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Improved measurement technique for the characterisation of phase change materials using the T-history method

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1. Introduction

Recently the interest in Phase Change Materials (PCMs) has grown significantly amongst researchers [1-9]. 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. Nevertheless, accurate knowledge of the thermal properties of PCMs is a prerequisite before design processes and real time deployments of any TES applications.

The T-history method 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 aim to reduce the temperature and the heat storage uncertainty associated with the PCMs measurement [3-9]. Reduction of these uncertainties is important since it should provide better material utilisation. This paper presents an improved measurement technique for the characterisation of PCMs using the T-history method. The main modifications involved in the measurement process are briefly summarized below.

Primarily, 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. [5] was adjusted for the data analysis in order to take the subcooling phenomenon into account. The calculated results on heat capacity were presented as heat density in given temperature intervals, as suggested by Mehling et al. [10]. Moreover, the determination of the total phase change heat in case of both cooling and heating cycles showed that the reduction of relevant temperature and heat storage uncertainties was achieved.

2. Materials and method

The application of the T-history method, as proposed by Zhang et al. [3], 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 [3]. The samples within the tubes are firstly heated to the temperature above the PCM's 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 [3]. As indicated in the introductory section, important contribution of this study is the development of the precise T-history setup. The main experimental setup of this work is summarized below.

A BINDER KMF 115 (BINDER GmbH) environmental chamber was used as the temperature controlled facility. It provides precise thermal control between -10 °C and 100 °C. This temperature range was found acceptable for the investigation of the selected RT21 (RUBITHERM® GmbH) PCM sample, with the typical phase change temperature of 21 °C. According to the manufacturer's specification the heat storage capacity for the investigated PCM, evaluated between 15 °C and 30 °C, is 134 kJ/kg. Distilled water was used as the reference material since its thermal properties, mainly in terms of the specific heat capacity, are well-known. Test tubes for the RT21 and the reference sample were designed and custom built. The length of the tubes was 43 cm with the internal diameter of 1.3 cm and the wall thickness of 1 mm (see figure 1). This way the Biot's number was kept below 0.1 and the lumped capacitance model could be applied [3]. The mass of the PCM sample within the test tube was 41 g.

Continuous temperatures of the samples and the environment temperature were measured using thermistors (Newark MA100GG103A model). In comparison to other conventional temperature sensors, thermistors were selected for this study due to their high sensitivity [11]. 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 [12]. These sensors require the application of the suitable linearisation technique prior to any utilisation. Therefore, an appropriate instrumentation system for thermistor linearisation, signal amplification and filtering had to be developed in order to minimise the temperature uncertainty associated with the measurements. Detailed explanation of the sensor linearisation and calibration procedure is given in [13]. The achieved temperature uncertainty was below 0.3 °C. 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). In total, three thermistors were deployed in this T-history implementation.

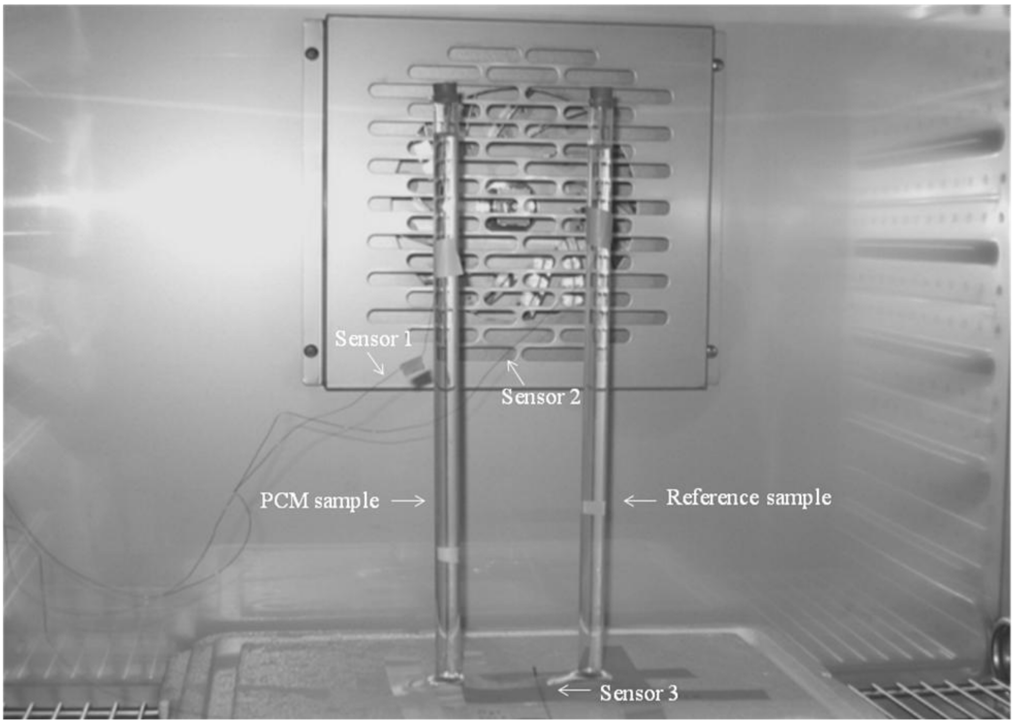

Figure 1. T-history experimental setup inside the BINDER KMF 115 environmental chamber.

Furthermore, both PCM and reference samples were subjected to alternating heating and cooling cycles between 11 °C and 30 °C. At the beginning of every 3 h long cycle the chamber's temperature was sharply changed between those two points. Each measurement included five cooling and five heating cycles. The results from different cycles within the same experimental run were averaged to reduce random errors and improve measurement precision. Five consecutive runs were performed in order to confirm the measurement repeatability. 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. The selection of the sampling rate proved to be important in the T-history implementation. This observation is further explained in the third section on the results and discussion.

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. [5]. This model uses the concept of enthalpy and its relation with temperature. The enthalpy-temperature (*H(T)*) curves were also determined here. 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. Subsequently, the obtained data on enthalpy temperature dependency i.e. the *H(T)* curves were used to determine the heat release/storage density in given temperature intervals. High precision of the obtained T-history data enabled the determination of the degree of subcoling. The calculated degree of subcooling was also presented in given temperature intervals and with high precision. For this, the calculations of the heat capacity in given temperature intervals had to be modified. Namely, the sign of the PCM temperature history cooling curve slope was taken into consideration. Thus, the heat release and the subcooling phenomenon had been able to be distinguished and properly evaluated.

The implemented representation format i.e. heat density in given temperature intervals was chosen because it allows easier comparison between the data acquired by different researchers for the same phase change material [10]. 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 capacity 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 phase change heat between 15 °C and 30 °C, in case of both cooling and heating cycles, was determined for the RT21 case. This was done in order to compare our heat capacity 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. In the cooling case, heat storage capacity was evaluated with and without taking the subcooling effect into account.

3. Results and discussion

Figure 2 shows the heat stored/released for the RT21 in the given temperature intervals upon cooling and heating cycles. RT21 showed a certain degree of subcooling (see figure 2b) which is not reported in the material sheet by the manufacturer. The subcooling was low and lasted shortly under the given measurement conditions. Therefore it could only be observed when the measurements were acquired at a high sampling rate as done in this study. Also, it can be observed that the heat capacity in the case of the cooling cycle shows a relatively sharp peak value at the temperature of 21.1 °C (see figure 2a) 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 capacity is distributed across a wider temperature range (see figure 2c). These results indicate different behaviour of the PCM 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 PCMs. Different behaviour upon freezing/melting affects the TES system design in terms of real time PCM discharging/charging strategies.

Total heat storage capacity for the RT21 between 15 °C and 30 °C for both cooling and heating cycles is shown in figure 3. The results from five different experimental runs are presented (see figure 3) and they indicate good repeatability.

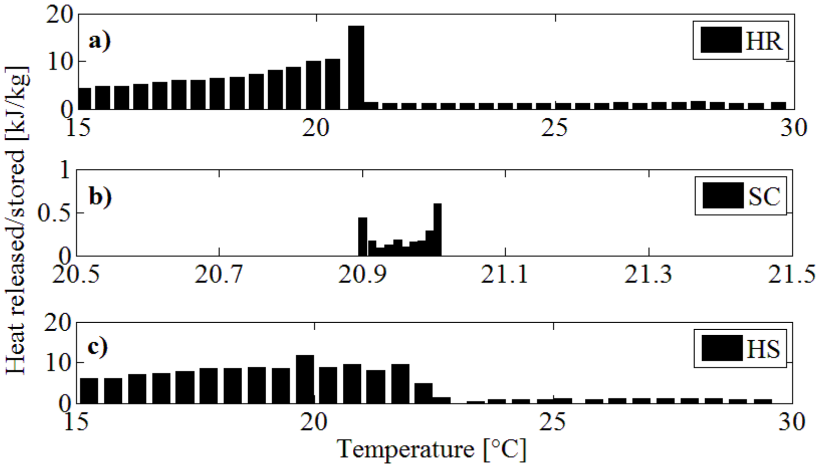

Figure 2. Experimental results for the heat storage in the given temperature intervals for the RT21 PCM (m=41 g). a) Heat Released (HR) upon sample freezing, b) degree of SubCooling (SC) upon sample freezing, and c) Heat Stored (HS) upon sample melting.

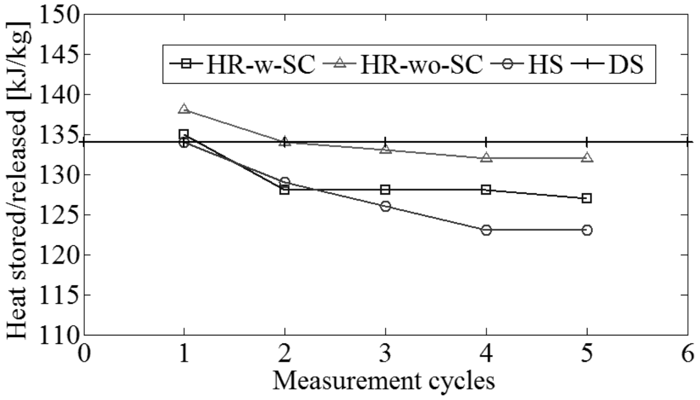

Figure 3. Experimental results for the heat storage of the RT21 sample (m=41g) evaluated in the 15 – 30 °C temperature range (HR SC – Heat Released with taking SubCooling effect into the account, HR no SC – Heat Released without taking SubCooling effect into the account, HS – Heat Stored, DS – heat Data Sheet value).

As previously said, during the PCM cooling cycles, total heat storage capacity is calculated with and without taking the subcooling effect into account (HR-w-SC and HR-wo-SC in figure 3). It can be observed that the heat results upon cooling, obtained without taking the subcooling into the account, showed better agreement with the RT21 data sheet value. However, the heat results upon cooling when taking subcooling into consideration showed better agreement with the heat storage results upon heating.

4. Conclusions

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 characterisation 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. The subcooling effect lasted shortly and could be observed only when the sampling rate was high enough. On the other hand, data processing methodology, taking the subcooling into consideration, proved to be valuable. Namely, this resulted in the reduction of the uncertainty associated with heat storage capacity between the cooling and heating measurements. Finally, the data representation format (heat capacity in given temperature intervals) revealed the differences in the PCM behaviour upon cooling and heating conditions.

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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