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# Characterisation of commercial phase change materials with potential application in gypsum boards for buildings

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## Abstract

Currently, there is an expanded utilisation of lightweight construction structures in buildings, which results in a low structure's thermal storage capacity of the envelope due to the application of thermally unsuitable materials. PCMs incorporated into building structures components are potential alternatives to manage the inadequate thermal energy storage capacity of lightweight structures. To provide a guide for selecting and applying commercial PCMs in construction, nine organic and inorganic bulk materials were selected, and their thermophysical properties were characterised. Thus, the enthalpy of melting/crystallisation, the melting/crystallisation temperature, the stability of 50 cycles, and the verification of the presence of the subcooling phenomenon by DSC and the T-history method were evaluated.

Since the adequate methods to incorporate the PCMs in gypsum are suspension and vacuum impregnation, their thermal properties, together with density and viscosity, need to be considered, properties that are not typically reported in the datasheets of commercial PCMs.

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Furthermore, the temperature dependence of the viscosity and density of the solid/liquid PCMs were measured by a rheometer and densimeter/pycnometer, respectively. Based on liquid and solid density values, the volumetric expansion of PCMs during the melting process was calculated. Finally, the characterisation parameters were compared with those provided by the suppliers of the different companies. The characterisation's results indicate that for both organic and inorganic PCMs, the fusion temperature (21-26°C) and the density values (0.777-1.515 g/cm<sup>3</sup> for liquid state and 0.895-1.860 g/cm<sup>3</sup> for solid state) were consistent with the values provided in the datasheet from the suppliers'. Viscosity values were found to be higher than expected, and the enthalpy was found to be lower (19-30%) when compared with the technical datasheets from manufacturers'. The cycling stability study results were consistent only for the organic samples, without displaying phase segregation or subcooling problems. Based on the thermophysical characterisation, it was possible to establish that three organic RT-21, RT-21(TA), RT-25, and three inorganic SP-21E, PCM 21C, HS-24P PCMs would be suitable products for their inclusion into gypsum boards under the conditions analysed. These findings provide new insights regarding the applicability and development of new strategies and materials for passive or active heating/cooling applications in buildings.

**Keywords:** *commercial phase change material; density; viscosity; volumetric expansion; thermal properties; gypsum board; building applications.*

## 1. Introduction

Amongst the energy consumers sector, one of the largest is building, responsible for more than a third of the world's final energy consumption [1]. Overall, the building sector is responsible for 30% of energy consumption and 28% of CO<sub>2</sub> emissions [2], of which thermal comfort appliances such as hot water, heating and cooling make up about 70%. Along the way, the building energy performance has been improved by different means. In this sense, the application of energy efficiency measures based on thermal energy storage (TES) rises as an alternative to decreasing energy consumption and emissions [3].

TES solutions can be integrated into buildings in the form of sensitive, latent or thermochemical storage [4]. Amongst the TES technologies, latent heat storage using PCM provides an effective solution. It has a high-energy storage density within a narrow thermal gradient as PCM's fusion and crystallisation process are almost isothermal. Further, TES applications can be classified as active or passive. Passive solutions are characterised by a heat exchange without mechanical action through natural convection between the indoor environment and the storage material [5]. In contrast, active applications are based on an exchange of heat through the assistance of a mechanical component (*e.g.* fan, pump) [6]. An essential current feature of using TES materials in passive applications is the capacity to reduce energy demand in buildings through greater thermal inertia, reducing temperature peaks and improving indoor thermal comfort without additional energy consumption [3,7].

The expanded utilisation of lightweight building structures might result in the structure envelope's low thermal storage capacity due to the application of unsuitable materials. PCM incorporated within the building structures components –different material used in the

construction and assembling of a building— is a potential alternative in managing the inadequate TES capacity of lightweight structures [8]. The relevance of the PCM-based TES in structures firmly relies upon thermal, physical, chemical and financial criteria. Thus, the principal objective of PCMs in building envelopes as latent heat thermal energy storage is to deal with peak heating/cooling loads. Kuznik et al. carried out a series of studies related to incorporating gypsum panels with PCM in lightweight buildings. In [9], an optimal value of the PCM wallboard thickness is investigated. The results showed that a doubling of the building's thermal inertia is reached with a gypsum board thickness of 1 cm. In the following study, Kuznik et al. [10] demonstrate that 5 mm of PCM lightweight wallboard enhances the building room's thermal inertia. The available storage energy is twice higher with PCM. The authors estimated that this value corresponds to an equivalent concrete layer close to 8 cm. In the other study [11], the authors indicated that the PCM wallboards enhance natural convection and achieve no thermal stratification in the room, contrary to the other without composite. Sonnick et al. [12] studied a prefabricated wooden house equipped with 1 ton of salt hydrate-based PCM with a 21°C melting temperature. The monitoring during 87 days showed a 57% reduction of the temperature fluctuations.

In latent heat storage using PCMs, heat gains can be stored during the day and discharged at night —cycles of daily temperature fluctuations— consequently reducing the requirement for mechanical cooling in a structure [13]. Even though the application of such technology based on latent heat through the application of PCMs might be seen as a logical way to replace or support active heating/cooling systems, their implementation requires thorough characterisation of the thermophysical properties of the PCMs. This process is fundamental for creating new applications of the PCMs in buildings and not only to predict the impact of

latent heat storage on indoor condition and energy savings [13] but to ensure a complete melting and solidification processes in such narrow thermal ranges.

Widely used techniques for the characterisation of PCMs are thermal gravimetric analysis (TGA) and also differential scanning calorimeter (DSC) [14,15]. For example, Haillet et al. [16] analysed the thermal performance of 11 different phase change materials such as solid-solid transition materials, dicarboxylic acids, sugar alcohols, polymeric hydrocarbons, aromatic hydrocarbons and urea, in the temperature range 120-150°C using TGA and DSC, coupled with quadrupole mass spectrometer (QMS) gas analysis. The results showed that only a few organic materials demonstrated potential for thermal storing purposes, requiring further examination concerning long-term stability. Del Barrio et al. [17] characterised different sugar alcohols as PCM for TES applications using DSC and HotDisk-based method. The study evaluates five pure sugar alcohols' critical thermal and physical properties and three eutectic blends; to later be compared with those frequently applied PCM within 70°C and 180°C. The main finding of this investigation established that sugar alcohols are attractive materials for latent heat storage. Even though the promising features of sugar alcohols, a verity of problems, such as thermal endurance and stability, must be examined further.

Similarly, Bayón et al. [18] studied the feasibility of thermotropic liquid crystals as latent heat storage materials performing DSC and TGA analysis together with polarised light microscopy and rheological measurements. The study concluded that regardless of the encouraging results displayed by those materials, the long-term thermal stability should be further studied. Additionally, Miró et al. [19] and Gasia et al. [20] included health hazard analysis to consider the potential impact of PCMs on people and their effect on the

environment. Miró et al. [19] tested five different materials within a 150°C and 200°C temperature range. To check the long-term performance of the PCMs, thermal stability and cycling stability analyses were carried out. The study concluded that the appropriate materials at that temperature range were benzanilide and D-mannitol; in a closed system, hydroquinone was also considered. Moreover, Gasia et al. [20] characterised sixteen materials as phase change materials from the cycling (100 cycles) and thermal stability point of view in the temperature range between 120°C to 200°C. Thus, they determined that under the studied temperature range, high-density polyethylene (HDPE) and adipic acid were appropriate materials as PCMs.

Maldonado et al. [21] selected nine phase change materials, and their thermophysical properties were characterised for an application between 210°C and 270°C. Since these were chemicals typically used in the industry, a health hazard evaluation was carried out. Then, a thermophysical characterisation was performed, evaluating the phase change temperature and the enthalpy of fusion; the thermal stability was analysed by TGA performed up to 50 cycles. Those authors concluded that Myo-inositol could be used in a closed system and that solar salt is adequate for its use in such temperature range.

When looking for building applications, there are several options for commercial PCMs to purchase. However, the main restriction for these applications is finding the appropriate materials that fulfil all the application requirements under study. As such, Navarro et al. [22] characterised eleven commercial organic PCM in the melting temperature range 21-28°C to be used in a mixture with mortar (bulk and micro-encapsulated PCM) or as a new layer in the wall (macro-encapsulated PCM). This thermophysical characterisation was carried out using DSC and thermal cycling up to 10000 cycles. Additionally, the thermal conductivity of the

PCM was measured. Results revealed that MC DS5038X is a suitable option due to its long-term stability properties. The literature includes several papers on the study and evaluation of different PCM candidates for numerous applications. Some of them related to building-integrated photovoltaic-thermal (BIPVT) system using four commercial RT18HC, RT21, RT21HC, and RT25HC PCM types [23], compact plate-fin heat exchanger with encapsulated RT35HC, RT44HC or RT64HC [24], single-slope solar still using commercial salt hydrate-based PCM 28/315 [25] and multi-slope solar still with paraffin-based PCM [26]. In all studies, it was found that PCM addition could significantly enhance the overall performance of devices by storing the solar heat during sunshine hours and releasing it during hours with lower and zero solar radiation. Moreover, the literature includes several papers on studying and evaluating different PCM candidates for several applications. However, there is no similar assessment on the selection of a PCM to be included in gypsum boards for building applications, considering the material requirements to ensure good incorporation in it, *i.e.* viscosity and density.

Therefore, the present investigation's objective is to select suitable PCMs to be incorporated in a gypsum board as a lightweight construction material for building applications, considering a temperature range according to the climate of the North of Chile [27]. To do so, nine different bulk PCMs were tested (micro-encapsulated PCMs were disregarded due to the high price and already available composites in the market, such as COMFORTBOARD by KNAUF [28]). Since the adequate methods to incorporate the PCMs in gypsum are suspension and vacuum impregnation [29], the thermophysical properties of the PCMs were assessed, together with density and viscosity properties that are not typically reported in the datasheets of commercial PCMs. Thus, this study represents an exhaustive characterisation of several organic and inorganic PCMs evaluating the melting temperature for the application in



gypsum boards for lightweight buildings in Chile. The determination of thermophysical properties (*i.e.* temperature and enthalpy of fusion and crystallisation), thermal stability, viscosity, and density at different temperatures were also evaluated.

## **2. Materials and methods**

### **2.1. Materials**

For this study, nine commercial organic and inorganic bulk PCM samples were tested. These PCMs were acquired from different international companies, Rubitherm GmbH (Germany), RGEES LLC (United States) and PCM Energy P. Ltd (India). The technical specifications and suppliers of each of these PCMs are detailed in Table 1.

### **2.2. Analytical methods**

#### **2.2.1. Viscosity**

To determine the viscosity of the samples, a Brookfield Rheometer DV-III Ultra with Thermosel and SC4-18 needle was used with a 8 mL sample volume. Measurements were carried out for the nine samples from 30°C to 45°C in triplicate. The measurements were made at different controlled speeds between 5 and 150 RPM. The reported viscosities were obtained when the torque percentage was 50%. The closest values were taken from a set of tests for each temperature, calculating their average and standard deviation. A complete data set can be found in supplementary information (Table S1).

### **2.2.2. Density in liquid state**

To determine the density of PCMs in a liquid state, a Mettler Toledo DE50 density meter was used. Briefly, 10 g of each sample was placed in sealed glass jars and then placed in an oven at 30°C for 24 hours until the complete fusion of each sample was reached, and subsequently, the density was measured. The equipment was calibrated for each of the required temperatures, 25°C, 30°C, 35°C, 40°C and 45°C. Afterwards, the density was measured in triplicate at the indicated temperatures. A complete data set can be found in supplementary information (Table S2).

### **2.2.3. Density in solid state**

The density of the PCMs in a solid state was determined at 10°C, 15°C and 20°C in triplicate, using a pycnometer –instrument which bases its principle on the displacement method– for this procedure, four different types of mass weights were carried out:

- Empty pycnometer (PP)
- Pycnometer with a solid body (PS)
- Liquid filled pycnometer (PA)
- Pycnometer with the solid body inside and filled with the liquid used (PSA)

It is essential to bear in mind that the liquid used to fill the pycnometer depends on the type of sample; hence, distilled water was used for organic PCMs and n-Dodecane in the case of inorganic PCMs. After obtaining these measurements, the corresponding calculations were performed. The gross relative density of the solid, for the liquid at the working temperature, is obtained with Eq. (1):

$$Z = \frac{D_S}{D_A} = \frac{\frac{M_S}{V_S}}{\frac{M_A}{V_A}} = \frac{P_S - P_P}{P_A + P_S - P_P - P_{SA}} \quad (1)$$

Where:

Z: gross relative density of the solid. It is obtained from the four weighings.

D<sub>S</sub>: gross solid density.

D<sub>A</sub>: density of the liquid. In the case of water, it is obtained from tables for the working temperature.

M<sub>S</sub>: mass of solid.

M<sub>A</sub>: mass of the liquid's volume dislodged by the solid when introduced into the pycnometer filled with fluid.

V<sub>S</sub>: volume of solid.

V<sub>A</sub>: volume of liquid dislodged.

Error propagation must be applied using Eq. (2) to obtain the error  $\Delta Z$ . Since the same scale is used for all four weights, the error of appreciation will be the same for all of them.  $\Delta P_S = \Delta P_A = \Delta P_P = \Delta P_{SA} = \Delta P = 10^{-4}$

$$\Delta Z = \left[ \frac{2 \cdot [|P_S - P_P| + |P_A - P_{SA}|]}{(P_A + P_S - P_P - P_{SA})^2} \right] \cdot \Delta P \quad (2)$$

Eq. (3) is used to obtain the gross density of the introduced body.

$$D_S = Z \cdot D_A \quad (3)$$

The following linear equations give the density of the liquid at a specific temperature.

$$\text{Water} = \rho_w(T/K) = 1111,9 - 0.3834 (T/K)$$

$$n - \text{Dodecane} = \rho_n(T/K) = 969,36 - 0.7045 (T/K)$$

The gross density error is obtained using Eq. (4).

$$\Delta D_S = \Delta Z \cdot D_A \quad (4)$$

Finally, the density of the unknown solid, applying the correction by mass of occupying air, is obtained from Eq. (5) and its respective error from Eq. (6):

$$D_S^* = Z(D_A - da) + da \quad (5)$$

$$\Delta D_S^* = (D_A - da) \Delta Z \quad (6)$$

Where  $da$ , corresponds to the density of the air. A complete data set can be found in supplementary information (Table S2).

The volume changes and partial expansion of various PCMs or mixtures during the melting process must be considered for its inclusion in TES frameworks. To assess these parameters, the densities of solid and liquid samples were extrapolated to the individual melting points to then determine the decreased density value due to the phase change [37]. The expansion during volume change was assessed as the ratio  $\Delta V/V_{solid}$  and was expressed as a percentage.

### 2.3. Thermophysical characterisation

To analyse the temperature and enthalpy of fusion and crystallisation of the PCMs, the NETZSCH DSC 204 F1 Phoenix® equipment was applied, using a nitrogen gas protective environment, integrated mass flow controller, and a volumetric flow of 70 mL/min. The equipment was calibrated with five high purity standards (*i.e.* C<sub>10</sub>H<sub>16</sub>, In, Sn, Bi, Zn). The calibration validation was carried out using C<sub>10</sub>H<sub>16</sub>, In, Sn periodically according to the equipment manual. The containers used were aluminium micro-crucibles with sealed lids (40 µL) and 10 mg of sample. Only one scanning rate was considered: 0.5 °C/min, to be consistent with the slow ambient rates expected in building applications [38–40]. Also, the peak temperature has been considered as the representative temperature of a phase change material.

The heating ramps in each of the samples were (4 cycles): Initial temperature of 0°C, heating at 55°C, constant temperature of 55°C for 10 min, and cooling to 0°C.

### 2.4. Cyclic stability tests

For this analysis, the NETZSCH DSC 204 F1 Phoenix® device was applied, with the descriptions and characteristics indicated previously. The containers used were also aluminium micro-crucibles with sealed lids (40 µL) and 10 mg samples.

The heating ramps in each of the samples were (50 cycles): Initial temperature of 10°C, heating to 45°C with 0.5 °C/min rate, isotherm at 45°C for 10 min, and cooling to 10°C with 0.5 °C/min rate.

## **2.5. T-history method**

The charging and discharging capacity of commercial PCMs was carried out using the T-history method. For this, a JEIOTECH thermostatic bath, model RW3-1025P, which controls the operating temperature, was used. PCE temperature sensors type-K (accuracy  $\pm [0.4\% + 1^{\circ}\text{C}]$ ), to record the temperature variations of the sample, and a PCE-T390 Data-logger for recording the data were utilised. Test tubes were used as containers to hold the sample into the thermostatic bath during the experimentation. A volume of 15 mL of each sample was taken. The results were carried out in duplicate, with three technical replicates.

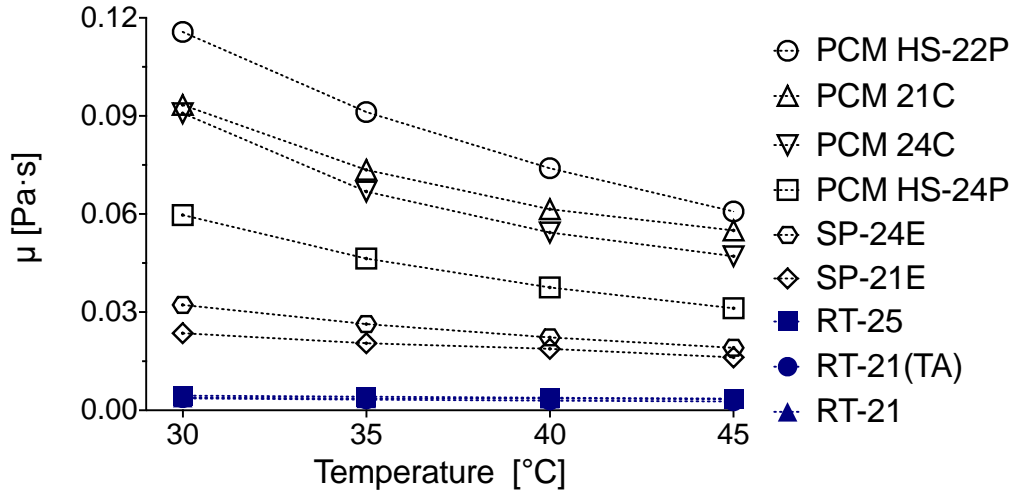
The heating-cooling ramps in each sample were (3 cycles): Initial temperature of  $40^{\circ}\text{C}$  with an isotherm of 1 hour, cooling at  $5^{\circ}\text{C}$  in 6 hours, isotherm at  $5^{\circ}\text{C}$  for 1 hour, and finally, heating at  $40^{\circ}\text{C}$  in 6 hours.

## **3. Results and discussion**

### **3.1. Viscosity**

The viscosity measurement results and their standard error of the mean (SEM) at different temperatures of liquid commercial PCMs are shown in Fig.1. The viscosity measurements were carried out in triplicate for each PCM, with negligible variations amongst replicate samples (*i.e.* standard deviations,  $n=3$ ) between 0.00001 to 0.0002 Pa·s. The organic PCMs (RT-21, RT-21(TA), and RT-25) had a viscosity between 0.0039 and 0.0045 Pa·s. The inorganic commercial PCMs presented much higher viscosity, in fact, higher than expected, between 0.024 and 0.12 Pa·s. This is most probably due to the presence of some additives included in the manufacturing process of PCMs. Aiming the potential application of these

PCMs in gypsum boards as presented in this investigation, this high viscosity would represent a problem since it would make it more difficult to impregnate the gypsum board with such materials.



**Fig. 1.** Dynamic viscosity of commercial PCM samples as a function of temperature.

Organics (solid symbols), inorganics (open symbols) ( $n=3$ ). SEM bars are displayed.

Previous studies measured the viscosity of some of these PCMs at lower temperatures, and Ferrer et al. [41] even derived an empirical equation to calculate the viscosity of organic PCM (Eq. (7) and Eq. (8)):

$$\mu(T)[Pa \cdot s] = (-3.66 \times 10^{-8} \cdot T^3 + 6.14 \times 10^{-6} \cdot T^2 - 4.35 \times 10^{-4} \cdot T + 1.41 \times 10^{-2}) \cdot c$$

(7)

$$c = 0.001 \cdot T_m^2 - 0.0215 \cdot T_m + 0.5815 \quad (8)$$

Where  $T$  is the temperature at which the viscosity wants to be determined in °C,  $c$  is the correction parameter for each PCM, and  $T_m$  is the melting temperature of the material in °C. The advantage of such calculation is to have a numeric approximation before the experimental validation of such value.

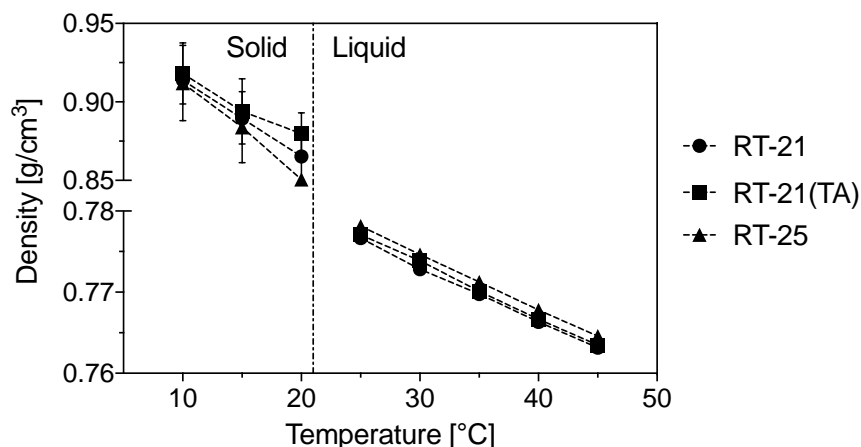
Table 2 compares the viscosity values obtained in this investigation with those reported in the literature and those obtained with the empirical equation proposed by Ferrer et al. [41]. In this Table, it is possible to observe that the viscosity values measured for the PCM RT-21 between 30-45°C are higher compared to the value obtained from the literature at 30°C and to those obtained employing the empirical equation proposed by Ferrer et al. [41].

### **3.2. Density**

The densities in liquid and solid phase –at different temperatures– were determined from the total number of commercial PCM samples. The results showed that the density measurement's values are related to the property of the matter since the density decreases as the temperature increases [42]. Because the samples have different natures (three of an organic nature and six of an inorganic nature), independent graphs were made for each sample composition (*i.e.* organic Fig. 2; inorganic Fig. 3).

Fig. 2 shows the density behaviour in both: liquid and solid state for the three organic PCM used. The densities obtained in a liquid state presented a similar behaviour, with densities varying between 0.7782 g/cm<sup>3</sup> and 0.7635 g/cm<sup>3</sup>. The densities obtained in the solid state initially show similar behaviour, with densities between 0.9181 g/cm<sup>3</sup> and 0.9120 g/cm<sup>3</sup> at 10°C, and then a variation of densities between them of 0.8798 g/cm<sup>3</sup> and 0.8505 g/cm<sup>3</sup> when increasing the temperature and reaching 20°C.

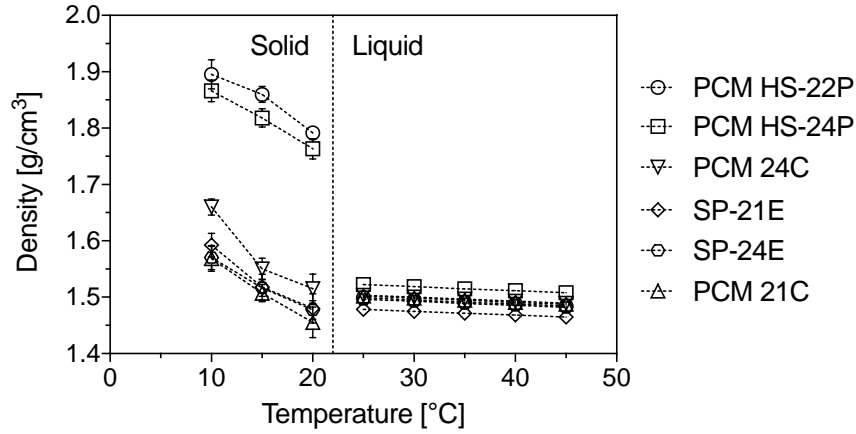




**Fig. 2.** Density of organic commercial PCM vs. temperature ( $n=3$ ). SEM bars are displayed.

Similarly, samples of the solid and liquid state of inorganic PCMs are presented in Fig. 3. When comparing the behaviour in a liquid state, the PCMs offered a variable response, showing at their extreme points (PCM HS-24P and SP-21E) densities between  $1.522 \text{ g/cm}^3$  and  $1.478 \text{ g/cm}^3$ . However, PCM HS-22P, PCM 21C, PCM 24C and SP-24E, showed densities with less variation in the range of  $1.504 \text{ g/cm}^3$  to  $1.496 \text{ g/cm}^3$ . For solid state densities, a group of PCMs with higher densities (PCM HS-22P and PCM HS-24P) is observed again, with values between  $1.895 \text{ g/cm}^3$  and  $1.866 \text{ g/cm}^3$  at  $10^\circ\text{C}$ . However, PCM SP-21E, PCM 21C, PCM 24C and SP-24E, showed densities in the range of  $1.660 \text{ g/cm}^3$  to  $1.569 \text{ g/cm}^3$  at  $10^\circ\text{C}$ .

Marginal variations amongst replicates for both organic and inorganic PCMs in liquid state were observed. The variations amongst replicates samples, for both organic and inorganic PCM in a solid state, were more noticeable, possibly because the technique used to measure solid densities involves more significant human error.



**Fig. 3.** Density of inorganic commercial PCM vs. temperature ( $n=3$ ). SEM bars are displayed.

The density data considering a temperature range of 10°C-20°C for the solid state and 25°C-45°C for the liquid state were fitted as a linear function of the temperature. To calculate the volume change ( $\Delta\rho$ ) during melting, the solid and liquid density values were extrapolated to the individual melting point. Table 3 shows the results obtained in the calculation of the volume change and their respective volumetric expansion ( $\Delta V/V_{solid}$ ).

As it is possible to observe in Table 3, the PCMs that decrease their density considerably when the material melts and that have the highest values of percentage of volumetric expansion are the inorganics PCMs HS-22P and HS-24P, both from the company RGEES LLC. PCMs HS-22P and HS-24P showed values of 0.274 g/cm<sup>3</sup> and 0.199 g/cm<sup>3</sup> regarding their density variation and values between 18.25% and 13.08% of volumetric expansion, respectively. Subsequently, they are followed by the organic PCMs of the Rubitherm company (RT-21, RT-21 (TA) and RT-25) and finally the inorganic PCMs of the Rubitherm company (SP-21E and SP-24E) with those of the company PCM Energy P. Ltd (PCM 21C and PCM 24C) that show a slight increase in density when melting.

The obtained values warn us that these parameters should be considered when contemplating any of these PCMs for use in future research, either in encapsulation or, in general, in thermal storage systems.

Table 4 compares the supplier's density values and the experimental values, both in liquid and solid state at the temperatures specified in the technical datasheets.

For density readings in a liquid state, in the samples RT-21, RT-21(TA) and RT-25, a positive difference not exceeding 1% was observed. For the SP-21E and SP-24E samples, the maximum difference of all readings was obtained, with differences greater than 5.1% and 6.4%, respectively. Finally, PCM HS-22P and HS-24P, unlike the previous results, showed a negative difference of 3.2% and 1.6% concerning what the supplier reported. For the PCM 21C and PCM 24C samples, it was impossible to compare because the supplier's information is not available.

The same analysis was performed for solid state density of samples RT-21, RT-21(TA), and RT-25, in which a difference of 1.7% was observed. PCM SP-21E and SP-24E showed higher densities of 1.2% and 1.1%, respectively. Finally, the PCMs HS-22P and HS-24P samples showed a difference of 1.1% and a negative difference of 0.2%, respectively. As in the previous case, the PCM 21C and PCM 24C samples could not be compared due to this information was not available in the datasheet.

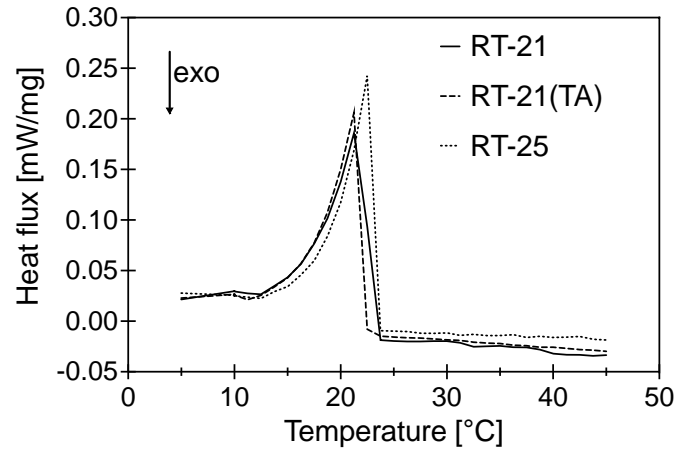
The physical parameters of viscosity and density were determined to establish the greatest number of factors that could influence the comparison and final determination of these materials' capacity for its use as PCM. Concerning viscosity, this property is not included in

the datasheet provided by any of the suppliers. Consequently, it was necessary to have this data to establish if it is a determining property in phase change materials. However, the suppliers did provide the density data, and the values obtained in this investigation are similar to those reported by Rubitherm GmbH (Germany), RGEES LLC (United States) and PCM Energy (India) (Table 1).

### **3.3. Thermophysical characterisation**

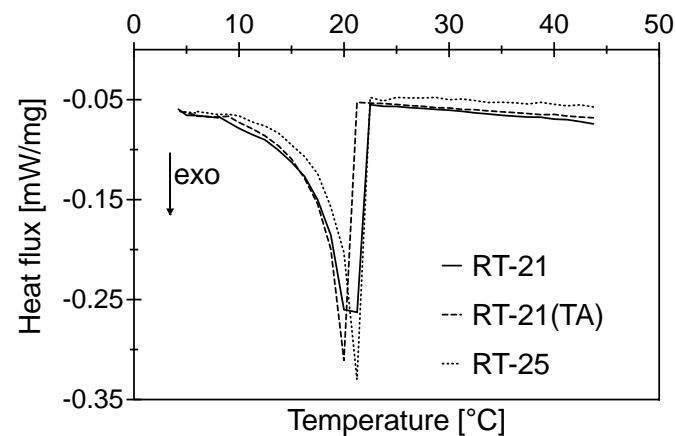
The analysis of temperatures and enthalpies of fusion and crystallisation was performed on all commercial PCM samples. Only the RT-21, RT-21(TA), and RT-25 samples showed positive results in this analysis, which means it was possible to determine the  $T_f$ ,  $T_c$ ,  $\Delta H_m$ ,  $\Delta H_c$ . For the remaining samples, hydrated salts: PCM HS-22P, HS-24P, SP-21E, SP-24E, PCM 21C and PCM 24C, it was impossible to determine these parameters due to typical inconveniences of this type of salts, such as subcooling and phase segregation amongst others (Fig. S2). In general, inorganic salts have shown subcooling problems since they do not solidify at their freezing point, even when they are subcooled several degrees below such point during feasibility assessments for subsequent applications according to cooling-heating cycles; phenomenon widely studied by various authors [43].

Fig. 4 shows the behaviour of three of the PCMs (samples RT-21, RT-21(TA), and RT-25) that presented phase changes (fusion and crystallisation) during the heating and cooling cycles. The results indicated that the steepest curve corresponds to PCM RT-25, with a 120.2 kJ/kg fusion enthalpy.



**Fig. 4.** Fusion DSC curves for organic PCM samples.

In Fig. 5, the behaviour of these three PCMs is shown when they are subjected to the crystallisation process. In this case, defined curves were observed, of which the most pronounced corresponds to PCM RT-25, with a crystallisation enthalpy of 116.5 kJ/kg. Regarding thermochemical characterisations, it is possible to determine the specific heat and enthalpy (latent heat) of materials from the heat flow. Materials with a high enthalpy of phase change heat are attractive elements for application in building materials, for instance, the application of PCM-concrete [39].



**Fig. 5.** Crystallisation DSC curves for organic PCM samples.

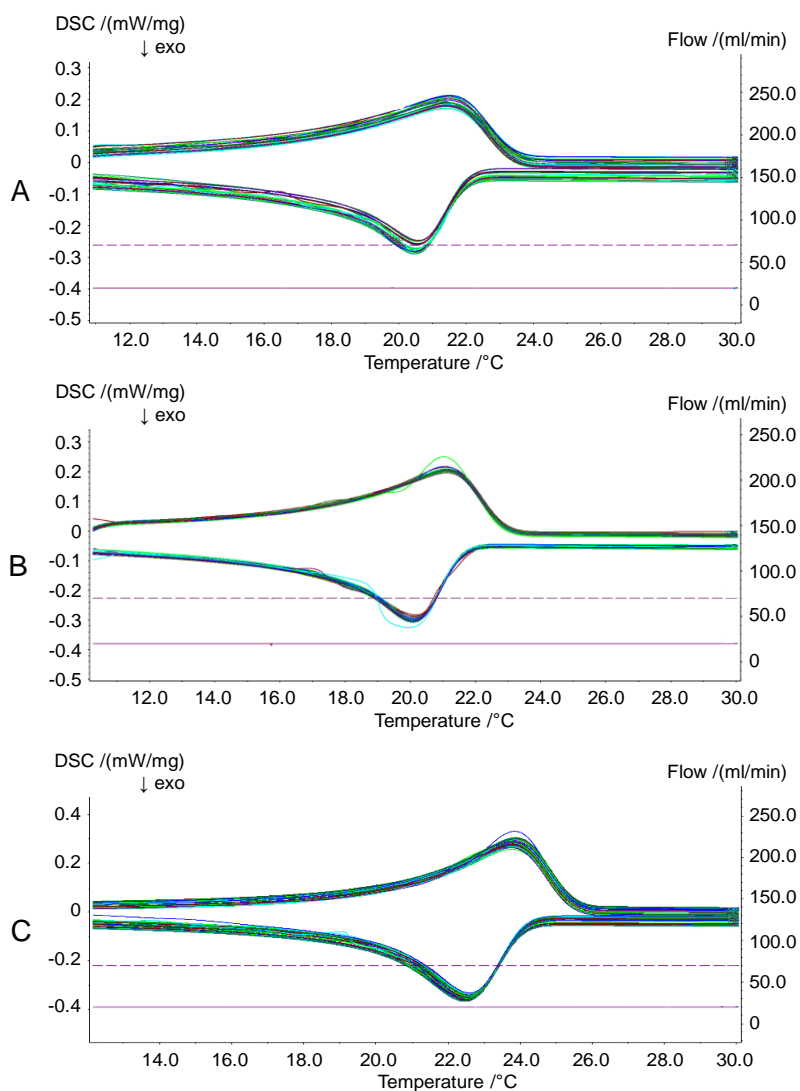
Table 5 details the results obtained from the DSC study, compared with the data provided by the supplier.

In this table (Table 5), it is possible to see that both the fusion and crystallisation peak temperature results are within the range provided by the supplier for all three organic PCMs. However, in practice, heat fusion values are between 19% and 30% lower for PCM RT-25 and RT-21(TA), respectively, when compared with the supplier's values. Similarly, crystallisation heat values are lower than those reported by suppliers between 21% (RT-25) and 34% (RT-21(TA)). As it is to be understood, the fusion and crystallisation heat values indicate the energy storage capacity (in the form of heat) of materials. The heat storage capacity for each of the organic PCMs studied was diminished in the experimental process. The differences in the enthalpies of fusion and crystallisation determined here could be due to the methodological differences in determining these values, which each supplier does not specify, and therefore are unknown to the user. In the case of PCM RT-21 and RT-21 (TA), it is observed that they present different temperatures and transition heats between them, considering that they correspond to the same PCM. However, when assigning the respective standard deviations to Table 5, it is observed that the transition values obtained are the same in reality.

### **3.4. Cyclic stability**

Based on the thermal characterisation results, it was decided to continue with only three samples (RT-21, RT-21(TA) and RT-25) to study cyclic thermal stability. Fig. 6 shows the 50 cycles of the stability study of the RT-21, RT-21 (TA) and RT-25 samples, which showed that for all three cases, these PCMs melt and crystallise in the same way. The samples do not

present significant phase segregation problems, or subcooling, indicating that they are stable compounds for later application.



**Fig. 6.** Stability curve (50 cycles) for organic PCMs **A)** RT-21, **B)** RT-21(TA), **C)** RT-25.

Table 6 shows the temperature and enthalpy of fusion and crystallisation of the three organic PCMs tested for cyclic thermal stability. The values reported in this table correspond to the average of 50 cycles performed for each sample.

When comparing these results with the supplier's values, it is possible to observe that both the fusion and crystallisation temperatures for the three organic PCM studied are within the range provided. However, the differences in enthalpies of fusion and crystallisation persist for all cases. Observing values lower than those of the control between 1.2% (RT-25) and 11.2% (RT-21(TA)) for the fusion stage and lower values between 7.2% (RT-25) and 25.5% (RT-21(TA)) for the crystallisation stage.

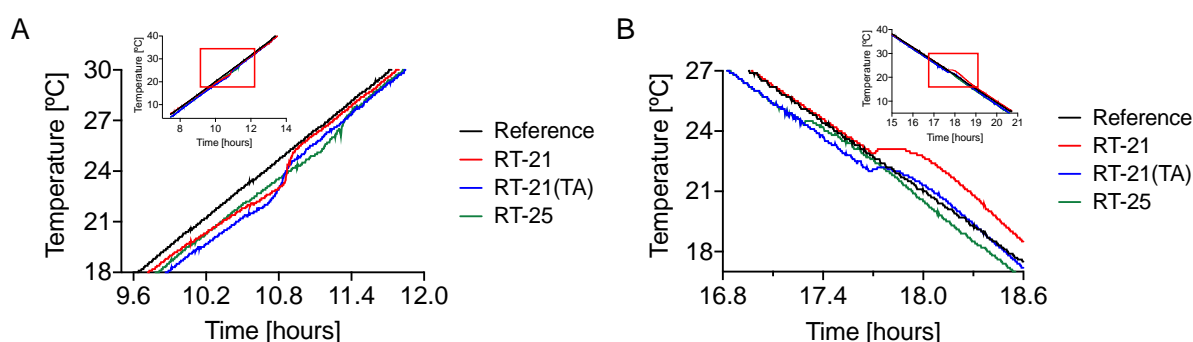
According to the information regarding the PCM's thermal stability, it has been established that the phase change materials must have constant enthalpies and temperatures of fusion and crystallisation during charge/discharge cycles for proper operation and subsequent application. Amongst other factors affecting its applicability is phase segregation, a frequent PCM phenomenon whose composition is based on hydrated inorganic salts and affects the fusion/crystallisation process and thus the energy storage capacity. Similarly, another frequent phenomenon in hydrated inorganic salts is subcooling, a phenomenon linked to the material's inability to crystallise and release the latent heat absorbed in the fusion, which causes the material to only store sensitive heat [44].

In the case of the PCM of organic nature analysed, it was possible to determine the temperatures and enthalpies of fusion and crystallisation. Besides, it was possible to determine that the parameters obtained are close to those provided by the supplier. The organic PCM used showed no subcooling or phase segregation. These observations are under the literature, where it is emphasised that organic PCMs do not present these phenomena compared to inorganic PCMs, mainly hydrated salts. These observations allow us to conclude that organic PCMs are promising for their application in building materials [44].



### 3.5. Thermal behaviour of samples studied with T-history method

After obtaining the results of temperatures and enthalpies of fusion and crystallisation, the study of charging and discharging was carried out using the T-history method, where a larger volume of sample (15 mL) is used to determine the phase change of the PCM since the sample size influences its behaviour [45]. This study is carried out mainly of those PCMs composed of hydrated sales, which did not have a stable behaviour in the previous DSC tests. Fig. 7 shows the behaviour in heating A) and cooling B) for the organic PCMs (RT-21, RT-21(TA) and RT-25).

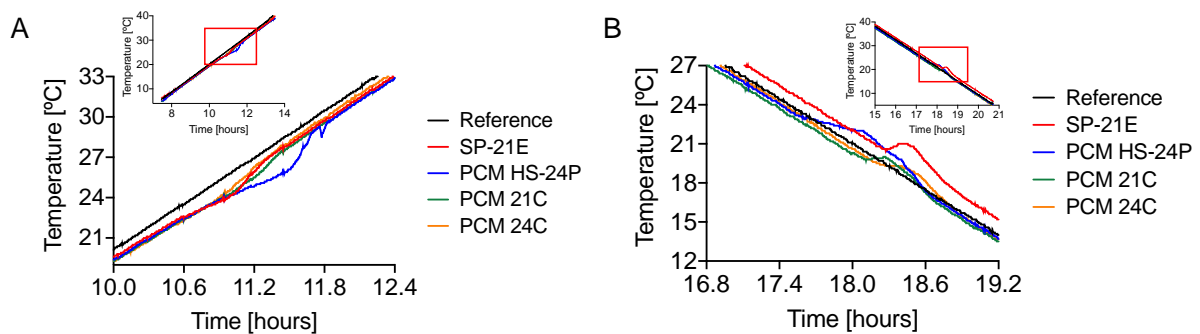


**Fig. 7. A) Heating and B) cooling cycles for organic PCMs (RT-21, RT-21(TA), RT-25).**

It is possible to observe from Fig. 7 that there is no subcooling for all the organic PCM considered in this experiment. It is known that the phenomenon of subcooling is not a characteristic phenomenon of organic compounds. Therefore, for PCMs RT-21, RT-21 (TA), and RT-25, the phase change temperature is considered between the melting point temperature and the inflexion point temperature. These temperature values vary concerning the curve generated for each of the PCMs. As the temperature tends to decrease during the transition period continuously, the difficulty arises to mark the exact limits of each state. Therefore, the inflexion point was taken at the end of the phase change process and

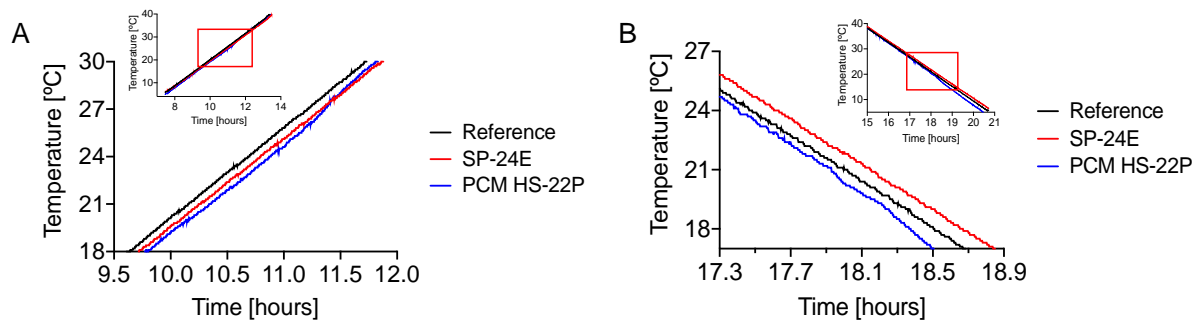
considered the beginning of the solid state. Thus, PCM RT-21 registered phase change for fusion and crystallisation at 21°C and 23°C, respectively, RT-21(TA) at 20°C and 22°C, then RT-25 at 24°C in both stages.

Similarly, the inorganic PCMs tested (Fig. 8), SP-21E, PCM HS-24P, PCM 21C and PCM 24C have a certain degree of subcooling so that the phase change temperature is considered between the melting temperature and solid state temperature. The difference between these temperatures is the degree of subcooling for each PCM ( $\Delta T$ ), obtaining values of 1.8°C, 1.9°C, 1.5°C and 2.8°C, respectively. Even so, all these PCMs show phase change of fusion and crystallisation, indicating that in some way, when taking a larger volume of sample, it is possible to observe this behaviour.



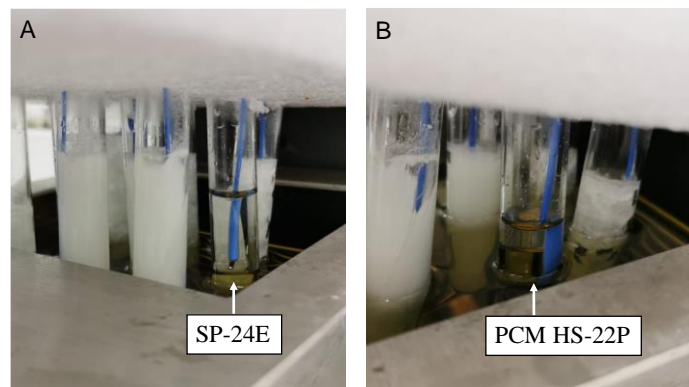
**Fig. 8. A)** Heating and **B)** cooling cycles for inorganic PCMs that showed phase change (SP-21E, PCM HS-24P, PCM 21C, PCM 24C).

However, as shown in Fig. 9, the PCMs SP-24E and HS-22P do not display any phase change, remaining in a liquid state regardless of temperature reduction. This situation may be due to unstable phases since they are saline mixtures. Possible separation and segregation of the solid phase at the bottom of the test tubes might occur. For this reason, these PCMs were discarded for subsequent tests.



**Fig. 9.** A) Heating and B) cooling cycles for inorganic PCMs that showed no phase change (SP-24E, PCM HS-22P).

In Fig. 10, the behaviour of these PCMs (SP-24E and HS-22P) during experimentation is shown. It is possible to observe that both PCMs remained in a liquid state (initial state for the T-history test) during the period in which the experiment was carried out. This is a recurring phenomenon, again due to subcooling. As explained above, subcooling problems are common in hydrated salts where the subcooled liquid remains in a metastable state. The introduction of a crystalline nucleus in the PCM causes a spontaneous crystallisation of all this. Several studies have focused on investigating nucleating agents that can be added in smaller amounts to the material to induce nucleation in the PCM and eliminate subcooling [46].



**Fig. 10.** Behaviour of inorganic PCMs: A) SP-24E and B) PCM HD-22P during the T-history test.

Table 7 summarises the melting and crystallisation temperatures obtained by the T-history method, using DSC and those delivered by the supplier.

The majority of the data obtained in this study were within the range established by the suppliers, without presenting considerable variations or data dispersion (*i.e.* standard deviation). However, PCM 21C and PCM 24C are the samples that showed the greatest data dispersion of fusion and crystallisation temperature, respectively (find values of standard deviation in Table 7). In particular, the results of charging and discharging cycles of organic PCM showed agreement with the suppliers' data due to the high stability of PCM of organic nature compared to those of inorganic nature.

Meanwhile, the inorganic PCMs showed inconsistencies regarding the data reported by the suppliers. The PCM SP-24E and PCM HS-22P did not show a favourable behaviour during the tests carried out because they cannot change phase either by the thermophysical characterisation method or by the T-history method. Unlike the other inorganic PCMs, this situation makes them unstable for subsequent studies since they present severe nucleation problems and are more likely to subcooling. Now, because subcooling is one of the main problems of commercial inorganic PCMs. When they are manufactured, a nucleating agent is added to overcome this drawback, so it might happen that we did not grasp the amount of nucleating agent necessary to achieve the crystallisation at the time of sampling.

On the other hand, the PCM 24C presents a phase change in the fusion and crystallisation process at lower temperatures than those reported by the supplier, making it an ambiguous product when analysing its application in future investigations. These phenomena have been described and characterised previously, showing that inorganic PCMs tend to modify their

thermal behaviour. In general, although inorganic PCMs: PCM 21C, PCM 24C, SP-21E, and HS-24P, obtain lower fusion and crystallisation temperatures than expected (data provider) because they all have subcooling in the crystallisation stage, it was possible to complete the charging and discharging cycles tested.

As previously stated, inorganic PCMs have certain advantages and potentialities, mainly from the construction point of view. They could be functional materials with a lower cost compared to those with an organic base. Due to their nature, they are less abundant and present a series of other complications in their application, especially in view of the safety of these materials. Nonetheless, considering the potentialities, it is relevant to improve inorganic PCM applications and thus overcome complications such as those presented in this work and the related literature. The presence of subcooling complicates the use of these materials in construction techniques such as in impregnation since the PCM would also be dispersed in the construction material, hampering the nucleating agent function, and therefore causing the PCM not to function properly.

It is essential to highlight that, overall, the results presented in this study are sometimes in discrepancy (*e.g.* inorganic salts, mainly DSC results) or not entirely in line with what is reported by the manufacturers (*e.g.* density results). Although the variations may not always be significant, in some cases, the PCMs have failed in fulfilling or completing their thermophysical characterisation cycles. The latest excels the importance of having a detailed description of the thermal behaviour of these materials when looking at further applications. Hence, it is crucial to account for a better and more specific material description from suppliers.

#### 4. Conclusions

A deep search was carried out to select PCMs, including bulk organic and inorganic, from commercial origin to be used in the temperature range of building applications by characterising their thermophysical properties. The results obtained in this study evidence the following:

- PCMs HS-22P, HS-24P, PCM 21C and PCM 24C presented a higher viscosity than expected, with values between 0.024 and 0.12 Pa·s. Thus, viscosity is considered an important parameter to consider when selecting a PCM for incorporation into construction materials
- When comparing the density in liquid state, the PCMs of organic origin present a positive difference not exceeding 1% compared with the supplier's information in all cases. While PCMs of inorganic origin present differences greater than 5.1% (SP-21E), 6.4% (SP-24E), and negative differences of 3.2% (HS-22P), 1.6% (HS-24P).
- For densities in the solid state, PCMs of organic origin showed positive differences of 1.7% in all cases. PCMs of inorganic origin showed positive differences of 1.2% (SP-21E), 1.1% (SP-24E), 1.1% (HS-22P), and a negative difference of 0.2% for HS-24P.
- The DSC measurements showed that organic compounds (RT-21, RT-21(TA) and RT-25) comply with the properties described by the supplier. However, the phase change enthalpies obtained are lower than those provided by the suppliers, with differences for heat fusion between 19% and 30% for PCMs RT-25 and RT-21(TA), respectively, and differences for crystallisation heat between 21% and 34% for PCMs RT-25 and RT-21(TA), respectively.

- Concerning the inorganic bulk compounds studied by DSC (SP-21E, SP-24E, HS-22P, HS-24P, PCM 21C, and PCM 24C), these failed to complete the tests.
- The T-history studies discarded the SP-24E and HS-22P inorganic bulk PCMs since the permanent presence of subcooling in each of the cycles performed.
- PCM 24C was eliminated from the T-history studies. Although subcooling is observed, it manages to complete the cycles. Still, the parameters obtained are far from those reported by the supplier, so attention is recommended for building applications.
- It was possible to establish that the products RT-21, RT-21(TA), RT-25, SP-21E, PCM 21C, and HS-24P showed consistent temperature values compared to the values reported by the suppliers. Thus, these PCMs would be suitable products for their inclusion into gypsum boards under the conditions analysed.
- The results obtained indicate that the PCMs RT-21, RT-21(TA), RT-25, SP-21E, PCM 21C, and HS-24P have adequate properties to be applied in a more complex system. Here we suggest further assess these constituents included as a functional component like in gypsum boards and determine their effectiveness as heat storage materials.

Finally, we recommend that companies that manufacture PCMs—include more detailed product features and characterisation parameter in their database and adequately inform consumers.

**Conflict of interest:** the authors declare no conflict of interest.

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**Table 1.** Technical specification and suppliers of PCMs under study.

PCM	Composition type	Manufacturer	Provider Data						Literature		
			T <sub>f</sub> [°C]	T <sub>c</sub> [°C]	Latent heat capacity [kJ/kg]	$\rho_{liq}$ [g/cm <sup>3</sup> ]	$\rho_{sol}$ [g/cm <sup>3</sup> ]	$\mu$ [Pa· s]	T <sub>f</sub> [°C]	Latent heat capacity [kJ/kg]	Reference
PCM 21C	Inorganic mixture	PCM Energy P. Ltd	21.1	20.8	156	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
PCM 24C	Inorganic mixture	PCM Energy P. Ltd	24.9	24.8	162	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
PCM-HS22P	Inorganic mixture	RGEES LLC	23	22	185	1.540	1.840	n.a.	23	185	[30]
PCM - HS24P	Inorganic mixture	RGEES LLC	25	24	185	1.540	1.820	n.a.	24	185	[31]
SP-21E	Inorganic mixture	Rubitherm	22-23	21-19	160	1.400 (35°C)	1.500 (15°C)	n.a.	21	160	[32]
SP-24E	Inorganic mixture	Rubitherm	24-25	23-21	190	1.400 (35°C)	1.500 (15°C)	n.a.	27.35	97.53	[33]
RT-21	Paraffin	Rubitherm	18-23	22-19	155	0.770 (25°C)	0.880 (15°C)	n.a.	21	133.6	[34]
RT-21(TA)	Paraffin	Rubitherm	18-23	22-19	155	0.770 (25°C)	0.880 (15°C)	n.a.	21	134	[35]
RT-25	Paraffin	Rubitherm	22-26	26-22	148	0.760 (40°C)	0.880 (15°C)	n.a.	26.6	232	[36]

Note: T<sub>f</sub> –fusion temperature; T<sub>c</sub> –crystallisation temperature;  $\rho_{liq}$  – liquid density;  $\rho_{sol}$  –solid density;  $\mu$  –viscosity; n.a. –not available.

**Table 2.** Viscosity of RT-21 compared to literature data ( $\pm$  standard deviation).

Temperature [°C]	Measured viscosity, present study [Pa·s]	Experimental viscosity from [41] [Pa·s]	Viscosity calculated with Eq. 7 [Pa·s]
20	n.a	0.00409	0.004319
25	n.a	0.00363	0.003706
30	$0.0039 \pm 0.00005$	0.00316	0.003191
35	$0.0036 \pm 0.00002$	n.a	0.002756
40	$0.0036 \pm 0.00002$	n.a	0.002388
45	$0.0034 \pm 0.00006$	n.a	0.002069

Note: n.a. –not available.



**Table 3.** Volume changes and fractional expansion values for each PCM.

PCM	$\Delta\rho$ [g/cm <sup>3</sup> ]	$\Delta V/V_{solid}$ [%]
RT-21	0.081	10.42
RT-21(TA)	0.095	12.24
RT-25	0.042	5.40
SP-21E	0.017	1.18
SP-24E	0.059	3.95
PCM HS-22P	0.274	18.25
PCM HS-24P	0.199	13.08
PCM 21C	0.063	4.17
PCM 24C	0.060	3.97

**Table 4.** Supplier and experimental densities in liquid and solid state of PCMs ( $\pm$  standard deviation).

PCM	Provider data		Experimental data	
	$\rho_{liq}$ [g/cm <sup>3</sup> ]	$\rho_{sol}$ [g/cm <sup>3</sup> ]	$\rho_{liq}$ [g/cm <sup>3</sup> ]	$\rho_{sol}$ [g/cm <sup>3</sup> ]
RT-21	0.770 (25°C)	0.880 (15°C)	$0.777 \pm 5.77 \times 10^{-6}$ (25°C)	$0.895 \pm 4.22 \times 10^{-3}$ (15°C)
RT-21(TA)	0.770 (25°C)	0.880 (15°C)	$0.777 \pm 5.77 \times 10^{-6}$ (25°C)	$0.894 \pm 3.60 \times 10^{-2}$ (15°C)
RT-25	0.760 (40°C)	0.880 (15°C)	$0.768 \pm 5.77 \times 10^{-6}$ (40°C)	$0.884 \pm 3.92 \times 10^{-2}$ (15°C)
SP-21E	1.400 (35°C)	1.500 (15°C)	$1.472 \pm 1.53 \times 10^{-5}$ (35°C)	$1.518 \pm 3.95 \times 10^{-2}$ (15°C)
SP-24E	1.400 (35°C)	1.500 (15°C)	$1.489 \pm 6.08 \times 10^{-5}$ (35°C)	$1.517 \pm 2.61 \times 10^{-2}$ (15°C)
PCM HS-22P	1.540	1.840	$1.491 \pm 7.21 \times 10^{-5}$	$1.860 \pm 2.44 \times 10^{-2}$
PCM HS-24P	1.540	1.820	$1.515 \pm 1.04 \times 10^{-4}$	$1.818 \pm 2.80 \times 10^{-2}$
PCM 21C	n.a.	n.a.	$1.495 \pm 3.75 \times 10^{-4}$	$1.507 \pm 2.61 \times 10^{-2}$
PCM 24C	n.a.	n.a.	$1.497 \pm 1.53 \times 10^{-5}$	$1.550 \pm 3.29 \times 10^{-2}$

Note:  $\rho_{liq}$  –liquid density;  $\rho_{sol}$  –solid density; n.a. –not available.

**Table 5.** Comparison of the thermophysical characterisation results carried out with DSC, with data provided by the suppliers ( $\pm$  standard deviation).

PCM	Composition type	Provider data			Experimental data							
		T <sub>f</sub>	T <sub>c</sub>	$\Delta H$	T <sub>f</sub> [°C]			$\Delta H_f$	T <sub>c</sub> [°C]			$\Delta H_c$
		[°C]	[°C]	[kJ/kg]	Peak	Onset	Endset	[kJ/kg]	Peak	Onset	Endset	[kJ/kg]
PCM 21C	Inorganic mixture	21.1	20.8	156	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
PCM 24C	Inorganic mixture	24.9	24.8	162	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
PCM HS-22P	Inorganic mixture	23	22	185	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
PCM HS-24P	Inorganic mixture	25	24	185	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
SP-21E	Inorganic mixture	22-23	21-19	160	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
SP-24E	Inorganic mixture	24-25	23-21	190	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
RT-21	Paraffin	18-23	22-19	155	21.8 ± 0.5	17.7 ± 0.8	23.3 ± 0.7	115.5 ± 2.9	20.9 ± 0.3	18.0 ± 0.2	22.0 ± 0.4	109.9 ± 2.8
RT-21(TA)	Paraffin	18-23	22-19	155	21.4 ± 0.5	18.5 ± 0.6	23.6 ± 0.8	108.7 ± 3.3	20.5 ± 0.4	17.6 ± 0.1	21.6 ± 0.6	102.9 ± 2.9
RT-25	Paraffin	22-26	26-22	148	24.2 ± 0.4	21.4 ± 0.5	25.8 ± 0.5	120.2 ± 2.6	23.1 ± 0.3	21.0 ± 0.3	24.6 ± 0.6	116.5 ± 2.4

Note: T<sub>f</sub> –fusion temperature; T<sub>c</sub> –crystallisation temperature; Peak –peak temperature; Onset –onset temperature; Endset –endset temperature;  $\Delta H$  –latent heat capacity;  $\Delta H_f$  –latent heat capacity of fusion;  $\Delta H_c$  –latent heat capacity of crystallisation; n.a. –not available.

**Table 6.** Enthalpies and temperatures of fusion and crystallisation for the 50 cycles ( $\pm$  standard deviation).

PCM	Scanning rate			
	0.5 °C/min			
	$T_f$ [°C]	$\Delta H_f$ [kJ/kg]	$T_c$ [°C]	$\Delta H_c$ [kJ/kg]
RT-21	$22.0 \pm 0.3$	$152.6 \pm 0.9$	$21.3 \pm 0.5$	$116.1 \pm 1.0$
RT-21(TA)	$21.5 \pm 0.4$	$137.6 \pm 1.2$	$20.5 \pm 0.4$	$115.5 \pm 1.1$
RT-25	$24.2 \pm 0.3$	$146.2 \pm 0.7$	$22.9 \pm 0.5$	$137.4 \pm 0.9$

Note:  $T_f$  –fusion temperature;  $T_c$  –crystallisation temperature;  $\Delta H_f$  –latent heat capacity of fusion;  $\Delta H_c$  –latent heat capacity of crystallisation.

**Table 7.** Comparison of fusion and crystallisation temperatures obtained by the T-history method, DSC and those delivered by the supplier ( $\pm$  standard deviation).

PCM	Composition type	T-history		DSC		Provider data	
		T <sub>f</sub> [°C]	T <sub>c</sub> [°C]	T <sub>f</sub> [°C]	T <sub>c</sub> [°C]	T <sub>f</sub> [°C]	T <sub>c</sub> [°C]
PCM 21C	Inorganic mixture	23 $\pm$ 2.8	20 $\pm$ 0.9	n.a.	n.a	21.1	20.8
PCM 24C	Inorganic mixture	22 $\pm$ 1.0	20 $\pm$ 2.1	n.a	n.a	24.9	24.8
PCM HS- 22P	Inorganic mixture	n.a	n.a	n.a	n.a	23	22
PCM HS- 24P	Inorganic mixture	25 $\pm$ 0.8	23 $\pm$ 0.9	n.a	n.a	25	24
SP-21E	Inorganic mixture	23 $\pm$ 1.7	21 $\pm$ 1.6	n.a	n.a	22-23	21-19
SP-24E	Inorganic mixture	n.a	n.a	n.a	n.a	24-25	23-21
RT-21	Paraffin	21 $\pm$ 0.5	23 $\pm$ 0.2	21.8 $\pm$ 0.5	20.9 $\pm$ 0.3	18-23	22-19
RT-21(TA)	Paraffin	20 $\pm$ 0.4	22 $\pm$ 0.4	21.4 $\pm$ 0.5	20.5 $\pm$ 0.4	18-23	22-19
RT-25	Paraffin	24 $\pm$ 0.6	24 $\pm$ 0.5	24.2 $\pm$ 0.4	23.1 $\pm$ 0.3	22-26	26-22

Note: T<sub>f</sub> –fusion temperature; T<sub>c</sub> –crystallisation temperature; n.a. –not available.