the results obtained by applying the standardized calibration using three different calibration materials to the DSC and with an additional baseline correction as outlined above if required (Figure 4). Here the reference temperature was set to 30 °C. The right graph of Figure 7 depicts the temperature deviation between the plotted enthalpy curves. The maximum temperature deviation during melting and crystallization is about 0.52 K and 1.13 K, respectively. For the nucleation temperature, a temperature variation of 0.38 K is observed. The curves show a good agreement in the sensible liquid part (Figure 8, left graph). The difference in enthalpies at 20 °C is in the range of 10 kJ/kg, which is less than 5% of the total enthalpy change measured between 20 and 30 °C (Figure 8, right graph).
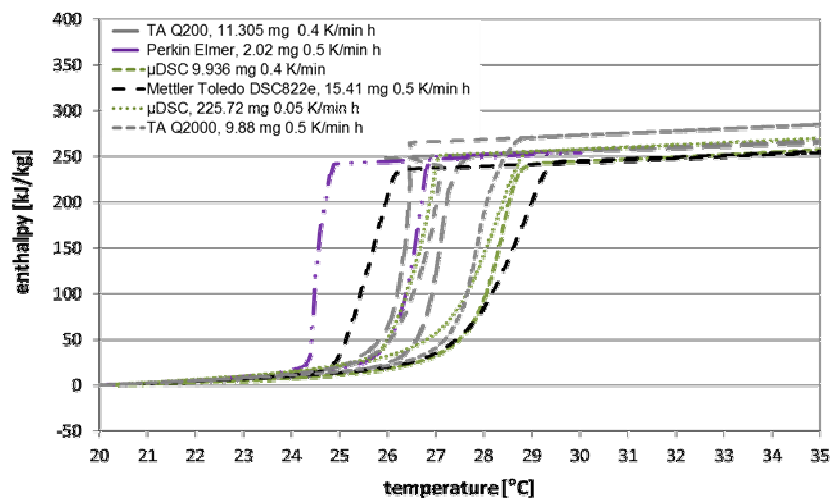

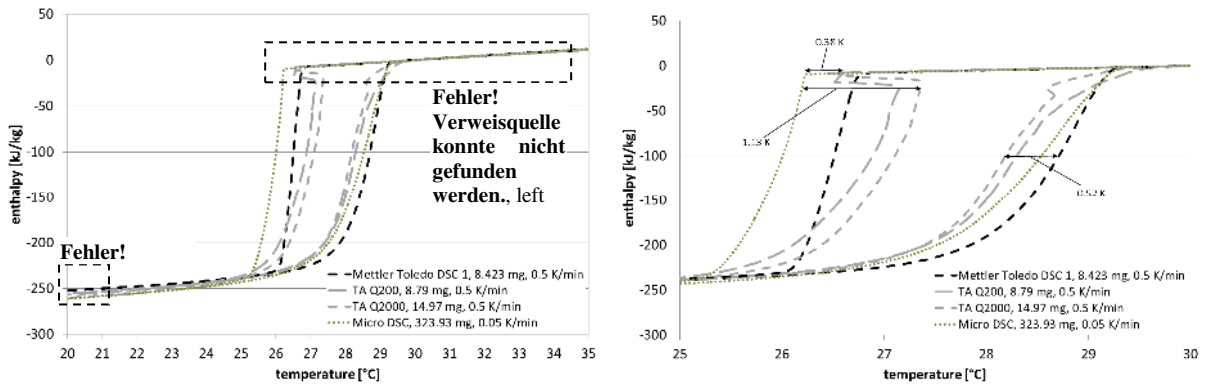*Figure 6. Results of the second RRT with procedure according to PCM-RAL*

Figure 7. RRT results after applying a standardized calibration and a correction of the baseline.
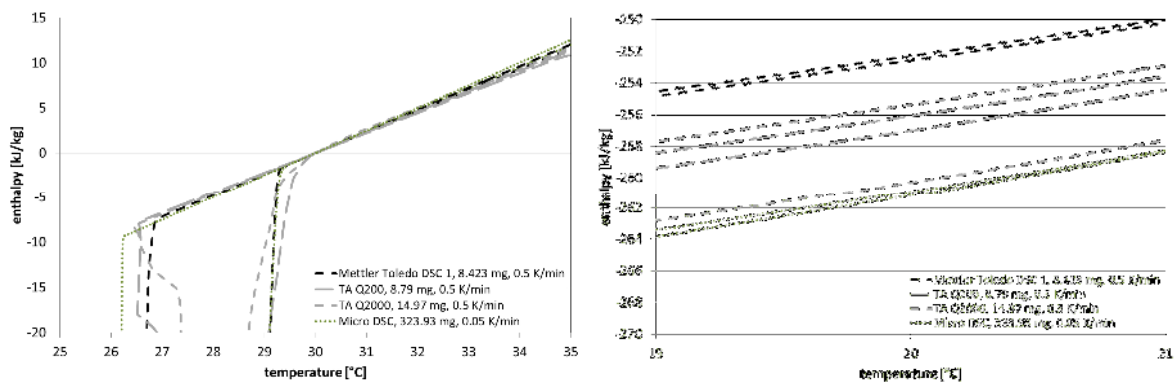

Figure 8. Details of the enthalpy curves of Figure 7

The left graph in Figure 9 depicts more results of a second group of measurements which have been measured partly according to the defined procedure (only heating curve measured, only heat of fusion integrated, or heating rate was very low for the used sample mass). For comparison the measurement with Mettler Toledo DSC1 is also plotted into the graph. The comparison of heat of fusion and heat of crystallization is plotted on the right graph of Figure 9. Table 2 lists the main parameters as well as the main results of all DSC measurements obtained with the last RRT. The standard deviation printed in the table as well as the graph illustrates the good agreement of results obtained for the onset values. All results show also good agreement in heat of fusion and heat of crystallization except from the results obtained with the Netzsch DSC 404.
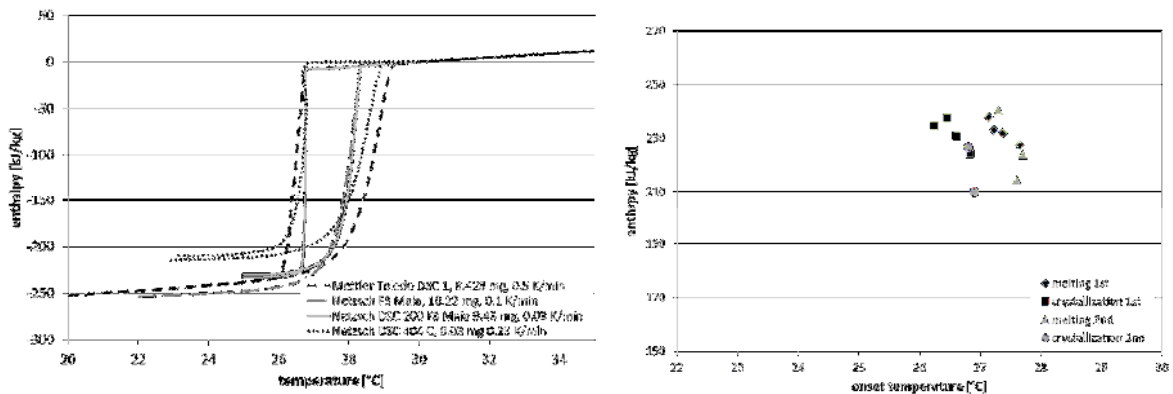

Figure 9. Left: comparison with a second group of DSC measurements; right: comparison of heat of fusion, heat of crystallization plotted against the onset temperatures

Table 2. Main results of the final DSC RRT

		Sample mass [mg]	Heating rate [K/min]	Cooling rate [Kmin]	Heat of fusion [kJ/kg]	Onset fusion [°C]	Offset fusion [°C]	Heat of cryst. [kJ/kg]	Onset cryst. [°C]	Offset cryst. [°C]
1st group	Mettler Toledo DSC1	8.42	0.5	0.5	227.28	27,.65	29.24	224.25	26,83	26.05
	TA Q200	8.79	0.5	0.5	231.81	27.37		230.9	26.61*	
	TA Q2000	14.97	0.5	0.5	232,9	27.23	29.7	237.5	26.46*	24.64
	Setaram Micro DSC	323.93	0.05	0.05	237.81	27.14	29.33	234.6	26.24	25,86
	mean value				232.45	27.35	29.45	231.81	26.54	25.52
	standard deviation				3.74	0.19	0.23	4.95	0.95	0.62
2nd group	Netzsch F3 Maia	10.22	0.1	0.1	240.19	27.3	28.5			
	Netzsch DSC 200 F3 Ma	9.43	0.03	0.03	223.7	27.7	28.3	226.6	26.8	26.6
	Netzsch DSC 404	8.03	0.25	0.25	214.1	27.6	29.1	209.9	26.9	26
	mean value				226	27.53	28.63	218.25	26.85	26.3
	standard deviation				10.77	0.17	0.34	8.35	0.05	0.30

*nucleation temperature

DISCUSSION

The results of the RRTs show continuous improvements in the comparability. The determination of suitable heating and cooling rates for the characterization is the basis to measure a temperature close to the real sample temperature. For the measured Parafol 18-97 all applied DSCs require a heating rate below 1 K/min if a sample mass of around 10 mg is measured. Much lower heating and cooling rates have to be applied if the sample mass is higher. The Micro DSC (manufacturer Setaram) is an example for a DSC that requires a sample mass of around 300 mg and, therefore, a heating rate of only 0.05 K/min. While the Micro DSC is designed to measure with such low heating rates, for other DSCs the resolution has to be considered as too low, so thatheating and cooling rates lead to a poor signal to noise ratio. This renders measurements above and below the phase transition difficult. The measurements with the Netzsch DSC 200 F3 Maia and DSC 404 might be below the resolution what might be the reason for the differences to the other results in the solid and liquid state of the measured PCM.

The RRT revealed also that a standardized calibration is necessary to gain good agreement in the results for enthalpy. It is advisable to calibrate by using several calibration materials and to choose calibration materials which show melting temperatures lower and higher than the PCM´s melting temperature to avoid extrapolation. The calibration has to be done using the heating rate which is determined via the heating rate test and applied to the PCM sample.

The correction of baselines is another important step to increase the quality of the measurement results. Many DSC show a baseline drift which makes a comparability of results impossible as this drift is different for every DSC as well as might be different in every measurement.

The results presented here show a very good agreement if it was possible to apply the complete measurement procedure. The results presented in Figure 7, Figure 8 and Table 1 show good agreement but it is better for the heating curve than for the crystallization curve (Figure 7). An explanation for this might be that the nucleation is a statistical effect and not well defined. In addition, the thermal inertia of the DSC furnace influences the results. Very small deviations can be found for the onset values of the melting peak which is determined to 27.35 °C ± 0.19 K for the first group of DSCs. The standard deviation of 0.19 K seems to be an acceptable value considering the different shapes of the measured curves. The expected melting temperature for pure Octadecane is 28.15 °C as outlined above. The obtained result is 0.8 K lower. The differences in enthalpies taken out of the graph (Figure 7) are below 10 kJ/kg which is less than 5% of the enthalpies measured between 20 and 30 °C. The mean value for the heat of fusion is determined to 232.45 kJ/kg ± 3.74 kJ/kg which is also lower

than the expected value of 241.65 kJ/kg reported for pure Octadecane. The result determined by using the Netzsch F3 Maia has the smallest deviation from this value. However, it is difficult to estimate the influence of the impurities on the phase transition data of the investigated Parafol 18-97 which might be a reason for the lower values obtained for melting temperature and heat of fusion.

CONCLUSIONS

The characterization of PCMs using DSCs requires a careful procedure to achieve reliable results. The comparison of measurements done for the same material at different institutions using different DSC revealed significant differences without applying a standardized measurement procedure. The results presented in this paper show clearly that not only a procedure for the measurement of the sample is required; the procedure has to include the calibration and the data analysis, too. An accurate calibration using the heating rate which will be applied to the sample is essential for the characterization of PCM via DSC. It is also essential to measure PCM slowly. Suitable heating and cooling rates have to be determined by applying a heating and cooling rate test as described. An offset and a drift of the baseline can be eliminated by an analysis with correction of the.

All this steps improve the comparability of different DSC measurements and, therefore, hopefully also the quality of PCM characterization by using DSCs.

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