Determining the Heat of Fusion and Specific Heat of Microencapsulated Phase Change Material Slurry by Thermal Delay Method

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Abstract: This paper details an experimental study that was performed to investigate the specific heat of microencapsulated phase change material (mPCM) slurry and its heat of fusion at the PCM phase change transition temperature. Six samples (mPCM slurry concentrate with the water solution of propylene glycol used as a main base liquid) were prepared. As the concentrate contains 43.0% mPCM, the actual mass fraction amounts to 8.6, 12.9, 17.2, 21.5, 25.8, and 30.1 wt%, respectively. The thermal delay method was used. Samples were cooled from 50 °C to 10 °C. A higher concentration of microcapsules caused a proportional increase in the specific heat of slurry at the main peak melting temperature. The maximum value of the specific heat changed from 9.2 to 33.7 kJ/kg for 8.6 wt%, and 30.1 wt%, respectively. The specific heat of the mPCM slurry is a constant quantity and depends on the concentration of the microcapsules. The specific heat of the slurry (PCM inside microcapsules in a liquid form) decreased from 4.0 to 3.8 kJ/(kgK) for 8.6 wt%, and 30.1 wt% of mPCM, respectively. The specific heat of the slurry (PCM inside microcapsules in a liquid form) was higher than when the PCM in the microcapsules is in the form of a solid and increased from 4.5 to 5.2 kJ/(kgK) for 8.6 wt% and 30.1 wt% of mPCM, respectively.

Keywords: PCM; microencapsulation; thermal delay method; specific heat

1. Introduction

The Thermal energy storage (TES) is one of the most promising technologies for the efficient use of heat from renewable sources [1,2]. The profitability of TES is due to the fact that it enables the supply of energy during peak hours and its storage when there is a delay between supply and demand. There are physical or chemical methods for storing thermal energy. The most common way to store thermal energy is to use physical processes that rely on sensible (SHS) or latent heat storage (LHS). They differ by the presence of a phase change phenomenon. The use of phase change material (PCM) as a working medium in the LHS method allows (in contrast to the SHS method) to achieve a higher storage capacity of energy per unit of mass and a small temperature change. It is expected that the thermally ideal PCM material will have a high thermal capacity and a constant range of phase change temperature. Organic materials (paraffine, fatty acid, ester, glycol, alcohol, ...), inorganic (salt hydrate, nitrate salt, a carbonate salt, chloride salt, sulphate salt, ...) and their mixtures (eutectic mixtures) are being researched [3–6]. The current state of knowledge is that the main limitation of PCM is its low thermal conductivity, which affects the heat exchange inside the tank [7]. In addition, solid-phase PCM materials can't be easily transported inside the system. The solution is the combination of single-phase fluid as a continuous phase and phase change materials (PCM) particles as a dispersion. The resulting slurry has been included in the group of latent functional thermal fluid (LFTF) [8].

1.1. Microencapsulated PCM Slurry as a Latent Functional Thermal Fluid

Latent functional thermal fluid can be divided into five categories: (1) Ice slurry, which is a mixture of fine ice crystals, water and additives that lower the freezing point of the solution and reduce the size of the crystals; (2) an emulsion in which PCM is dispersed directly in the base liquid; (3) a PCM slurry in which the PCM encapsulated in the capsule is dispersed in the base liquid; (4) clathrate hydrate slurry, where the water molecules form the lattice structures and the molecules of the other substance fill the lattices; (5) shape stabilized slurry, where PCM is infiltrated in high-density polyethylene and is dispersed in water to form slurry [9].

Encapsulation is the most commonly proposed type of PCM slurry among the five discussed above [9]. In the 1940s the technology of PCM microencapsulation has been developed in the National Cash Register Company [10], which made it possible to obtain micro- or even nanometer-sized capsules [11–14]. A slurry of microencapsulated PCM (mPCM) using both latent heat (PCM) and sensible heat (base liquid) is appropriate for energy storing, as well as energy transferring medium. Unlike pure base liquids or nanofluids, this type of slurry is suitable also for low-temperature changes. As above, these type of fluids, can be used in ventilation, air conditioning and refrigeration [7,15–18]; as a heat/cold storage for stabilization of thermal conditions in buildings in the 24-h cycle [12,19]; reducing the temperature of PV panels [20–22]; heating [23–27] or in engines cooling [28].

Many studies indicate that microencapsulated PCM forms long-term stable slurries easily. Numerous studies are carried out to identify the flow and heat exchange characteristics of mPCM slurries before they are used on an industrial scale [29]. These include experimental studies to determine the specific heat and heat of fusion of mPCM slurry.

1.2. Specific Heat and Heat of Fusion of mPCM Slurry—A Previous Study

Differential scanning calorimetry (DSC), differential thermal analysis (DTA), and the conventional calorimetry method are used to determine the specific heat and heat of fusion of different materials. The devices used in the DSC and DTA methods have limitations in their application to the testing of substances of different composition [30]. As it results from [2,31], the T-history method proposed by Yinping and Yi [32] is an alternative to the above-mentioned methods, allowing to obtain research results with similar accuracy. Additionally, it has other advantages, the most important of which is the ability to perform measurements simultaneously with a larger number of samples. Kravvaritis et al. [33] presented an improved version of the T-history method (the so-called "thermal delay method"). The main improvement concerns the method of processing measurements, allowing for acceleration and automation of the processing of test results.

The fact that an increase in the mass fraction of PCM in an emulsion/suspension causes an increase in its phase transition heat is not in doubt [7,34], while the influence of the mass fraction of PCM on the specific heat of the slurry when PCM is in the liquid state and when PCM is a solid is not fully recognized. This is due to the small number of publications by which this topic was discussed.

Wang et al. [35] determined the thermophysical properties of paraffin/water emulsions with and without the addition of graphite nanoparticles. It was shown that the apparent specific heat of the emulsion (relative to the base liquid-water) increased when PCM was in solid-state and decreased when PCM was liquid. Fisher et al. [36] who studied physical and rheological properties of phase change dispersion composed of water and the paraffin RT25HC (mass fraction 5–40%) obtained similar results, or Wang et al. [37] who used a microencapsulated (n-hexadecane) slurry with a mass of 10–30 wt%. and a propanol-water mixture as the base fluid.

The results of subsequent studies are in contradiction with the above-mentioned results. Morimoto et al. [38] examined the phase change emulsion made of an aqueous solution and fine particles of n-hexadecane and n-octadecane as a phase change material. The research results show that the increase in the mass fraction of PCM causes a decrease

in the specific heat of the emulsion, both when PCM is in the form of liquid and solid. Similar results are presented in the work of Wang et al. [39]. The authors determined the specific heat of the emulsions based on polyalcohol (PVA) and polyethylene glycol-600 (PEG-600). The research was carried out in terms of mass fraction of paraffin to glycol: 10, 15, 20, 25, 30% by weight. The decrease in the specific heat of the suspension when PCM is in the form of a solid and when PCM is in the form of a liquid was also observed in the studies by Ho et al. [40] who studied the thermophysical properties of aqueous slurries of microencapsulated PCM n-eicosane with 2, 5 and 10 wt%. particle concentrations.

Sivapalan et al. [41] studied the specific heat of paraffin wax-water emulsion containing 10 wt%, 20 wt%, 33 wt%, and 50 wt% nanosized particles of paraffin wax. While the increase in the mass of PCM particles resulted in an increase in the heat of phase transition, the influence of PCM on the specific heat of the emulsion is not clear. Both the increase and the decrease of the specific heat value of the emulsion are observed, and due to the small number of samples, the ranges of variation are difficult to determine.

The properties of slurries with PCM microcapsules are also described in [42–44], but a small number of measurements do not allow to draw clear conclusions regarding the effect of PCM microcapsules on the specific heat of slurry. A large part of the articles concerns the determination of the specific heat or the phase change heat of new PCM materials [45–54] that can be used as an additive to the working fluid to create another type of slurry/emulsion.

The presented literature review shows that; (a) two methods (DSC and T-history with its modifications) are mainly used to determine the specific heat of PCM material in solid, liquid, and phase change states; (b) there are few publications on the specific heat testing of slurries containing encapsulated and microencapsulated PCM; (c) there are misleading data on how an increase in the mass of mPCM affects the thermal properties of the sludge, in particular, the specific heat value when the slurry contains microcapsules with PCM in a solid or liquid state; (d) there is evidently no information about encapsulated PCM sludge based on propylene glycol, which is a heat carrier used in solar installations, preventing them freezing in winter.

The results of detailed tests of the slurry with the addition of mPCM included in the work constitute a contribution to the global material database created for the needs of convective heat exchange studies. Research on heat exchangers with mPCM slurry as a working fluid requires the recognition of the basic properties of the medium in the phase transition temperature range in order to properly interpret the heat transfer indicators. This work fills the information gap in the study of the basic properties of slurries based on commonly available raw materials and propylene glycol as the base liquid. The tested slurry can operate at temperatures below 0 °C, and there are practically no studies on this matter, as indicated in the literature review above.

This article presents new results of detailed studies on the impact of microencapsulated PCM (6 different concentration values) on specific heat and heat of fusion of slurry. An mPCM slurry concentrate product called Micronal® DS 5039 X Manufacturer name: Microtek Labs, Location: 2400 East River Road Dayton, Ohio and the ERGOLID EKO® Manufacturer name: Boryszew, Location: Boryszew, Poland (aqueous solution of propylene glycol) as base fluid, were used as the components of the examined slurry. The results were obtained based on the modified T-history method, the so-called "thermal delay method".

2. Materials and Methods

2.1. Slurry Properties

Microencapsulated PCM slurry concentrate is an water solution of polymethyl methacrylate shell with mPCM paraffin. The particle size ranges between 1–5 μm. The average amount of solids in the slurry is 43.0%. This product is formaldehyde-free, not prone to damage, and withstands high temperatures. Other, more detailed information about concentrate may be found in articles by Dutkowski and Fiuk [55,56] or technical brochures of the current manufacturer [57]. It can be used as active or passive in heating/cooling [12].

Samples of mPCM slurries by mechanical mixing of concentrate with a base liquid were prepared–the samples were mixed for 30 min using a magnetic stirrer. The ERGOLID EKO® (an aqueous solution of propylene glycol and contains 37% pure propylene glycol and 63% water with a minor fraction of additives) was used as a base fluid. Samples of microencapsulated phase change material slurries were prepared according to the ratio of concentrate/propylene glycol: 20:80, 30:70, 40:60, 50:50, 60:40, and 70:30, respectively.

2.2. Experimental Set-Up

The specific heat and heat of fusion of mPCM slurry were determined based on experimental set-up carried out according to the "T-history" method. The recorded change in the sample temperature of the slurry and the reference liquid during the experiment formed the basis for determining the apparent specific heat and latent heat of mPCM slurry. Since the method allows measurements to be carried out with any number of samples seven test tubes were used. Its outside diameter was 16 mm, length 160 mm, and a wall thickness of 1 mm. The tubes on the test bench contained: distilled and deionized water (reference liquid) and six mPCM slurry samples. The mass of the sample was measured with an uncertainty of ±0.001 g. The temperature of the liquid contained in the tubes was measured using individually made K-type thermocouples. Each thermocouple was individually marked (in the range of 10 °C–70 °C) relative to the model glass thermometer with an elementary scale 0.02 °C. The thermocouple indication error did not exceed ±0.2 K. All voltage signals from thermocouples were archived using the Memograph RSG40 recorder from Endress and Hauser. The test tubes with liquids and the thermocouples located in their central part were installed on one supporting structure. The whole structure was placed in an electrically heated chamber, and then in the room where the actual experiment was carried out. The layout of the station is shown in Figure 1a. Figure 1b shows a photo of the measuring section located in a chamber with adjustable air temperature.

2.3. Test Conditions and Procedure

Liquid samples of known mass were poured into test tubes. The test tubes were then placed in holders attached to the supporting structure. The arrangement of the tubes relative to the support structure ensured free, convective air movement. A thermocouple was inserted into each of the tubes in such a way that its tip was in the center point of the liquid's volume. In addition, another thermocouple was attached to the structure to measure the temperature of the air surrounding the tubes. The complete system was placed in the test chamber. The electric heater was used to change the air temperature inside it. Due to the regulated electric power supplied to the heater, it was possible to change the rate of temperature increase in the chamber. The change in temperature of air and liquids placed in test tubes was observed on the recorder's display. When the temperature in the chamber and the temperature of the liquid in the tubes were uniform and amounted to around 50 °C, it was assumed that the system was prepared for proper tests. The 50 °C temperature is two times the PCM phase transition value found in the microcapsules and allows a significant number of measurement results to be obtained that are necessary to determine the specific heat of the slurry when the PCM is in the liquid state. After reaching the assumed temperature, the supporting structure with test tubes and the recorder was placed in an unheated room at a temperature of about 7 °C. This is the temperature that allows a significant number of measurement results to be obtained, in order to determine the specific heat of the slurry when the PCM is in the solid-state. The temporary temperature values displayed by the recorder were written to the memory with the frequency of 1 s. The data obtained from the measurements were used to determine the specific heat of the slurry (when PCM inside microcapsules was in the liquid state, as well as in the solid-state) and to determine the heat of phase transformation. In order to avoid the influence of accidental errors on the calculated value of specific heat, the measurement results were replaced with regression line functions. The linear regression equations were selected individually for each of the experimental characteristics. In order to improve the

effectiveness of this method, each of the characteristics was replaced by a few curves so that the coefficient of determination was not lower than $R^2 = 0.995$.
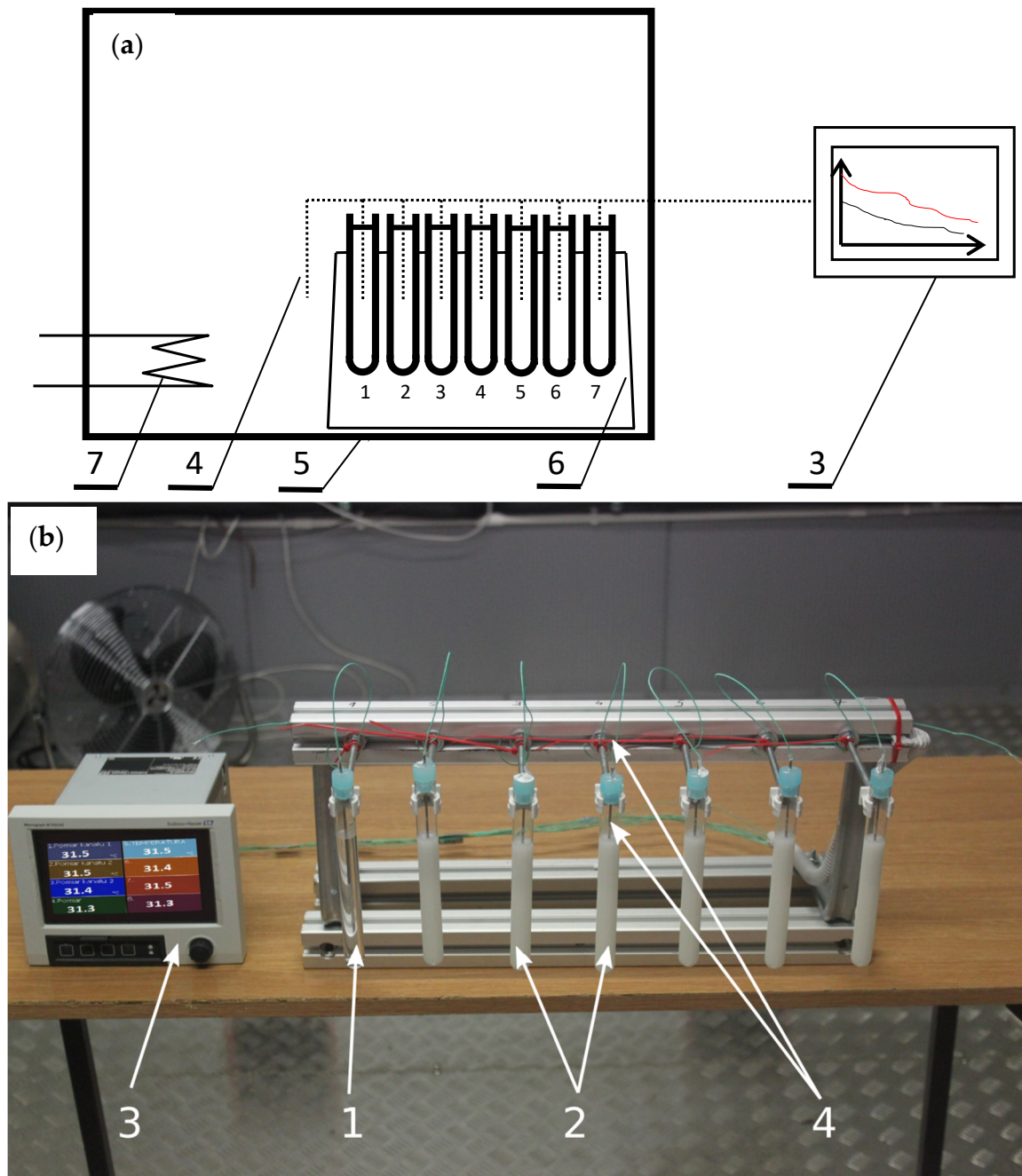
Figure 1. Schematic of the test bench and (**a**) overview of the measuring section inside the temperature-controlled chamber (**b**); 1—sample with reference liquid (distilled water), 2—test samples with different concentration of suspension, 3—data acquisition module, 4—K-type thermocouple array, 5—test chamber/room, 6—sample support structure, 7—electric heater with power regulation.

The presented results are the average of three measurement series, each of them based on the "thermal delay method" proposed by Kravvaritis et al. [33]. According to the authors of the "thermal delay method", it is an improved version of the T-history method because it provides results with less error. In the experimental part, these methods do not differ from each other. The difference occurs at the stage of processing the obtained measurement results. The original T-history method examines the time needed for the PCM sample to

reach the same temperature as the standard liquid at a given moment. In "thermal delay methods", the basis for determining the specific heat value is the temperature that the PCM reaches in relation to the temperature of the standard liquid after a specified time. The smaller the time step, the more precise the results of the calculations are obtained, and the individual measurements can be considered as realized in the quasi-static process ($T_i \approx$ const). According to this method, during cooling, the heat released by the liquid and the glass tube within one-time step $\Delta\tau$ (in this work $\Delta\tau = 1$ s) equals the heat given to the environment,

$$m \cdot c_p \cdot (T_i - T_{i+1}) + m_g \cdot c_{p\,g} \cdot (T_i - T_{i+1}) = \alpha \cdot S \cdot \int_i^{i+1} (T(\tau) - T_{amb}(\tau))d\tau \qquad (1)$$

where m—mass of liquid in the test tube, m_g—mass of glass test tube, c_p—specific heat of the liquid in the test tube, c_{pg}—specific heat of the glass, T_i—liquid temperature in the test tube at an (ith) time, T_{i+1}—liquid temperature in the test tube after the time step ($i + 1$), T_{amb}—ambient temperature at time τ, α—heat transfer coefficient on the outside of the test tube, S—heat exchange surface on the outside of the test tube.

The right side of Equation (1) can be written as,

$$\alpha \cdot S \cdot \int_i^{i+1} (T(\tau) - T_{amb}(\tau))d\tau = \alpha \cdot S \cdot \left(\int_i^{i+1} T(\tau)d\tau - \int_i^{i+1} T_{amb}(\tau)d\tau \right) \qquad (2)$$

where term $\int_i^{i+1} T(\tau)d\tau$ expresses the area under the temperature change curve of the liquid in the test tube, while term $\int_i^{i+1} T_{amb}(\tau)d\tau$ expresses the area under the ambient temperature change curve. In a sufficiently short time $\Delta\tau$, the area under the curve can be calculated as the area of the rectangle with the dimensions $\Delta\tau$ and the average temperature of the fluid in this time interval. Therefore, assuming that the ambient temperature is approximately a constant value, Equation (2) takes the form:

$$\alpha \cdot S \cdot \int_i^{i+1} (T(\tau) - T_{amb}(\tau))d\tau = \alpha \cdot S \cdot [0.5(T_i + T_{i+1}) \cdot \Delta\tau - 0.5(T_{amb\,i} + T_{amb\,i+1}) \cdot \Delta\tau], \quad (3)$$

after transformations,

$$\alpha \cdot S \cdot \int_i^{i+1} (T(\tau) - T_{amb}(\tau))d\tau = \alpha \cdot S \cdot [0.5\Delta\tau(T_i + T_{i+1} - 2T_{amb\,i})]. \qquad (4)$$

The Equation (1) after taking Equation (4) into account can be written for the reference liquid-water (subscript w) and the tested slurry of any concentration (subscript s), as a system of equations:

$$\begin{cases} m_w \cdot c_{p\,w} \cdot (T_{w\,i} - T_{w\,i+1}) + m_g \cdot c_{p\,g} \cdot (T_i - T_{i+1}) = \alpha \cdot S \cdot [0.5\Delta\tau(T_{w\,i} + T_{w\,i+1} - 2T_{amb\,i})] \\ m_s \cdot c_{p\,s} \cdot (T_{s\,i} - T_{s\,i+1}) + m_g \cdot c_{p\,g} \cdot (T_i - T_{i+1}) = \alpha \cdot S \cdot [0.5\Delta\tau(T_{s\,i} + T_{s\,i+1} - 2T_{amb\,i})] \end{cases}. \qquad (5)$$

After transformations, the specific heat of the slurry can be expressed as:

$$c_{p\,s} = \frac{m_w \cdot c_{p\,w} + m_g \cdot c_{p\,g}}{m_s} \cdot \frac{(T_{w\,i} - T_{w\,i+1})(T_{s\,i} + T_{s\,i+1} - 2T_{amb\,i})}{(T_{s\,i} - T_{s\,i+1})(T_{w\,i} + T_{w\,i+1} - 2T_{amb\,i})} - \frac{m_g \cdot c_{p\,g}}{m_s}. \qquad (6)$$

The specific heat of the slurry (c_{ps}) is a constant value in the initial cooling phase, i.e., when the PCM is in the liquid state. When the value of (c_{ps}) starts to change, then the temperature at which this occurs (T'') is the limit and determines the beginning of the PCM phase transformation. When the specific heat ceases to change, then the temperature at which this occurs (T') is the limiting temperature, and from now on, the specific heat is a constant value, characteristic for the slurry of microencapsulated PCM in the solid-state. It can therefore be stated that,

$$c_{p\,s\,(lip)} = const, \text{ for } T \geq T'', \tag{7}$$

$$c_{p\,s\,(solid)} = const \text{ for } T \leq T' \tag{8}$$

and heat of phase transformation (crystallization) in the temperature range T'' to T':

$$h = \int_{T''}^{T'} c_{p\,s}(T)\, dT \cong \sum_{i=liq}^{i=solid} c_{p\,s}(T) \cdot (T_{i+1} - T_i). \tag{9}$$

Additionally, to ensure that the temperature distribution inside the tubes was uniform and the lumped capacity assumption the Biot number should meet the condition Bi < 0.1.

3. Results and Discussion

3.1. T-History Cooling Curves for the mPCM Slurries

Figure 2 presents the results of experimental research on the change in sample temperature of the slurry with the mass fraction and changes in the temperature of the reference liquid (water) and the surrounding air temperature. It is noted that the temperature of the samples decreases over time. In the case of a slurry of PCM microcapsules, the temperature profile changes as the PCM crystallization process commences. This process takes place when the sample temperature is around 18 °C. The higher the concentration of PCM, the reflection of the phase change process on the temperature characteristics is more pronounced and the process takes more time.

The plot of temperature over time indicates that it becomes increasingly lower in each subsequent time step. Only during the phase change, the sample temperature was constant for a certain period of time. The lack of local temperature depression before the phase transition confirms the lack of subcooling effect. This is due to the fact that for organic PCM substances (including paraffin filling in microcapsules used in research) no subcooling effect is observed [5].
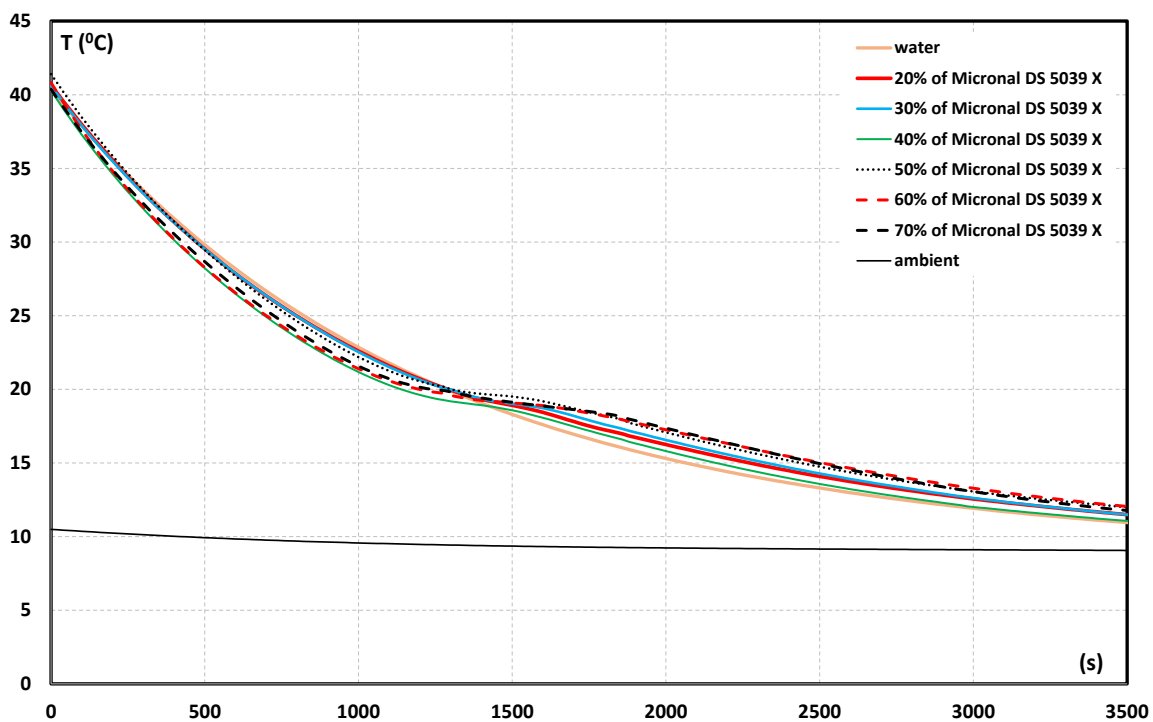

Figure 2. T-history cooling curves for the mPCM slurry, reference liquid (water) and surrounding air.

3.2. Specific Heat and Latent Heat of mPCM Slurries

The specific heat of the slurry was calculated according to Equation (6) based on temperature change over time. As a result, for each time step of 1 s it was possible to calculate the instantaneous specific heat of the slurry. The results of the calculations are shown graphically in Figure 3.
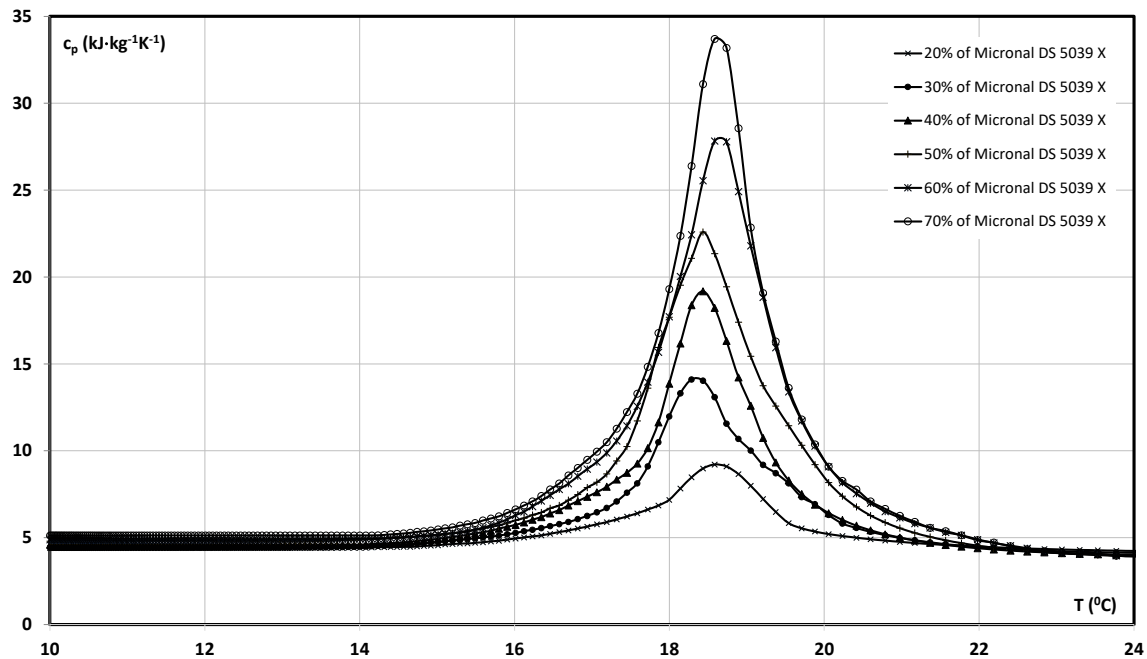
Figure 3. Evaluation of specific heat profiles for mPCM slurries vs. temperature.

In Figure 3 three sections can be observed. The first of them covers a temperature range from 10 °C to about 15 °C when the specific heat of the slurry appears to be constant; the second in the temperature range of 15–22 °C when a distinct change in specific heat is observed with the temperature change, and the third range (temperature 22–24 °C) when the specific heat of the slurry again appears to be constant. It was deduced that phase change occurs during sample cooling when values of the specific heat of the slurry deviate from the constant values (straight lines approximating the results of cp calculations). Hence, it was assumed that the temperature of 22 °C corresponds to the start of the crystallization process, which ends when the temperature reaches 15 °C.

The maximum of specific heat is at the temperature of about 18.5 °C. The obtained phase change temperatures are lower than the quantities given by the manufacturer and also confirmed by the authors' own research [55,56]. As stated in the work of Kousksou et al. [58], it is a common phenomenon that the start of the emulsion crystallization process does not take place at the phase transition temperature, but lower, depending on the rate of sample cooling. In studies of PCM emulsions, according to the authors of the work Morimoto et al. [38] the crystallization process took place at 14 °C lower than the melting point of each emulsion tested.

Figure 3 shows that with the increase in the mass fraction of microcapsules, the maximum value of specific heat during PCM phase transformation increases. For 8.6% mass fraction of PCM in the base liquid, the maximum specific heat value was 9.2 kJ/(kgK) and increased proportionally to 33.7 kJ/(kgK) when the PCM share in the slurry was 30.1%. It can be seen that the value of the specific heat of the slurry when the PCM in the microcapsules is in the solid-state (i.e., for $T < 14$ °C) and when the PCM encapsulated in the microcapsules is in the liquid state (i.e., for $T > 22$ °C) is a constant value. The highest values of specific heat were noted when PCM was solid. That has been confirmed for

mPCM slurry by the experimental results presented in the work of Allouche et al. [7] or for PCM emulsions according to Wang et al. [39].

The influence of mass fraction of microcapsules on the value of specific heat and heat of phase transformation of slurry is in details presented in Figures 4 and 5.
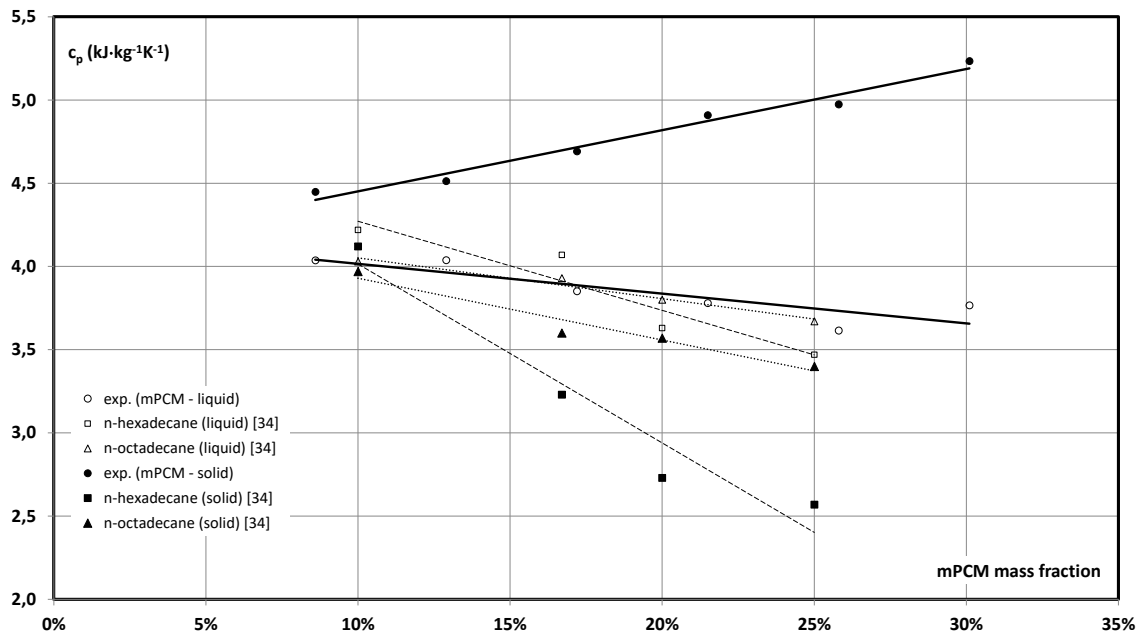
Figure 4. Influence of PCM mass fraction on specific heat of mPCM slurry.

Figure 4 shows the effect of PCM mass fraction on specific heat of the slurry when PCM is in solid-state and when PCM is in liquid-state. The presented characteristics show that higher values of specific heat are present when PCM is in a solid-state. Additionally, the specific heat of the slurry, when PCM in microcapsules is in liquid form, decreased from 4.04 kJ/(kgK) to 3.77 kJ/(kgK) for 8.6 wt%, and 30.1 wt% of mPCM, respectively. The specific heat of the slurry, when the PCM in the microcapsules is solid, increased from 4.45 kJ/(kgK) to 5.23 kJ/(kgK) for 8.6 wt% and 30.1 wt% of mPCM, respectively.

Figure 5 shows that when the mPCM content tends to zero, cp tends to a value of about 4.2 kJ/(kgK) both, when the PCM is in the solid and liquid state. The value of $c_p =$ 4.2 kJ/(kgK) corresponds to the specific heat of the water. It is known that the specific heat value of aqueous propylene glycol solution varies from 4.2 kJ/(kgK) to 4.0 kJ/(kgK) when the glycol concentration increases from 0 to 20%. It seems that the results obtained are too high. According to the authors, this value is influenced by additives (e.g., surfactants) contained in the mPCM concentrate or other substances in the base liquid–a water solution of propylene glycol. Hence, the characteristics presented in Figure 4 take into account the influence of not only mPCM material but other substances added with the concentrate, unknown to the authors.

The publication [52] shows that the specific heat value of 5 different substances tested by the authors takes higher values when PCM is in a liquid state. In addition, when PCM is in a specific state (either a liquid or a solid) the c_p value is not constant but increases. E.g. for Mannit $c_{p(s)}$ increased by 47%–from 1.9 kJ/(kgK) to 2.8 kJ/(kgK) when the PCM temperature increased from 100 °C to 147 °C. The work [53] shows the opposite, i.e., when PCM is in a solid-state, then the cp value is greater than the cp value when PCM is a liquid. It is not possible to assess whether changes in the specific heat of a single-phase PCM form with a change in its temperature were also observed, as the authors averaged these values. As concluded in [59], the presentation of the results of specific heat and phase change heat in the form of the effective PCM thermal capacity $c_{p;eff}$ characteristics from temperature is of greater practical importance. This presentation of test results contains much more information than the average value in the table. From the characteristics, it is possible to

determine the effective specific heat as a function of temperature (both when the PCM is in a liquid state and a solid), which is of key importance, e.g., during simulation of heat exchange issues.

For comparison, Figure 4 contains the specific heat values of the emulsion containing PCM particles obtained by Morimoto et al. [38]. First of all, according to [38], the specific heat of emulsions with PCM in the solid-state is lower than the specific heat of emulsion with PCM in the liquid state. Secondly, the increase in the mass fraction of PCM causes a decrease in the value of specific heat of emulsions with PCM in the liquid state. On the contrary to [38], from the work of Wang et al. [39], it can be concluded that in the case of the emulsion (particle paraffin in the mixture of polyolinyl alcohol and polyethylene glycol) the higher the proportion of PCM is in the solid-state in the emulsion, the higher is its specific heat. It should therefore be concluded that the type of emulsion components and their mass content influence the value of its specific heat in a different way. Probably a similar situation may occur in the case of a slurry containing PCM in the form of microcapsules. Further tests are required, with other types of PCM and a base liquid, aimed at verifying this hypothesis.
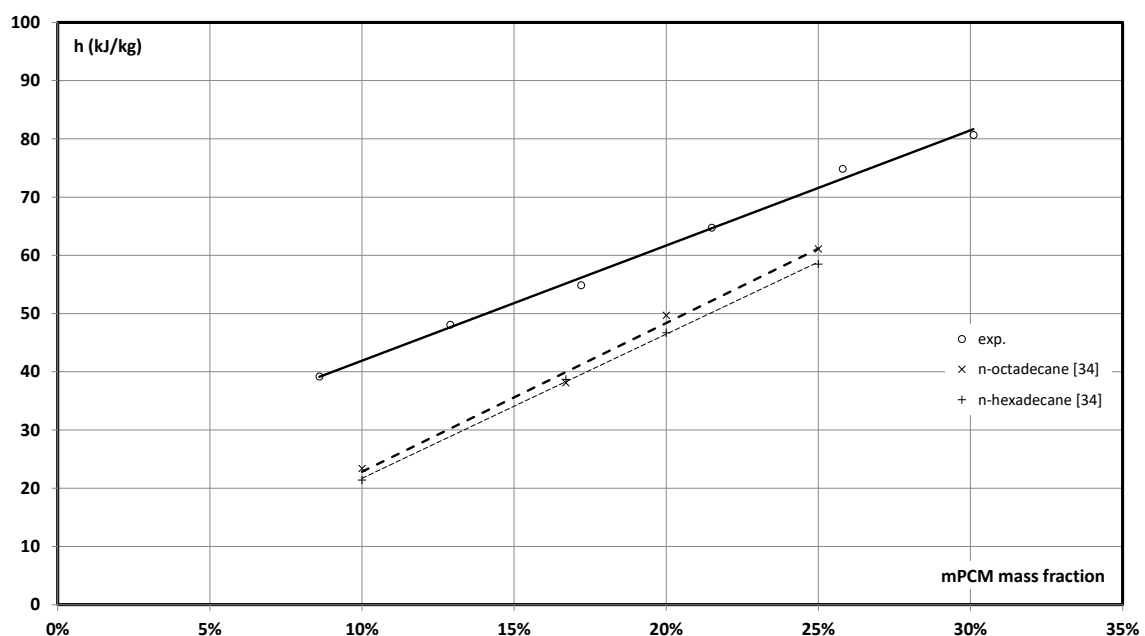

Figure 5. Influence of PCM mass fraction on phase change heat of mPCM slurry.

Figure 5 shows the influence of PCM mass fraction on the heat of phase transition. It is noted that the increase in the mass fraction of PCM results in a proportional increase in the heat of phase transition of the slurry. For the slurry, the latent heat changed from 39.2 kJ/kg to 80.67 kJ/kg respectively, when the mass fraction of mPCM was changed from 8.6% to 30.1%. The obtained trend in the phase change transformation of mPCM slurry is analogous to that for emulsions, for which the results were published in the work of Morimoto et al. [38], and to other data available in the literature concerning emulsions with PCM particles.

It can be noticed from Figure 5 that when the mPCM value tends to the maximum, i.e., the one present in the concentrate (approx. 43%), the expected latent heat will be approximately 100 kJ/kg. This value is consistent with the data delivered by the producer of the concentrate [57].

The quoted publications show that different results are obtained for different substances, and sometimes the results are contradictory. Sometimes the specific heat of solid PCM is greater than the specific heat of liquid PCM. Sometimes an increase in PCM concentration causes an increase in c_p, and sometimes its decreases. Hence, it is required to

conduct numerous experimental studies, their data publication in order to expand the material database. Therefore, the acquisition of knowledge indicates whether different behavior/characteristics of the material are the result of different chemical composition or an incorrectly carried out experiment.

4. Summary and Conclusions

Experimental studies were carried out to determine the specific heat and heat of phase transition of a slurry, composed of microencapsulated phase change material and an aqueous solution of propylene glycol as a base liquid. The research was carried out based on the modified "T-history method"–the so-called "thermal delay method". It is not a new method, but commonly used method due to good results. The experiment was carried out for six types of mPCM slurries with the following mass fraction of microcapsules in the base liquid was 8.6, 12.9, 17.2, 21.5, 25.8, and 30.1 wt%, respectively. Since the main peak melting temperature of the slurry is about 25 °C, the experiment was carried out during the cooling of samples from the temperature of 50 °C to 10 °C. The obtained results constitute a new contribution to the construction of the material database dedicated to mPCM slurries. This is particularly important in the context of the possibility of using the slurries as a working fluid in heat exchange systems. Conducting and further developing research in independent research centers in the future will add value to the results of experimental research developed so far. As a result, it will be possible to definitively determine whether the cause of different, qualitative changes in the value of the specific heat of the PCM slurry is the influence of their different chemical composition or the error of the measurement method. The authors of the experiment conducted research on other properties of slurry, e.g., viscosity. Currently, the search for mutual relations between the results of experimental research is being investigated [60,61].

Based on the experimental studies carried out, the following conclusions can be drawn:

1. Phase transition of PCM microencapsulated (analogous to PCM emulsions) may occur at a lower temperature, depending on the rate of cooling of the sample. The value of the main peak crystallization temperature of mPCM slurry was about 18.5 °C.
2. An increase in the concentration of microcapsules caused a proportional increase in specific heat in the main peak melting temperature of mPCM slurry. The value of the maximum specific heat changed from 9.2 kJ/(kgK) to 33.7 kJ/(kgK) respectively for 8.6 wt%, and 30.1 wt% of mPCM.
3. The specific heat of the slurry when PCM in microcapsules is in liquid form is lower than the specific heat of the slurry when PCM in microcapsules is in liquid form.
4. Specific heat of the slurry (when PCM in microcapsules is in liquid form) decreased from 4.04 kJ/(kgK) to 3.77 kJ/(kgK) respectively for 8.6 wt% and 30.1 wt% of mPCM.
5. The specific heat of the slurry (when the PCM in the microcapsules is in the form of a solid) increased from 4.45 kJ/(kgK) to 5.23 kJ/(kgK) for 8.6 wt%, and 30.1 wt% of mPCM respectively.

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