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Investigating PCM activation using transient plane source method

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Abstract

Heat storage solutions with phase change materials (PCM) as main heat storage material have larger storage capacity and more even storage temperature than traditional water-based systems at the same conditions. The efficiency of the PCM storage depends primarily on its ability to receive and deliver heat in a phase transition mode. To plan and verify a PCM storage, methods are needed to determine if the PCM is in phase transition under different thermal loading. This study investigates differential scanning calorimetry (DSC), which is a common method for the characterization of PCM, and the transient plane source (TPS) method for capturing the phase transition. For the latter, a small water tank is studied in laboratory to provide alternate thermal loading to the encapsulated PCM. The TPS method has shown to be appropriate to differentiate between solid and liquid PCM. However, there exist several limitations in the method that has to be solved before the PCM can be used to visualize the phase transition of PCMs.

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Keywords: phase change material; phase transition; TES; DSC; TPS

1. Introduction

The energy use for heating buildings accounts for 40% of the total energy use in developed countries. This leads to a large contribution to the greenhouse gas emissions in society [1]. Therefore, policies aiming to decrease the energy use for heating has been implemented in many parts of the world. Different examples of how to reduce the energy use for heating are to retrofit old buildings by e.g. changing windows and heating system. Another way to reduce the greenhouse gas emissions is to utilize renewable energy sources, such as solar thermal energy, waste heat recovery and free cooling by outdoor air more efficiently. The use of these energy sources is limited because they cannot provide

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a constant energy supply. There is also a variation of the heating power demand in buildings over the year and between the hours of the day. This creates a mismatch between the peak heating and cooling power demand of buildings and the availability of renewable energy sources. However, thermal energy from any energy source can be stored for later use in a thermal energy storage (TES). The development of efficient TES concepts can substantially contribute to reducing the demand for supplying energy and heating power in buildings. Today, the storage of excess thermal energy for heating and cooling of buildings, and for production of hot tap water, is usually done in water tanks. These tanks need a large volume to be efficient for utilizing renewable energy sources. Heat storage solutions with phase change materials (PCM) as main heat storage material, have larger storage capacity and more even storage temperature than traditional water-based systems at the same conditions. Despite these benefits of PCM based TES systems, the technology has not yet penetrated the market. Lack of design tools and guidelines for PCM based TES is identified as one of the reasons for preventing a greater use of this type of TES solutions. Such tools should reveal for designers how much heat can be stored and extracted from a PCM storage in time, and under given circumstances. This in turn requires reliable measurement techniques which would make it possible to evaluate that the PCM undergoes phase transition. Given that PCM melt over a range of temperatures (5-15°C) and that some types, like salt solutions, exhibit substantial sub cooling during crystallization (i.e. that a temperature significantly below the melting temperature has to be reached before a material begins to crystallize and release heat), temperature measurements alone are not reliable for evaluating the phase transition.

The aim of this study is to investigate and visualize when the PCM undergoes phase transition, and if possible, identify the transition temperatures. Two methods for measuring the heat transfer during melting and crystallization of PCM under different thermal loading are investigated. This will in the end lead to design specifications for how much energy that can be stored in a PCM based TES. The possibility to measure the thermal loading degree of the PCM makes it possible to monitor the efficiency of the TES to optimize its performance. Measurements using differential scanning calorimetry (DSC) reveal the activation temperatures and the change in enthalpy of the PCM. Based on the onset temperatures for solid-to-liquid or liquid-to-solid transitions, numerical simulations can be used to evaluate theoretically possible dynamics and effectiveness of heat loading and unloading in an encapsulated PCM. In this study, a small water tank is monitored in the laboratory to provide alternate thermal loading and unloading to the encapsulated PCM. The transient plane heat source (TPS) method is used together with thermocouples for performing comparative measurements and for visualizing the activation of the PCM.

2. Characterization of PCM

There are several different materials that can be utilized as PCMs. Depending on the range of the transition temperatures some are more feasible than others. The relevant PCMs for use in buildings are paraffin, fatty acids, salt hydrates and their eutectic mixtures [2]. The most important properties of the PCMs are the thermal conductivity (λ, W/(m·K)), the density (ρ, kg/m^3) and the specific heat capacity (c, J/(kg·K)). The product of the density and the specific heat capacity is normally referred to as the volumetric heat capacity. The ratio between the thermal conductivity and the volumetric heat capacity is the thermal diffusivity (a, m^2/s). An important relationship for determining the efficiency of a PCM is the thermal inertia or thermal effusivity. This is calculated by

$$e = \sqrt{\lambda \cdot \rho \cdot c} \tag{1}$$

where e (J/(m^2·K·s$^{1/2}$)) is the thermal effusivity which is a measure of the ability of a material to exchange thermal energy with the surroundings [3]. Salt hydrates generally have larger thermal effusivity than paraffin waxes mainly due to larger volumetric heat capacity. In other words, salt hydrates show faster response to varying heat loads and has a larger storage capacity per unit volume. Therefore, two different salt mixtures have been selected to be investigated in this study. The mixtures contain either sodium sulphate or sodium acetate which are mixed with water and different additives. The declared thermal properties for the mixtures are presented in Table 1.

Table 1. Declared thermal properties for the PCM mixtures ClimSel C24 and ClimSel C58 [4].

Name	Salt hydrate	Melting temperature (*°C*)	Latent heat (*kJ/kg*)	Density (*kg/m³*)	Thermal conductivity (*W/(m·K)*)	Storage capacity	
						Enthalpy change (*kJ/kg*)	Temperature range (*°C*)
ClimSel C24	Sodium sulphate	24	151.3	1380	0.5-0.7	195.7	15-30
ClimSel C58	Sodium acetate	58	288.5	1460	0.5-0.7	340.3	50-65

3. Laboratory measurements

There exists several methods to determine the thermal characteristics of PCMs. The most common one is the differential scanning calorimetry (DSC) but also the T-history method and guarded hot-plate method can be used [5]. Sasic Kalagasidis et al. [6] proposed the transient plane source (TPS) method as an alternative to the DSC for visualizing the PCM activation. They found that the TPS method provided temperature response curves of high resolution, but that issues with the bulk density of the specimen and the size of the sensor in relation to the granules of the solid PCM have to be resolved. In this study the DSC has been used to characterize the PCM and the TPS method has been used for comparative measurements and for visualizing the PCM activation in a pilot site setup of a PCM based TES.

3.1. DSC: Differential scanning calorimetry

The DSC is used to characterize a material by measuring its heat exchange with the surrounding. By using a special sensor of 120 thermocouples, the temperature of the specimen can be determined with an accuracy of ±0.2°C and a precision of ±0.02°C. The heating and cooling rate of the sample is 0.02-300°C/min and 0.02-50°C/min respectively [7]. By slowly raising and lowering the temperature, the heat flow to and from the sample can be determined with high accuracy. The slower the temperature is changed, the higher the accuracy of the measurement will be. In the DSC measurements presented here a 100 µl alumina crucible was filled with a sample of the PCM. The weight of the sample then determines the specific heat capacity of the PCM. The temperature scanning curve gives detailed information on the onset and endset temperatures for solid-liquid and liquid-solid phase transitions, see Fig. 1.

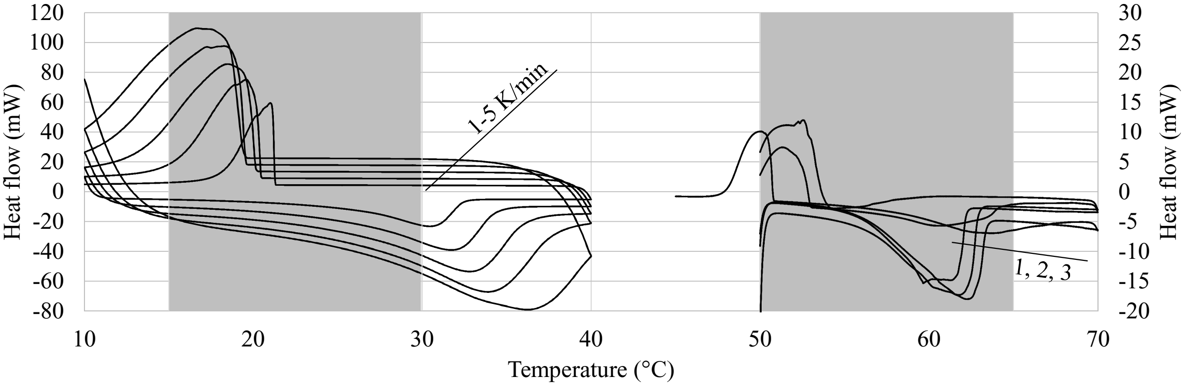

Fig. 1. DSC measurement results for a sample of ClimSel C24 (left) depending on the rate of heating and cooling and three samples of ClimSel C58 (right). The gray square marks the storage temperature range according to the product declarations [4].

The ClimSel C24 was conditioned in a heating cabinet at 35°C for 24 hours before removed from its delivery pouch. At this temperature the substance was liquid and three samples were placed in the crucibles. The method chosen for the measurement was a scanning between 10-40-10°C with a heating and cooling rate of 0.3°C/min. It was more difficult to get liquid samples of the ClimSel C58 with a good mixture because of the higher transition temperature which made the sample crystallize quickly when moved from the pouch. The specimen were conditioned in a heating cabinet at 65°C for 24 hours. The DSC measurements were performed by scanning 50-70-45°C with a heating and cooling rate of 0.3°C/min. The results are presented in Table 2.

Table 2. Results from DSC measurements of the ClimSel C24 and ClimSel C58.

Name	Sample number	Sample weight (*mg*)	Melting onset temperature (*°C*)	Melting endset temperature (*°C*)	Latent heat of fusion (*kJ/kg*)	Crystallization onset temperature (*°C*)	Crystallization endset temperature (*°C*)	Latent heat of crystallization (*kJ/kg*)
ClimSel C24	1	132.2	26.8	30.4	17.4	22.2	20.5	37.1
ClimSel C24	2	108.0	25.5	31.8	63.9	22.4	20.0	58.3
ClimSel C24	3	141.9	25.7	34.1	50.4	20.9	15.7	53.8
Average	-		26.0	32.1	43.9	21.8	18.7	49.7
ClimSel C58	1	60.9	58.1	62.1	180.0	52.9	50.1	48.9
ClimSel C58	2	79.9	58.5	62.8	169.2	53.6	50.9	67.9
ClimSel C58	3	80.0	57.3	63.2	159.6	50.8	48.1	57.6
Average	-		58.0	62.7	169.6	52.4	49.7	58.1

It is evident that it is difficult to sample the PCM with a good mixture of the content in the pouches. However, it is clear that there is a major sub cooling effect for both ClimSel C24 and ClimSel C58. The average difference between the melting and crystallization temperature are 8.8°C and 9.3°C for ClimSel C24 and ClimSel C58 respectively. In applications where PCMs are used, it is important to assure that these temperatures can be reached to utilize their full potential.

3.2. TPS: Transient plane source method

The thermal conductivity and volumetric heat capacity can be determined by using the transient plane source (TPS) method. The general and specific procedures of the method for measurements of thermal properties are described in SS-EN ISO 22007-2 [8]. A sensor composed of a 10 µm thick double nickel spiral, sandwiched between two layers of 25 µm thick kapton (polyimide film) is clamped between two samples. A constant electric power is supplied through the spiral while the temperature increase is registered. The relationship between the supplied energy and temperature increase makes it possible to calculate the thermal conductivity and volumetric heat capacity of the material.

Sasic Kalagasidis et al. [6] used the TPS method (6.4 mm sensor, 100 mW, 20 seconds) on two different PCMs by two approaches. The first approach was to measure the properties directly on the surface of the transport pouch. This proved to work less well due to the large heat dissipation in the metallic pouch. The second approach was to move the PCM from the pouch to a sample holder and place the sensor in direct contact with the PCM. Although the temperature response curves were distinctly separated from each other, the difference between the fully melted and crystallized samples was not as large as expected. It could not be clearly determined to what extent the samples were crystallized inside the sample holder. Therefore a third approach is tested in this study. The idea is to measure a larger sample of the PCM by filling a plastic bag with the material where the sensor is inserted in the middle of the bag which is then sealed. By this approach it should be possible to better control the phase transition of the PCM. The sensor is a 9.9 mm radius sensor where 100 mW is supplied during 80 seconds. The reliability of the measurements is evaluated by using the coefficient of variation (CV), i.e. the standard deviation divided by the average measurement result. The PCM ClimSel C24 was conditioned either in a refrigerator at 5°C or in heating cabinet of 31°C before the measurements. The results are presented in Table 3 and compared to Sasic Kalagasidis et al. [6].

Table 3. Thermal properties of ClimSel C24 determined by the TPS method compared to [6].

Name	Number of runs	Measurement temperature (*°C*)	Thermal conductivity (*W/(m·K)*)		Thermal diffusivity $\cdot 10^6$ (*m^2/s*)		Volumetric heat capacity (*$kJ/(m^3 \cdot K)$*)	
Solid	6	5-22	1.27	80.3%	0.29	129%	34.1	98.5%
Solid [6]	4	20	0.96	2.01%	0.30	1.15%	3.18	5.64%
Solid [6]	4	21	1.10	1.60%	0.44	1.12%	2.52	2.91%
Solid [6]	4	22	1.08	1.76%	0.36	1.27%	2.96	5.64%
Liquid	6	22-30	0.49	68.0%	4.23	205%	31.7	161%
Liquid [6]	4	25	1.32	0.53%	0.43	0.78%	3.05	5.39%

From the measurements performed in this study, it is possible to differentiate the PCM in solid and liquid phase based on the thermal conductivity and volumetric heat capacity. However, the temperature in the samples was difficult to maintain at a constant level which is shown by the large span in the measurement temperature for the solid (5°C-22°C) and liquid (22°C-30°C) samples in Table 3. Therefore there is a very large CV for all the measurements. The difference between the highest and lowest temperature increase imposed by the TPS sensor during the measurements differed with 0.09°C for the solid and with 2°C for the liquid PCM. A better control of the ambient conditions is needed to keep the samples at constant temperature for evaluating the properties with higher accuracy. The difference between these measurement results and the results in [6] could be based on the fact that the solid samples in that study were in form of granules stacked in the testing cup, while in this work it was a uniformly crystallized block. As shown in Fig. 1, the phase at a certain temperature depends on whether the sample is being heated or cooled.

3.3. Pilot site setup and measurement results

To evaluate the applicability of the TPS method in real PCM based TES applications a pilot site was setup in the laboratory. A metal container was filled with water and a plastic rod containing the PCM ClimSel C58. A metal flange in the rod distributes the temperature inside the rod. The temperature in the TES was changed by using a 1.4 kW electrical coil heater submerged in the water. The heater gives a potential temperature rise of the TES from 30°C to 70°C in 30 minutes. In the first testing sequence the TES was tested without heating by TPS in a 22°C constant temperature room. The thermal properties of the PCM filled rods in ambient conditions (not in the TES) was determined by single-sided TPS method where EPS was placed on the backside of the sensor. The thermal properties of the empty rod and ClimSel C58 with the corresponding CV are presented in Table 4.

Table 4. Thermal properties of ClimSel C58 in a plastic rod determined by single-sided TPS method with EPS on the backside. Empty rod and rod filled with PCM where the sensor was placed on pure plastic or close to the metal flange.

Name	Number of runs	Measurement temperature (*°C*)	Thermal conductivity (*W/(m·K)*)		Thermal diffusivity $\cdot 10^6$ (*m^2/s*)		Volumetric heat capacity (*$kJ/(m^3 \cdot K)$*)	
Empty rod[1]	4	22	0.21	5.53%	0.14	12.3%	1.52	7.79%
C58 plastic[2]	10	22	0.29	0.21%	0.44	4.10%	0.66	3.64%
C58 metal[2]	10	22	0.28	0.33%	0.50	1.99%	0.56	1.80%
C58 solid[3]	10	22	0.15	0.33%	1.56	1.23%	0.10	1.35%
C58 liquid[3]	4	22	0.15	15.0%	0.66	26.1%	0.23	17.1%

[1] 6.4 mm sensor, 20 mW, 20 seconds, [2] 6.4 mm sensor, 40 mW, 20 seconds, [3] 9.9 mm sensor, 40 mW, 20 seconds

The different test setups with the single-sided TPS measurements show the difficulties to get results of the thermal properties of the PCM with good precision. The influence by the metal flange on the TPS measurement is small as the results are close for the two cases where the sensor was placed on pure plastic or close to the metal flange. The difference between solid and liquid is clear where the thermal diffusivity is 2.4 times higher for the liquid PCM.

The test of using the TPS method inside the TES showed that the temperature increase in the sensor was stable between the measurement runs. However, the close contact between the sensor and the surface of the rod with PCM could not be maintained for a longer period of time. This meant that the temperature increase varied for setups with the same settings. The size of the sensor influenced positively as a 6.4 mm sensor had 14.4% CV while a 9.9 mm sensor had 4.8% CV. The average temperature increase in the sensor was 0.72°C for the smaller sensor and 0.3°C for the larger sensor after 40 mW had been supplied for 20 seconds. The influence by the water in the TES has to be studied more in the next steps of this project since the water has been considered as a solid uniform entity in this paper.

4. Conclusions

There is a lack of design tools for designers to calculate how much heat can be stored and extracted from a PCM based TES in time, and under given circumstances. Temperature measurements alone are not reliable for measuring the phase transition. Therefore, other techniques have to be used for characterizing the loading and unloading of the PCM based TES. There exist several methods to determine the thermal characteristics of PCMs. In this study the DSC and TPS methods were tested on two different PCMs in different settings. It was found that both PCMs had major sub cooling, i.e. the melting and crystallization temperature differed, when using the DSC. In practical applications it is not possible to use the DSC for measuring the activation of the PCM. The TPS method has proved to be appropriate to differentiate between solid and liquid PCM. However, there exist several limitations in the method that has to be solved before the PCM can be used to visualize the transition temperatures in PCMs. The TPS sensor supplies heat and therefore it is vulnerable to changes in the surrounding temperature. A better controlled temperature of the pilot TES will make it possible to calibrate the TPS method. The contact between the sensor and PCM in the TES also has to be secured better in future experiments. To that the influence by the moving water in the TES will be a major challenge for accurately and precisely evaluating the TPS measurements.

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