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Enthalpy-temperature evaluation of slurry phase change materials with T-history method

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Abstract

PCMs and PCSs are widely used to increase the energy efficiency of several building elements. For example in solar thermal applications, the adoption of PCSs can increase the performance of the energy storages and efficiency of the carrier fluid. For this purpose, an important step is the definition of the enthalpy-temperature curve of the PCS. The T-History is a widely adopted method to investigate the thermal behaviour of traditional PCMs. This paper describes the T-History characterisation method for a PCS based on micro-encapsulated n-eicosane suspended in water. Some suggestions on how to deal with the specificity of PCSs are provided.

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Keywords: phase change material (PCM); phase change slurry (PCS); T-history; material characterisation; energy storage.

1. Introduction

Nowadays, energy conservation and carbon emission reduction have become some of the most important challenges of the modern society. In this framework, the building sector consumes over 40% of the end use energy [1]. Worldwide governors and countries have started policies to encourage the adoption of sustainable solutions. Moreover, many researches have dealt with the investigation of new solutions to reduce energy consumption, use of fossil fuels and CO_2 emissions. These objectives can be reached by using high performance building design solutions, energy management strategies and coupling the buildings with systems based on renewable energy sources (RESs) [2, 3]. One of the most important problems in RES applications is the time delay between availability of

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energy and its consumption. For example, one of the most widely used RES exploiting systems in the building sector are solar collectors [4] and there is a time mismatch between solar energy availability and energy demand [5]. In this perspective, thermal energy storages (TESs) can play an important role, especially when the energy sources are not continuous. The most common way to store thermal energy is by exploiting sensible heat. Desirable characteristics of TES are high energy storage density, near constant operating temperature and good heat transfer performance [6].

Recently introduced innovative technologies to achieve these characteristics are systems based on latent heat thermal energy storage (LHTES). LHTES is a particularly attractive technique because it provides a high energy storage density with a small temperature swing. Many kinds of prototypal LHTESs were proposed in the literature [7]. The most promising ones are those based on phase change materials (PCMs).

The substances used as PCMs can be organic (such as paraffin and fatty acids), or inorganic (such as hydrate salts solutions). They both show a single melting temperature when they are pure and a melting range when they are mixtures. They act like an almost isothermal reservoir of heat due to the large amount of heat they absorb or release during their phase transition [8]. PCMs can be very useful in applications where the temperature control is important. PCMs can also be used to enhance the thermal inertia of buildings in order to improve their energy performance. For example, they can be embedded in construction materials [9] or they can be used in glazing [10]. Due to the high thermal inertia of PCMs, they are especially useful for application in energy storage tanks. Many examples of these solutions are available in literature [11]. Nevertheless, some drawbacks of this materials – such as low thermal conductivity, instability under extended cycles, phase segregation and subcooling – have limited a wide diffusion of the application of PCMs in storages [12]. To avoid some of these drawbacks, a possible solution is to mix a carrier fluid, such as water, and a PCM. The resulting two-phase fluid is called Phase Change Slurry (PCS). The main advantage of these fluids is to conserve the high thermal inertia of PCMs, combining it with higher thermal conductivity. Phase segregation and subcooling are also reduced. The following types of PCSs were highlighted in literature [13]: ice slurries (ice particles dispersed in water); emulsion slurries (homogenous mixture of PCM and carrier fluid); microencapsulated PCM slurries (microencapsulated PCMs and carrier fluid); shape-stabilised PCM slurries (fluid based on shape-stabilised PCM particles). The advantages of using microencapsulated PCM slurries (mPCSs) in different thermal applications were clear since the late ‘90s. The microencapsulation prevents the leakage of the PCM in the liquid carrier and the slurry can be easily pumped, reducing clogging risk and pressure drops. Moreover, mPCS have a higher surface to volume ratio than PCMs, which maximises the heat exchanged. In addition, they are always liquid and so they can be used as heat transfer fluids.

For these reasons, many examples of PCSs used in heat storage tanks can be found in literature [13]. Some of these tanks are specifically designed for RES, such as TES in residential solar energy systems [14]. To solve some drawbacks occurring with this technology, many solutions were proposed. Some authors improved the geometry of the storage tank and that of the heat exchanger, others introduced surfactants to further increase the effective thermal conductivity of the material [15]. According to the application, the most suitable PCS should be chosen. Firstly, the proper phase change temperature range has to be considered to match the thermal energy end uses. Moreover, the thermo-physical properties of the PCS should be known in order to quantitatively evaluate the possible performance improvements that can be achieved. For this reason, the characterisation of PCSs is necessary. An important step in this procedure is the definition of their enthalpy-temperature curve. Among the various methods to carry out this measurement, the Time History (T-History) method is widely adopted to investigate the thermal behaviour of traditional PCMs [16]. However, a peculiarity of PCSs is that their thermo-physical properties are not only a function of the PCM but also of its concentration. For this reason, different T-History experiments are necessary at various mass concentrations. Only few works on T-History for PCS are available in literature.

In the present work, the T-History is used to determine the enthalpy-temperature curve of a mPCS at two different mPCM concentrations. The chosen material is a mixture of water and micro-encapsulated n-eicosane, whose nominal melting temperature is 37 °C. Serale et al. [17] demonstrated that n-eicosane is especially suitable for storing energy in solar thermal heating applications. The experimental results of T-History experiments were compared to the theoretical data in order to evaluate their reliability and accuracy. Some considerations on the creaming phenomenon that appeared in the material are also discussed.

2. Material and methods

2.1. Thermal analysis methods

Thermal analysis methods are necessary to obtain the thermo-physical properties of PCMs. The most used thermal analysis methods for PCMs are: Differential Scanning Calorimetry (DSC) [19], Differential Thermal Analysis (DTA), Time History method (T-History) and Thermo Gravimetric Analyser (TGA) [18]. The last one is seldom used. DSC and DTA are similar methods, even though DTA is mostly used for qualitative measurements. To investigate the enthalpy-temperature curves, the most appropriate techniques are DSC and T-History. Both experiments require careful preparation and data post-processing. The sample has to be representative of the material under investigation and the specific boundary conditions of the experiment should be taken into account when the monitored data are post-processed. Cabeza et al. [18] developed general guidelines for referring the experiments of PCM characterisation to standard conditions.

2.2. Time history method

In this paper, the T-History method was chosen for the simplicity of the requested experimental setup. This is especially useful when the thermal properties are not completely provided by the manufacturer and the customer company do not hold the necessary instrumentation for carrying out complex thermal analyses. T-History represents an optimum compromise between the data reliability and the lower cost of the experimental set up compared to other methods. Moreover, T-History allows to analyse samples with a wider volume than other methods. This is an advantage for PCSs because the representative volume of the sample should be wide enough to guarantee the correct mixing of the two substances. Many examples can be found in literature where this method was adopted to characterise PCMs and PCSs [16].

The T-History was proposed by Zhang and Jiang [20] in 1999 as an alternative method to DSC or DTA and several contributions were subsequently published to improve it [16]. T-History requires at least two tubes. At least one tube is filled with the material under investigation and one is filled with a reference material. The reference material should be a substance with well-known thermal properties, such as distilled water. The characteristics of the tubes should guarantee a sufficiently small Biot number. The tubes are preheated above the PCM melting temperature ($T_o > T_m$) and then they are cooled by exposing them to air at ambient temperature. Duringthe cooling process, the curves of temperature versus time are recorded. Thermal properties can be determined by comparing these curves for the PCM and the reference material. In this paper, the T-History method improved by Marìn et al. [21] was used to determine the enthalpy-temperature curve of the samples.

2.3. Materials

The material under investigation was a PCS obtained by a mixture of water and micro-encapsulated n-eicosane. 20% and 50% of mPCM mass concentrations were analysed. Some mPCM characteristics were provided by the manufacturer or found in the scientific literature. The microcapsule size is about 17-21 µm, the nominal melting temperature in heating is 37 °C and the melting latent heat is 190-200 kJ/kg. Thermal conductivity and density of n-eicosane respectively are 0.230 W/(m K) and 856 kg/m^3 when in solid state, or 0.151 W/(m K) and 780 kg/m^3 when in liquid state. The experimental setup consisted of:

- Distilled water, used as reference material (specific heat of 4186 J/(kg K));
- Scale for sample weighting (sensibility of 0.01 g);
- 5 low-density polyethylene tubes with 15 mm diameter (a specific heat of 2300 J/(kg K) was considered);
- 7 T-type thermocouples, previously calibrated using a Pt-100 as a reference;
- DT85 datalogger with support for multiple SDI-12 sensor networks and 12V regulated output to power sensors;
- Haake F3 thermostatic bath for sample heating (temperature accuracy of 0.02 °C, operative range of -20/150 °C);
- Insulated thermostatic chamber for sample cooling (1°C internal temperature control accuracy);
- Ventilated oven and a webcam as auxiliary devices.

3. Description of the experiment

PCS thermo-physical properties are strictly related to the mass concentration of the PCM. For this reason, two weight concentrations were chosen. A comparison was carried out for 20 wt. % and 50 wt. %. The PCS was obtained by accurately mixing distilled water and microcapsulated n-eicosane. The concentration was verified during sample preparation and after the experiment. First, the samples were prepared by weighting the amount of materials on the scale. Afterwards, a gravimetric test was performed drying the samples in oven until constant weight [22]. For each concentration, four tubes were filled with the PCS sample and a fifth tube was filled with distilled water. The thermocouples were stably fixed in the middle of each tube.

After sample preparation, all the tubes were placed in the thermostatic bath. Two additional thermocouples further monitored its temperature. The bath temperature was set at 60 °C, which is a higher temperature than the nominal melting temperature of the PCS. When the thermodynamic equilibrium was reached, the tubes were moved into the thermostatic chamber. The temperature of the thermostatic chamber was set at a constant value of 18 °C to cool the samples below their melting temperature. The thermocouples previously used for measuring the water temperature in the thermostatic bath were used to measure the air temperature within the chamber. The data were recorded by the datalogger every 5 seconds. The preliminary temperature versus time curves were obtained in this phase. A webcam programmed with Matlab snapped a picture every 15 minutes to monitor how the experiment was progressing.

4. Results and discussion

The samples were labelled according to their theoretical mass concentration from preparation on the scale. However, the concentrations resulting from the gravimetric tests slightly differ. Table 1 reports these values.

Table 1. Sample weight concentration resulting from gravimetric tests.

Sample label	Mass concentration	Standard deviation
PCS 20 wt. % mPCM concentration	20 wt. %	± 0,7 %
PCS 50 wt. % mPCM concentration	49 wt. %	± 0,9 %

To evaluate the influence of mPCM concentration on the PCS enthalpy, tests were carried out for 20 wt. % and 50 wt. %. Fig. 1(a) reports the time vs temperature curves obtained for the four 20 wt. % samples, whereas Fig. 1(b) reports the results obtained for the 50 wt. % samples. It can be observed that the temperatures within the four samples were comparable for both experiments.

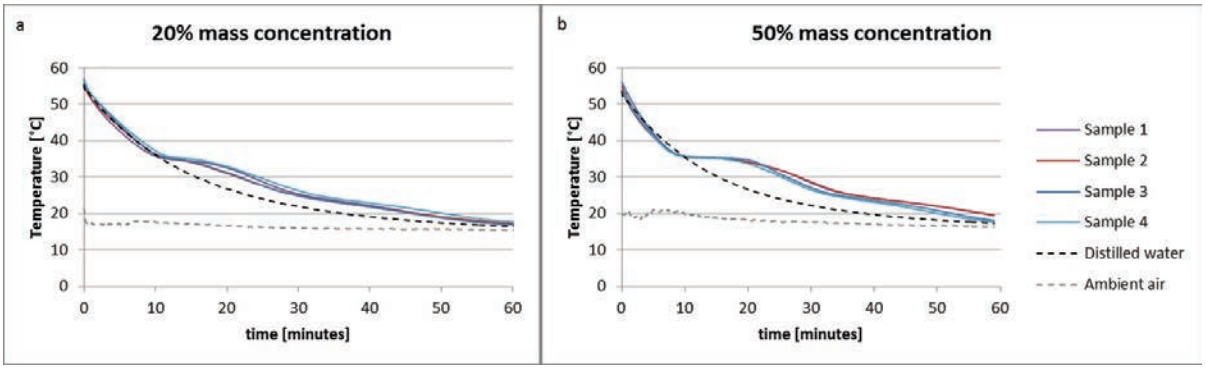

Fig. 1. Time vs temperature curves: (a) 20% mPCS mass concentration; (b) 50% mPCS mass concentration.

One of the possible drawbacks related to the adoption of PCSs is the creaming phenomenon [23], which is caused by the density differences between the suspended mPCM and water. The creaming is the movement of the suspended particles towards the superior part of the suspension as a result of gravity. After a period of time depending on the material, the two phases of the PCS are likely to show separation. In the case of n-eicosane, a layer of more concentrated mPCM appeared in the upper part of the mixture. This variation of concentration gradient during time could strongly affects the thermo-physical properties of the PCS and, as well, the T-History experiment. For this reason, PCM sedimentation was monitored during the experiments through a webcam. No visible separation between water and mPCM occurred within the duration of the tests (about one hour). Preliminary results showed that creaming became visible after three hours. The higher the concentration the slower the creaming appearance.

Fig. 2 shows the average enthalpy vs temperature curves that resulted from the elaboration of the measured data. As it was expected, the latent heat with 50 wt. % was significantly higher than with 20 wt. %. To determine the reliability of the test results, the measured values were compared with the theoretical ones, which were obtained by applying the equations described in [24, 25] with the microencapsulated n-eicosane thermal properties found in the literature. From the experimental tests, in the same temperature range, enthalpy values of 113,5 kJ/kg and 182,0 kJ/kg were respectively obtained for the 20 wt. % and 50 wt. % samples. These results are in accordance with the theoretical values since the discrepancy between them lies within the uncertainty typically estimated for T-History experiments [20]. However, a small difference was observed between the measured solidification range (35 °C) and the nominal melting temperature (37 °C). This is probably due to hysteresis of the material, since the melting temperature was provided by the manufacturer whereas the T-history measured the solidification temperature. There are two peaks on the enthalpy vs temperature curves; the bigger one can be attributed to liquid-rotator and liquid-crystal transitions, while the smallest one can be due to rotator-crystal transition [26, 27].

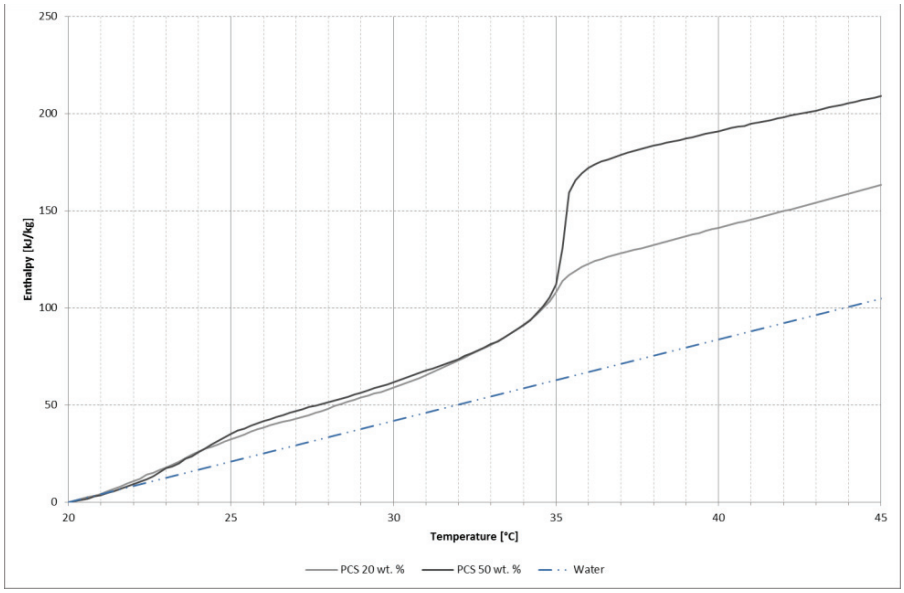

Fig. 2. Enthalpy vs temperature curves.

5. Conclusions

In this paper, a method to determine the thermo-physical properties of a PCS was discussed. T-History experiments on a PCS based on a mixture of water and microencapsulated n-eicosane were carried out to determine its enthalpy versus temperature curves. The obtained results were comparable with the expected theoretical values. Moreover, this paper highlights that T-History tests on samples at different concentrations should be performed for full characterization of PCSs. For this reason, 20 wt. % and 50 wt. % sample were investigated. A monitoring of the

creaming phenomenon was also necessary.

Future work will investigate more concentrations in order to describe the correlation between concentration and enthalpy-temperature curves of a PCS. Furthermore, an uncertainty analysis and a sensitivity analysis will be carried out. Additional studies on the creaming are also required and a procedure that allows to correct the T-History results considering this phenomenon would be necessary.

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