Improved measurement technique for the characterization of organic and inorganic phase change materials using the T-history method

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Abstract. In the past decade, the interest in phase change materials (PCM) has grown significantly due to their ability to store large amounts of thermal energy in relatively small temperature intervals. Accurate knowledge of thermo-physical properties is a prerequisite for any reliable utilization of these materials. The T-history method is widely used for the investigation of PCM. This paper presents an improved measurement technique for the characterization of PCM using the T-history method. The suggested improvements include the arrangements made in three different prospects: the experimental setup, data processing and data representation. T-history measurements of organic RT21 and inorganic SP22 A17 (RUBITHERM® GmbH) PCM were performed. The applied arrangements resulted in the temperature accuracy of ±0.3 °C and the reduction of uncertainty associated with heat stored/released between the cooling and heating measurements. The obtained results showed some important aspects of the T-history PCM investigation and could provide more effective design and development process of the thermal energy storage systems based on the investigated materials.

Keywords: PCM, Characterisation methodology, T-history method, Subcooling, Temperature uncertainty, Heat density.

1. Introduction

In the past decade, the interest in phase change materials (PCM) has grown significantly amongst researchers as indicated in the most recent review papers by Oró et al. [1] and Zhou et al. [2] as well as in an earlier one by Zalba et al. [3]. Namely, these materials, due to their ability to store large amounts of thermal energy in relatively small temperature intervals, can be effectively used for various thermal energy storage (TES) applications [4]. Nevertheless, according to Mehling and Cabeza [4], one of the limiting factors for the effective application of PCM is the lack of the experimentally determined material data. Accurate knowledge of thermo-physical properties is a prerequisite before the design process and the real time deployment of any TES application based on PCM or PCM slurries as indicated by Diaconu et al. [5] and Lu and Tassou [6].

The T-history method, introduced by Yinping et al. [7], is widely used for the investigation of phase change materials. The majority of the T-history studies reported in the literature during the last 20 years aimed to reduce the temperature and the heat storage uncertainty associated with the PCM measurement. Accordingly, Marin et al. [8] improved the mathematical evaluation model developed

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by Yinping et al. [7] by using the concept of enthalpy and its relation with the temperature. Furthermore, Lazaro et al. [9] developed a verification methodology for the T-history setup. The most recent T-history procedures include improvements in measurement arrangement and in the way of measurement processing as reported by Kravvaritis et al. [10, 11] for the "thermal delay method" and by Moreno-Alvarez at al. [12] for the "dT-history method". Peck et al. [13] introduced the utilization of the PCM T-history curve's inflection point as the end of the phase change period instead of the release point of subcooling as suggested in the definition of the original method [7]. They also suggested the horizontal placement of the test tubes to avoid natural convection. Reduction of the temperature and the heat storage uncertainties is very important for optimal utilization of PCM since the typical temperature ranges of PCM applications are in the order of ±10 °C around the phase change temperature [14].

This paper presents an improved measurement technique for the characterization of PCM using the T-history method. The main modifications involved in the measurement process are summarized below. Primarily, the suggested improvements include the selection of the thermally controlled environment and the temperature sensing modalities for the T-history setup. This was followed by the development of the adequate instrumentation and data acquisition system. In addition, the mathematical model given by Marin et al. [8] and elaborated by Kravvaritis et al. [10], based on the time delay between the T-history curves at any specified temperature , was adjusted for the data analysis in order to take the subcooling phenomenon into the account. The suggestions given by Sandnes and Rekstad [15] regarding the subcooling were also taken into consideration. The calculated results on heat capacity were presented as heat stored/released in given temperature intervals, as suggested by Mehling et al. [16]. Moreover, the total heat released/stored (between 15 and 30 °C) for organic as well as for inorganic PCM in case of both cooling and heating cycles were determined and compared.

2. Materials and methods
The application of the T-history method, as proposed by Yinping et al. [7], requires at least two test tubes, one filled with the investigated PCM material and the other one filled with the reference material. Reference material needs to have very well-known thermal properties especially in terms of the sensible and the latent heat capacity. Distilled water is usually used for this purpose. Test tubes need to be long and narrow in order to keep the Biot's number below 0.1 and ensure the application of the lumped capacitance model [7]. The samples within the tubes are firstly heated to the temperature above the PCM melting point. When the uniform temperature of both samples is achieved they are exposed to the environmental temperature below the melting point. Their temperature history has to be recorded throughout the whole process so the measurement results can be used to evaluate the thermal properties of the PCM [7]. As indicated in the section 1, important contribution of this study is the development of the precise T-history setup. The main experimental setup and method improvements are summarized below.

A BINDER KMF 115 (BINDER GmbH [17]) environmental chamber was used as the temperature controlled facility. Majority of the reported studies [7-15] do not discuss the details of the experimental setup in terms of the temperature controlled environment. The temperature controlled facilities within the reported experiments are custom built in such way that clear understanding of temperature control implementation is not present. For this reason, we decided to use a high performance commercial BINDER KMF 115 chamber with the guaranteed and precise temperature control. The manufacturer does not reveal the details regarding the temperature control mechanism of

the chamber. However, highly precise control from -10 to 100 °C with the temperature accuracy of ±0.2 °C within the chamber is guaranteed by the manufacturer. Guaranteed temperature accuracy is one of the main reasons the BINDER KMF 115 was selected as the temperature controlled environment for the T-history experiments. The chamber was also used for the sensor calibration so relatively high sensor accuracy was obtained. The exterior dimensions of the chamber are: width 88.5 cm, height 105 cm, and depth 73 cm plus the interior dimensions: width 60 cm, height 48.3 cm, and depth 35.1 cm (see figure 1). The chamber's temperature controlled range between -10 °C and 100 °C was found acceptable for the investigation of the selected organic paraffin RT21 and inorganic salt hydrate SP22 A17 (RUBITHERM® GmbH [18]) PCM samples. According to the manufacturer's specification RT21 has the melting area between 18 °C and 23 °C and the congealing area between 19 °C and 22 °C with the typical phase change temperature of 21 °C. The heat stored between 15 °C and 30 °C of this PCM is 134 kJ/kg. The melting area of the inorganic PCM SP22 is between 22 °C and 24 °C (typical being 23 °C) and the congealing area is between 19 °C and 21 °C (typical being 20 °C). The heat stored between 15 °C and 30 °C of the SP22 is 150 kJ/kg. Distilled water was used as the reference material in case of both PCM samples since its thermal properties, mainly in terms of the specific heat capacity, are well-known.
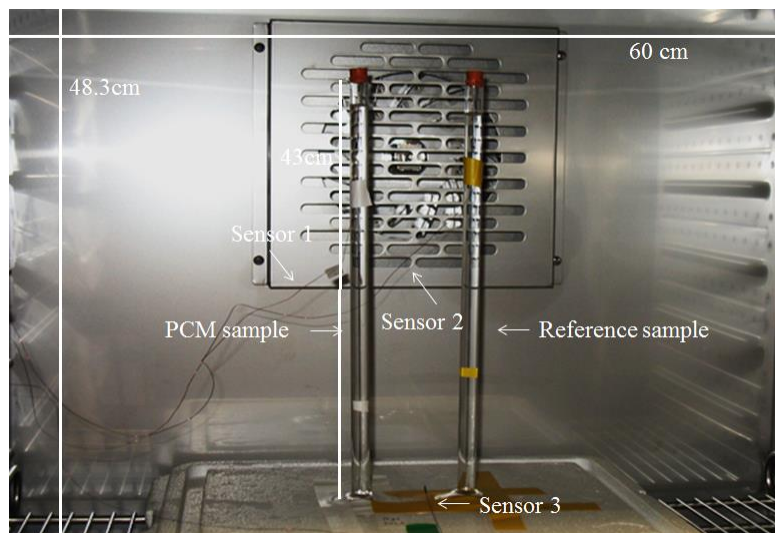

Fig. 1. T-history experimental setup inside the BINDER KMF 115 environmental chamber.

One of the aims of this experiment was to characterize relatively large PCM specimens (with the specimen's mass larger than 20 g) and so the results could be compared, in terms of PCM thermal characteristics, with the results obtained with smaller masses from experiments reported in literature [19, 20]. Therefore, the test tubes were designed and custom built with the aim to have the tubes of maximum possible volume to ensure that the mass of the specimen is above 20 g. The wall thickness of the test tubes was limited to 1 mm since the manufacturer (Dixon Glass Limited [21]) could not make thinner tubes. The height of the test tubes was also limited by the internal height of the chamber to below 48.3 cm. The tubes were made of SIMAX glass with the thermal conductivity of 1.2 W/mK. Given the aforementioned parameters the height and the internal diameter of the test tubes was determined so the Biot's number would be below 0.1 to justify the application of the lumped capacitance model [7]. This way the tubes' height and internal diameter were designed to be 43 cm

and 1.3 cm. In all experiments, both the RT21 and the SP22 were put in the test tubes of the same dimensions so the shared parameter for organic and inorganic specimens was volume. Since SP22 (density of 1.49 kg/l in solid and 1.43 kg/l in liquid form) is more dense than RT21 (density of 0.8 kg/l in solid and 0.77 kg/l in liquid form) this resulted in the respective masses of 73 g for SP22 and 41 g for RT21. Both masses were measured when samples were in liquid states.

Continuous temperatures of the samples and the environment temperature were measured using thermistors (Newark MA100GG103A model [22]). In comparison to other conventional temperature sensors, thermistors were selected for this study due to their high sensitivity [23]. This property makes them particularly responsive to the temperature changes during T-history measurements. The main disadvantage of thermistors is the nonlinear change of their resistance with temperature [24]. These sensors require the application of the suitable linearization technique prior to any utilization. Therefore, an appropriate instrumentation system for thermistor linearization, signal amplification and filtering had to be developed in order to minimize the temperature uncertainty associated with the measurements.

All the sensors were calibrated prior every measurement. The BINDER KMF 115 chamber was used as the temperature control facility in the calibration procedure. Calibration is not explained in detail in this paper since the whole procedure is thoroughly given in [25]. The thermistor linearization techniques were developed so the minimum uncertainty of ±0.1 °C is introduced by the thermistor alone. This adds to the uncertainty of ±0.2 °C associated with the calibration facility i.e. the BINDER KMF 115 chamber, resulting in the overall temperature accuracy of ±0.3 °C which is guaranteed in every measurement. Some studies in the literature suggest better accuracy (e.g. ±0.1 °C in [8]), sometimes even below 0.1 °C, without emphasizing the mechanism used for temperature control during the calibration procedures. To claim such accuracy without revealing the calibration details leaves room for discussion whether such accuracy is attainable. The accuracy of the sensors predominantly depends on the accuracy of the calibration facility. In addition, good quality calibration requires as many calibration points as possible to reduce the fitting errors. Therefore, to obtain the temperature accuracy better than ±0.1 °C is a very challenging task since firstly, very few exact temperatures are easily attainable in the laboratory environment and secondly, good quality calibration requires many temperature calibration points. For these reasons, the guaranteed accuracy of ±0.3 °C from this study seems very promising.

Since the PCM samples were placed in long tubes a methodology to avoid temperature gradients inside the samples was developed. Namely prior T-history measurements, three sensors were positioned on the outer surface of the PCM test tubes at different height levels (one near the top, one in the middle and the last one near the bottom of the test tube) and then the PVC foam insulation tape was wrapped around the test tubes, filled with the corresponding PCM samples. The samples were subjected to the step temperature programs and their temperature recorded with all three sensors. The tests were performed with the insulation of different thicknesses. The thickness was varied from 3 mm in the approximate 3mm steps. It was done for the two PCM samples until all three sensors showed the same temperature history. This was taken as a sign that the longitudinal thermal equilibrium within the samples was achieved so the corresponding thickness was marked as the optimal one. Furthermore, once the optimal thickness was determined it was assumed that the natural convection within the samples could be neglected since the longitudinal equilibrium was established. The optimal thicknesses of 6 mm and 1 cm were determined for the RT21 and SP22 samples. Once the optimal insulation thickness was determined the T-history measurement were performed. Two sensors were

positioned inside the PCM and water samples (Sensor 1 and Sensor 2 in figure 1) and one was inside the environmental chamber (Sensor 3 in figure 1). The tubes are shown without insulation in figure 1 for better visibility of both the test samples and the sensors. The sensor 1 and 2 were placed along the central axes of the test tubes at the depth of 12cm and secured with the rubber stopper used to seal the tubes. Namely, a narrow hole was made with the needle through the center of the 1 cm long rubber stopper and the sensors tunneled through it and tightly secured. In total, three thermistors were deployed in this T-history implementation.

Furthermore, both PCM and reference samples were subjected to alternating heating and cooling cycles between 11 °C and 30 °C in case of RT21 and between 8 °C and 30 °C in case of SP22. At the beginning of every 6 h long cycle the chamber's temperature was sharply changed between those two points. Each cycle was set to last 6h although measurement showed that within each cycle all three sensors were at the equilibrium temperature after 3h in case of both PCM measurements. Each measurement included five cooling and five heating cycles for RT21 and three cooling and three heating cycles for SP22. The results obtained from different runs corresponding to the adequate cycles within the experimental run were averaged to reduce random errors and improve measurement precision. Continuous temperature data were acquired. Data acquisition was performed using the 14-bit NI DAQ USB 6212 card at a sampling rate of 10 Hz [26]. The selection of the sampling rate proved to be important in the T-history implementation. This observation is further explained in section 3.

Another, relevant modification, made in this study is the adjustment of the data processing algorithm. As indicated previously, the main processing technique was based on the mathematical model given by Marin et al. [8] and elaborated by Kravvaritis et al. [10], based on the time delay between the T-history curves at any specified temperature. This model uses the concept of enthalpy and its relation with temperature. The enthalpy-temperature (H(T)) curves were also determined here as presented in section 3. Given the reported sampling rate, the time step used in enthalpy calculations was 1 s which resulted in high temperature precision of the obtained H(T) data for both heating and cooling cycle. Subsequently, the obtained data on enthalpy temperature dependency i.e. the H(T) curves were used to determine the heat released/stored in given temperature intervals. It was done by selecting a suitable temperature interval (0.5 °C in this study) and calculating the enthalpy difference between the end and the start temperature of each interval. In the heating case this simple subtraction procedure resulted in heat stored data in given temperature intervals. For the cooling case, depending on the actual values of the start and end temperatures of the given temperature interval the heat released upon cooling and the heat lost due to subcooling (heat used to raise the temperature of the PCM from the nucleating T_N to the phase change T_{PC} temperature) were distinguished. For this, the same subtraction procedure on the cooling enthalpy values was used. However, the obtained results were attributed to either heat released or degree of subcooling data in given temperature intervals depending on the intervals' boundary values. Namely, by evaluating the sign of the first derivative of temperature curve associated with the cooling enthalpy the nucleation T_N and the phase change temperature T_{PC} of the PCM were precisely determined. Thus, the heat data, obtained by the substraction of the corresponding cooling enthalpy values, in intervals with boundaries between the nucleation T_N and the actual phase change temperature T_{PC} point, were marked as the degree of subcooling in the given temperature intervals. Heat data in the given intervals with boundaries outside the mentioned range (T_N to T_{PC}) were marked as the heat released in given temperature intervals.

The implemented representation format i.e. heat stored/released in given temperature intervals was chosen because it allows easier comparison between the data acquired by different researchers for the same phase change material [16]. Also, the comparison between the data obtained for different materials with similar properties is facilitated by using this format. It gives better overview of the heat values at specific temperatures. This way, the selection of appropriate PCM for the certain application becomes more reliable, given the application's driving temperature range.

Finally, the total heat released/stored between 15 °C and 30 °C, in case of cooling and heating cycles, was determined for both investigated PCM. This was done in order to compare our heat released/stored results with the ones given by the manufacturer. The stated temperature range was selected because the manufacturer only gives the heat data in that particular range. When the total heat released/stored was evaluated in case of cooling the values were reported for both heat release with taking the heat lost upon subcooling into the account (HR-w-SC) and the heat release without taking the heat lost upon subcooling (HR-Usable). HR-w-SC was calculated by adding the actual heat released data upon cooling and the heat lost due to subcooling i.e. the heat used to raise the temperature of the subcooled PCM from T_N to T_{PC}. The HR-Usable represents the actual heat released upon cooling i.e. only the portion of heat which can be extracted from the corresponding PCM upon cooling. HR-Ideal was also evaluated and it represents the total heat content released upon PCM cooling when the subcooling effect is totally neglected. The total heat stored by the material upon heating is presented as the HS data.

3. Results and discussion

The results for the heat stored/released in given temperature intervals as well as the results for the total heat stored/released between 15 °C and 30 °C are presented in this section, firstly for the organic RT21 and then for the inorganic SP22 PCM.

3.1. Results for the organic RT21 PCM

Figure 2 represents T-history cooling curves for the RT21 PCM. For this material the subcooling degree of 0.1 °C is almost negligible with the nucleation temperature of 20.9 °C and the phase change temperature of 21 °C (Real RT21 curve in figure 2a and figure 2c). Figure 2b shows an ideal RT21 curve obtained when the subcooling is completely neglected. The time interval for the sample to raise its temperature from the nucleation to the phase change point lasted only 0.5 min (see Fig. 2c) so with a sampling period greater than 0.5 min the subcooling, in this case, would not be detected. However, this was possible with the used sampling rate of 10 Hz which was selected as the widely accepted sampling frequency for dc signals. A combined view of the real and ideal scenario is shown in figure 2c.

Figure 3 shows the enthalpy-temperature (H(T)) curves for the organic RT21 PCM for cooling and heating cycles with the normalized enthalpy value of 0 kJ/kg at 15 °C. Since the degree of subcooling is almost negligible in this case only a small hysteresis between the enthalpy curves is observed.

Figure 4 shows the heat stored/released for the RT21 in the given temperature intervals (see table 1) upon cooling and heating cycles obtained from the corresponding enthalpy values as explained in section 2. It can be observed that the heat released in the case of the cooling cycle shows a relatively sharp peak value in the temperature range from 20.8-21.3 °C (see figure 4a) which is in agreement with the typical phase change temperature of 21 °C, reported by the manufacturer. However, in the case of the heating cycle the peaks are less pronounced and the heat stored is distributed across a wider temperature range (see figure 4c). These results indicate different behavior of the organic materials

upon cooling and upon heating and therefore they should be taken into consideration during the design process of the thermal energy storage systems based on PCM. Different behavior upon freezing/melting affects the TES system design in terms of real time PCM discharging/charging strategies.
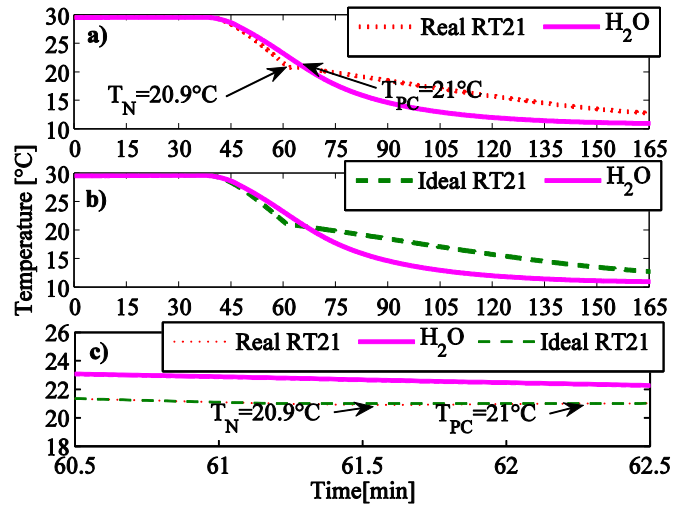

Fig. 2. T-history cooling curves for the organic RT21 PCM (m=41 g). a) Measured results for the PCM temperature (Real RT21) and the reference temperature (H_2O), b) Idealized results if subcooling effect is neglected for the PCM temperature (Ideal RT21) and the reference temperature (H_2O) and c) Combined zoomed in view of the measured (a) and idealized (b) temperature data.
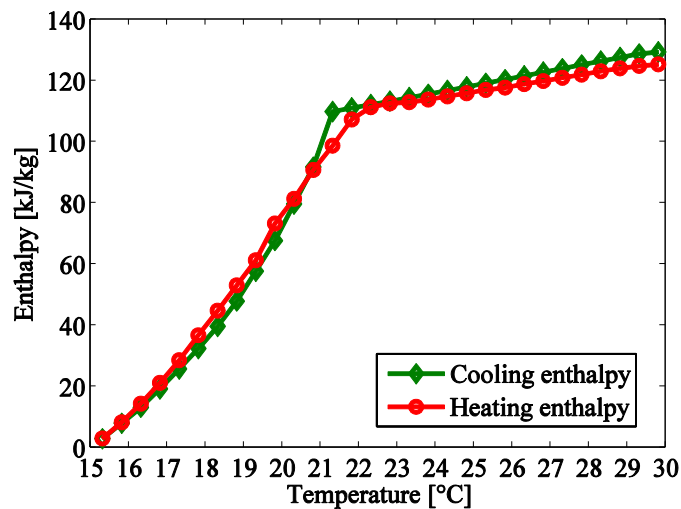

Fig. 3. Enthalpy-temperature (H(T)) curves for the organic RT21 PCM (m=41 g) for cooling and heating cycles with the normalized enthalpy value of 0 kJ/kg at 15 °C.
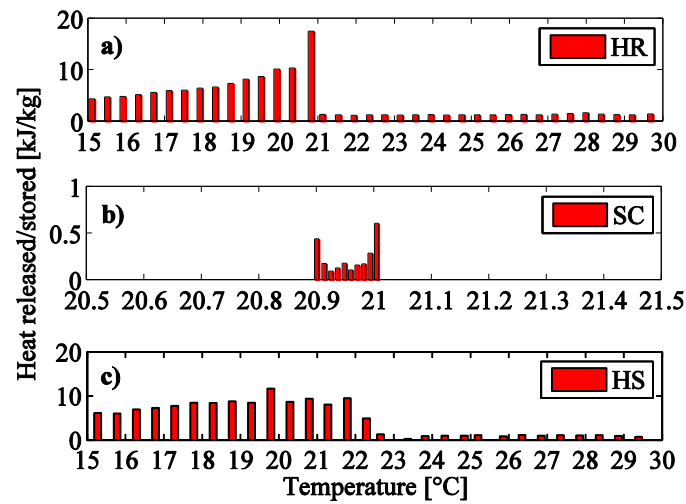
Fig. 4. Experimental results for the heat stored/released in the given temperature intervals for the organic RT21 PCM (m=41 g). a) Heat Released (HR) upon sample freezing, b) degree of SubCooling (SC) upon sample freezing, and c) Heat Stored (HS) upon sample melting.

Total heat released/stored data for the RT21 between 15 °C and 30 °C for both cooling and heating cycles are shown in figure 5. In all measurement runs it was observed that the values from the first cycle are always higher than the values from the consecutive cycles. The possible explanation for this could be the fact that before the first cycle within the measurement run a clean sensor is placed inside the sample and then the sample is cooled down and transformed into its solid form. After the first cycle, the sensor has undergone at least one solidification process within the sample so it seems to be acting as a nucleating agent. This means that a tiny portion of the solid material is formed around the sensor during the first cooling cycle and it becomes a nucleating seed in all the consecutive cycles. If this is taken into the account, then one should presume that the first cycle within each measurement reflects the most natural behavior of the PCM sample so the data obtained from the first cycle should be taken as the most accurate. The results from five different experimental cycles are presented (see figure 5) and they indicate good repeatability. As previously mentioned in section 2, during the PCM cooling cycles, total heat storage capacity is calculated with and without taking the heat lost due to subcooling into account (HR-w-SC and HR-Usable in figure 5). HR-Ideal was also evaluated and it can be observed that the total heat content released upon PCM cooling when the subcooling effect is totally neglected showed better agreement with the RT21 data sheet (DS) value. However, the heat results upon cooling with and without taking the subcooling (HR-w-SC and HR-Usable in figure 5) into consideration showed better agreement with the heat stored results upon heating. To quantify the previous statements the mean values of all data were estimated. The mean HS value was 127.8 kJ/kg and it showed a ±4.6 % deviation from the DS value. The mean HR-Ideal value was 133.6 kJ/kg. This value showed a negligible deviation of ±0.2 % from the DS values and an acceptable deviation of ±4.5 % from the mean HS values. The mean HR-w-SC and HR-Usable values were 130 kJ/kg and 129 kJ/kg. The HR-w-SC and the HR-Usable means showed a deviation of ±3 % and ±3.7 % from the DS values.

Table 1. Heat released/stored and the degree of subcooling in given temperature intervals for RT21 and SP22 PCM.

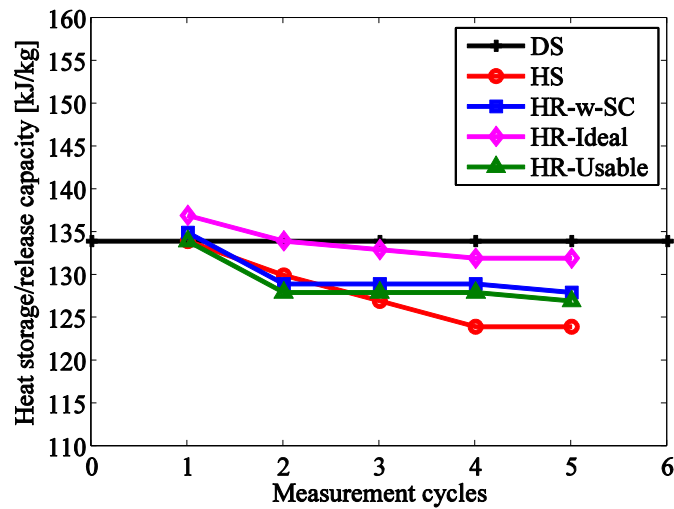| T intervals [°C]	RT21 HR [kJ/kg]	RT21 SC [kJ/kg]	RT21 HS [kJ/kg]	SP22 HR [kJ/kg]	SP22 SC [kJ/kg]	SP22 HS [kJ/kg]
15-15.3	3	0	3.1	2.5	0.9	0.9
15.3 -15.8	5.1	0	5.3	5	0.9	1.8
15.8-16.3	5.2	0	6.1	5.4	0.9	1.8
16.3-16.8	6	0	6.8	5.7	0.9	2
16.8-17.3	6.5	0	7.4	0.1	1	2.1
17.3-17.8	6.7	0	8.2	6.6	1	2.3
17.8-18.3	7.3	0	8	7.2	1	2.4
18.3-18.8	8.2	0	8.3	7.8	1.5	2.7
18.8-19.3	9.8	0	8.2	8.9	2.2	3
19.3-19.8	10	0	12	16.4	4.4	3.4
19.8-20.3	12	0	8.1	1.3	0.1	4
20.3-20.8	12.1	0	9.4	1.3	0	5.2
20.8-21.3	18.1	1	8	1.3	0	6.8
21.3-21.8	1.2	0	8.5	1.3	0	9.4
21.8-22.3	1.2	0	4.1	1.3	0	16
22.3-22.8	1.2	0	1.2	1.3	0	21.2
22.8-23.3	1.2	0	0.4	1.3	0	18.4
23.3-23.8	1.2	0	0.9	1.3	0	14.5
23.8-24.3	1.2	0	1	1.3	0	11.4
24.3-24.8	1.2	0	1	1.3	0	7.2
24.8-25.3	1.2	0	1.1	1.3	0	4.5
25.3-25.8	1.2	0	0.8	1.3	0	3
25.8-26.3	1.2	0	1.1	1.3	0	2
26.3-26.8	1.2	0	1	1.3	0	1.4
26.8-27.3	1.2	0	1.1	1.3	0	1.1
27.3-27.8	1.2	0	1	1.3	0	1.4
27.8-28.3	1.2	0	1.1	1.4	0	1.2
28.3-28.8	1.2	0	1	1.5	0	1.8
28.8-29.3	1.2	0	1	1.7	0	2
29.3-29.8	1.2	0	0.8	1.5	0	1.5
29.8-30	0.5	0	0.5	0.5	0	0.8

Fig. 5. Experimental results for the heat released/stored of the organic RT21 sample (m=41g) evaluated in the 15 – 30 °C temperature range (DS – heat Data Sheet value, HS – Heat Stored upon heating, HR-w-SC – actual Heat Released upon cooling with the addition of the heat lost upon SubCooling, HR-Ideal – Heat Released in an idealised case when subcooling is neglected, HR-Usable– actual Heat Released without taking the heat lost upon SubCooling into the account).

3.2. Results for the inorganic SP22 A17 PCM

Figure 6 represents T-history cooling curves for the SP22 PCM. For the inorganic SP22 PCM, as expected, the subcooling is much more pronounced with the nucleation temperature of 14.3 °C and the phase change temperature of 19.7 °C (Real SP22 curve in figure 6a and figure 6c). The subcooling effect lasted for around 20 minutes (see figure 6c). Figure 6b shows an idealized case when subcooling is neglected with the PCM and the reference cooling curves (Ideal SP22 and H₂O in figure 6b). A combined view of the real and ideal cooling scenario is shown in figure 6c.

Figure 7 shows the enthalpy-temperature (H(T)) curves for the organic SP22 PCM for cooling and heating cycles with the normalized enthalpy value of 0 kJ/kg at 15 °C. Since the degree of subcooling is significant in this case a large hysteresis between the enthalpy curves is observed.

Figure 8 shows the heat stored/released in the given temperature intervals (see table 1) upon cooling and heating cycles for the SP22. The degree of subcooling and the heat lost due to temperature rise of the subcooled PCM sample from the nucleation to the phase change point were also calculated and presented (see figure 8b). It can be observed that the heat released in the case of cooling shows a relatively sharp peak value in the temperature interval from19.3 to 19.8 °C (see figure 8a and table 1) which is in agreement with the typical phase change temperature upon cooling, reported by the manufacturer. In the case of heating the heat stored is distributed across a wider temperature range (see figure 8c and table 1) with the peak in the temperature interval from 22.3 to 22.8 °C which is in agreement with the typical melting temperature of 23 °C. Due to the large degree of subcooling, the results show even more significant difference in the cooling/heating behavior of the inorganic PCM compared to the cooling/heating behavior of the organic materials.
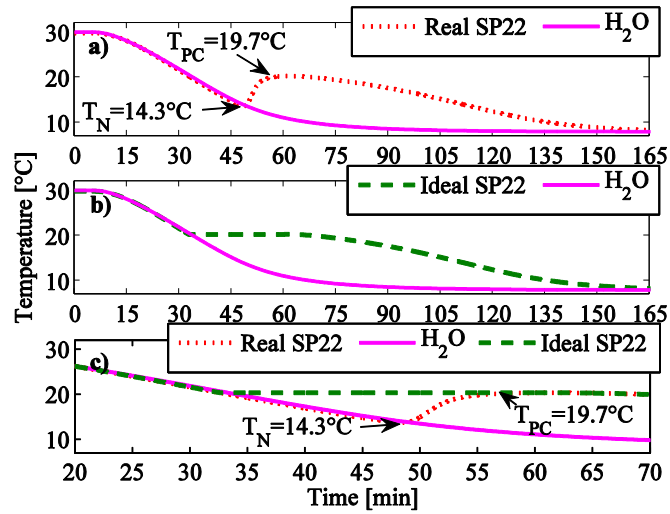
Fig. 6. T-history cooling curves for the inorganic SP22 PCM (m=73 g). a) Measured results for the PCM temperature (Real SP22) and the reference temperature (H_2O), b) Idealized results if subcooling effect is neglected for the PCM temperature (Ideal SP22) and the reference temperature (H_2O) and c) Combined and zoomed in view of the measured (a) and idealized (b) temperature data.
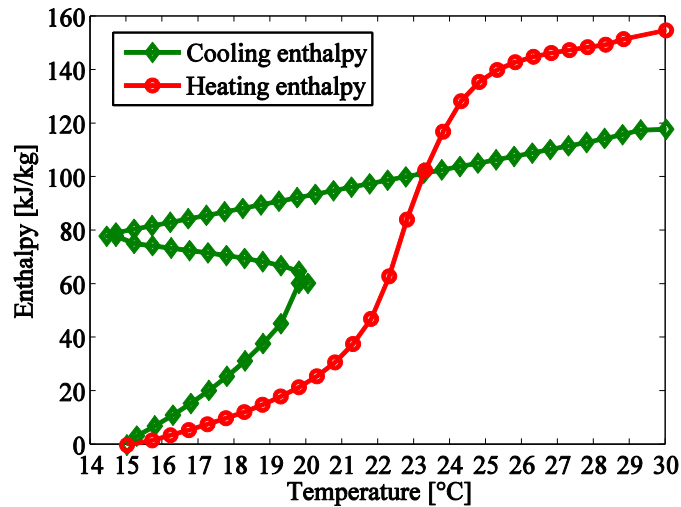

Fig. 7. Enthalpy-temperature (H(T)) curves for the organic SP22 PCM (m=73 g) for cooling and heating cycles with the normalized enthalpy value of 0 kJ/kg at 15 °C.

Total heat stored/released for the SP22 between 15 °C and 30 °C for both cooling and heating cycles is shown in figure 9. The results from three different experimental cycles are presented (see figure 9). The results from the first cycle are also higher than those from the consecutive cycles. It can be observed that the difference in the total heat content between heating and cooling cycles for the inorganic PCM is significant. The total heat stored upon heating (HS) shows good agreement with the material data sheet (DS) value reported by the manufacturer. Also, the total heat content upon cooling in case when subcooling effect is totally neglected (HR-Ideal) shows good agreement with both the total heat stored (HS) and the data sheet (DS) heat values.
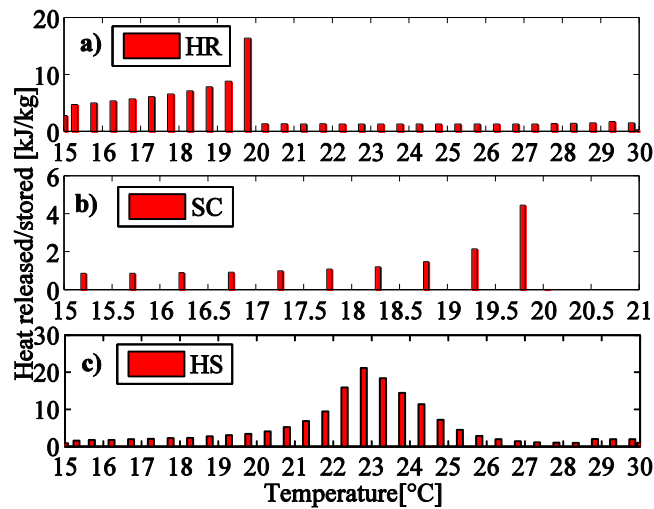
Fig. 8. Experimental results for the heat stored/released in the given temperature intervals for the organic SP22 PCM (m=73 g). a) Heat Released (HR) upon sample freezing, b) degree of SubCooling (SC) upon sample freezing, and c) Heat Stored (HS) upon sample melting.
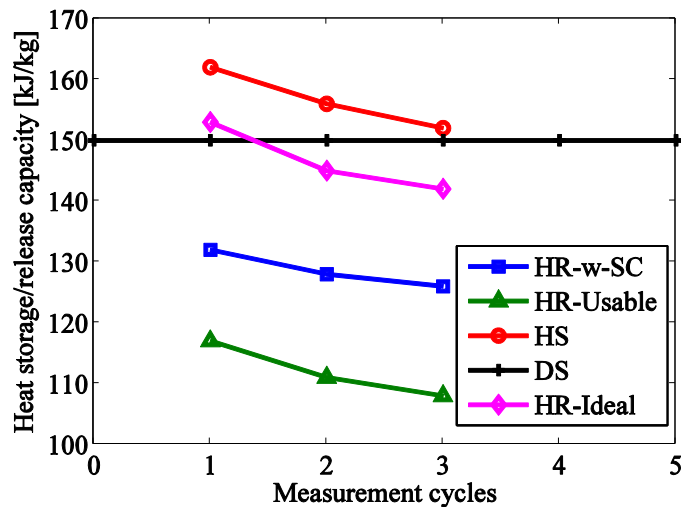

Fig. 9. Experimental results for the heat released/stored of the organic SP22 sample (m=73g) evaluated in the 15 – 30 °C temperature range (HR-w-SC – actual Heat Released upon cooling with the addition of the heat lost upon SubCooling, HR-Usable– actual Heat Released without taking the heat lost upon SubCooling into the account, HS – Heat Stored upon heating, DS – heat Data Sheet value, HR-Ideal – Heat Released in an idealised case when subcooling is neglected).

The situation is different for the total heat content of inorganic PCM upon cooling. Namely, the heat released with taking into account the heat lost due to subcooling (HR-w-SC) is closer to the heat stored upon heating than the heat released value without taking subcooling into account (HR-Usable). To quantify this behavior the mean values of all data were estimated. The mean HS value was 156.6 kJ/kg and it showed a ±4.4 % deviation from the DS value. The mean HR-Ideal value was 146.6 kJ/kg. This value showed a deviation of ±2.2 % from the DS values and an acceptable deviation

of ±6.3 % from the mean HS values. The mean HR-w-SC and HR-Usable values were 128.6 kJ/kg and 112 kJ/kg. The HR-w-SC and the HR-Usable means showed a deviation of ±14.2 % and ±25 % from the DS values.

4. Conclusion

It is concluded that the determination of PCM thermal properties using the T-history method significantly depends on the arrangement of the measurement setup as well as on the data processing methodology. The main setup improvements included the usage of the environmental chamber and thermistors for the precise temperature control and sensing. The reduction of the temperature uncertainty associated with the PCM characterization was achieved through the development of adequate instrumentation and data acquisition system. Also, it was observed that the data sampling rate affects the detection of the PCM subcooling phenomenon. In case of the organic PCM the subcooling effect lasted shortly and could be observed only when the sampling period was above 0.5 min.

It was also observed that the heat content values from the first cycle are always higher than the values from the consecutive cycles. The possible explanation for this could be the fact that before the first cycle a clean sensor is placed inside the sample. After the first cycle, the sensor undergoes at least one solidification process within the sample and it seems to be acting as a nucleating seed in the consecutive cycles. This means that one should presume that the first cycle within each measurement reflects the most natural behavior of the PCM sample so the data obtained from the first cycle should be taken as the most accurate.

Data processing methodology by taking subcooling into consideration, proved to be valuable since it revealed the importance of the subcooling effects on the process of heat extraction from the PCM upon cooling. Considering the values of all reported deviations for the RT21 it can be concluded that when the degree of subcooling is negligible the heat results from heating and cooling experiments agree to a satisfactory ±10% level of uncertainty. In contrast, considering the values of all reported deviations for the SP22 it can be concluded that when the degree of subcooling is significant the heat results from heating and cooling experiments differ greatly. It seems that the DS value adopted by the manufacturer fits the heating process, but the deviation of the cooling process is significant. This is expressed by 25 % smaller portion of the actual heat that can be extracted from the PCM upon discharging (HR-Usable) in comparison to the heat that can be stored within the material upon charging process. The observed behavior needs to be taken into consideration during the design process of TES systems.

The obtained results for RT21 and SP22 were compared to some reported in literature. Arkar and Medved [19] reported significant variation in the typical phase change temperature for the RT20 (former name of RT21 [18]) depending on the cooling rate used in their DSC tests. In case of 1 °C/min cooling rate (similar to the one in our measurements) the typical phase change temperature reported by Arkar and Medved [19] was 19.7 °C. On the other hand, the same temperature reported by Kravvaritis et al. [11] from their T-history studies was around 21 °C while Hasan [20] reported the temperature of 22 °C. Our typical RT21 phase change range from 20.8 to 21.3 °C agrees very well with the T-history results reported by Kravvaritis et al. [11]. The explanation of the 19.7 °C DSC result reported by Arkar and Medved [19] could be the fact that the sensors in the DSC tests are usually placed on the surface of the test crucibles. Hasan [20] also reported 139 kJ/kg (DSC result) and

143 kJ/kg (T-history result) for the total RT21 heat content evaluated between 15 to 30 °C and it agrees with the results obtained in this study to a satisfactory ±10% level of uncertainty. Finally, the typical SP22 phase change point of 21.6 °C reported by Hasan [20] is found in the middle between the SP22 solidification (19.3 to 19.8 °C) and melting (22.3 to 22.8 °C) intervals presented in this paper. The total SP22 heat content (evaluated between 15 to 30 °C), reported by Hasan [20], of 125 kJ/kg (DSC result) and 135 kJ/kg (T-history result) is significantly lower than the 150 kJ/kg data sheet value provided by the manufacturer. On the other hand, the 135 kJ/kg T-history result is almost in perfect agreement with the 134.3 kJ/kg obtained by averaging the mean HS (156.6 kJ/kg) and mean HR-Usable (112 kJ/kg) data presented in this study.

Finally, the averaging of heat results obtained from heating and cooling is one approach towards the quantification of the subcooling phenomenon in the design of PCM systems. However, the precise characterization of the PCM with a significant degree of subcooling as represented in this paper reveals much more information regarding the PCM properties than the simple averaging. The obtained results showed some important aspects of the T-history PCM investigation and as such may provide more effective design and development process of the thermal energy storage systems based on the phase change materials.

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Figure captions

Fig. 1. T-history experimental setup inside the BINDER KMF 115 environmental chamber.

Fig. 2. T-history cooling curves for the organic RT21 PCM (m=41 g). a) Measured results for the PCM temperature (Real RT21) and the reference temperature (H_2O), b) Idealized results if subcooling effect is neglected for the PCM temperature (Ideal RT21) and the reference temperature (H_2O) and c) Combined zoomed in view of the measured (a) and idealized (b) temperature data.

Fig. 3. Enthalpy-temperature (H(T)) curves for the organic RT21 PCM (m=41 g) for cooling and heating cycles with the normalized enthalpy value of 0 kJ/kg at 15 °C.

Fig. 4. Experimental results for the heat stored/released in the given temperature intervals for the organic RT21 PCM (m=41 g). a) Heat Released (HR) upon sample freezing, b) degree of SubCooling (SC) upon sample freezing, and c) Heat Stored (HS) upon sample melting.

Fig. 5. Experimental results for the heat released/stored of the organic RT21 sample (m=41g) evaluated in the 15 – 30 °C temperature range (DS – heat Data Sheet value, HS – Heat Stored upon heating, HR-w-SC – actual Heat Released upon cooling with the addition of the heat lost upon SubCooling, HR-Ideal – Heat Released in an idealised case when subcooling is neglected, HR-Usable– actual Heat Released without taking the heat lost upon SubCooling into the account).

Fig. 6. T-history cooling curves for the inorganic SP22 PCM (m=73 g). a) Measured results for the PCM temperature (Real SP22) and the reference temperature (H_2O), b) Idealized results if subcooling effect is neglected for the PCM temperature (Ideal SP22) and the reference temperature (H_2O) and c) Combined and zoomed in view of the measured (a) and idealized (b) temperature data.

Fig. 7. Enthalpy-temperature (H(T)) curves for the organic SP22 PCM (m=73 g) for cooling and heating cycles with the normalized enthalpy value of 0 kJ/kg at 15 °C.

Fig. 8. Experimental results for the heat stored/released in the given temperature intervals for the organic SP22 PCM (m=73 g). a) Heat Released (HR) upon sample freezing, b) degree of SubCooling (SC) upon sample freezing, and c) Heat Stored (HS) upon sample melting.

Fig. 9. Experimental results for the heat released/stored of the organic SP22 sample (m=73g) evaluated in the 15 – 30 °C temperature range (HR-w-SC – actual Heat Released upon cooling with the addition of the heat lost upon SubCooling, HR-Usable– actual Heat Released without taking the heat lost upon SubCooling into the account, HS – Heat Stored upon heating, DS – heat Data Sheet value, HR-Ideal – Heat Released in an idealised case when subcooling is neglected).

Highlights

>We implemented the precise T-history control and sensing setup. > Data processing algorithm was adjusted to take the effect of subcooling into account. > T-history measurements of organic and inorganic PCM samples were performed.>High temperature accuracy in PCM measurements was achieved.>Reduction of heat release/storage uncertainties between cooling and heating cycles was achieved.