1. Introduction

Because of the environmental context and to reduce dependency on fossil fuels, new solutions and technologies for thermal energy storage appear. The use of phase change materials (PCMs) allows to store and release large amounts of energy in reduced volumes by using latent heat storage through melting and solidifying at specific temperatures. Phase change materials receive a great interest for reducing energy consumption by easing the implementation of passive solar heating and cooling. They can be integrated to buildings as wallboards to minimize temperature’s fluctuations trough the phase change process [1].

Research on PCMs receives a great interest since the last decade. More and more works are published and excellent reviews on PCMs and their applications exist [2-6]. Some commercial products are available but to reach maturity, additional work is needed to predict performances of PCMs accurately [7]. To validate the models and to predict efficiency of PCMs, a perfect knowledge of thermophysical properties of the material is necessary [8]. However, according to some authors, data provided by the manufacturers can be inaccurate and generally optimistic [3]. Among essential properties, PCMs are characterized by the melting and the freezing temperatures, which are temperatures when the phase change process occurs. However, the process can be disturbed by subcooling or hysteresis [4]. Those two problems mean that the phase change transition is not homogeneous or does not occur at the specific phase change temperature of the material. Therefore, the phenomenon is non linear. To limit those problems, some techniques exist like additive injection or special containment for PCMs [2-5] [9].

PCMs’s behaviors are very complex: the relevant thermophysical properties with a meaningful accuracy are quite hard to measure. Generally, PCMs are characterized by calorimetric methods such as “differential scanning calorimetry” (DSC) [10], which use very small quantities of material. However, the low mass of sample may not be representative of the thermal behavior of a larger size used in the building application. An interesting approach, the guarded hot plates configuration, allows testing and characterizing PCMs contained into large size composite wallboards. The device, which includes thermal sources, heat flux sensors, thermocouples and a sample, is surrounded by an effective insulation. Integration of heat fluxes during phase change
process allows determining the performances of the wallboard. Results of various works permitted the validation of the experimental device behavior. Nowadays, it is reliable and inexpensive [11-14].

Through the characterization of a commercial composite PCM, this paper presents a method to characterize the thermophysical proprieties in situ that is potentially in real conditions. Results are compared with the manufacturer’s data [15] and data from literature [16-18].

2. Materials and methods

The experimental device used at the LGCgE (Laboratoire de Génie Civile et géo-Environnement) at Artois University is based on the measurement of temperatures and heat fluxes between the two lateral sides of the composite PCM [13]. The device, shown in figure 1, provides the total heat stored during the phase change process. Using thermoregulated baths, it allows imposing and measuring temperature variations with respect to selected time scales between the two faces. Thermoregulated baths allow regulation of the injected water temperature with a precision of about ± 0.3 °C (Julabo Model F34 HE).

![Figure 1: Experimental device used at the LGCgE [19]](image)

The experimental device allows measuring the peak melting and freezing temperatures of the composite PCM, the total heat storage capacity ($Q$), the specific heat ($c$) and the apparent thermal conductivities ($\lambda$) in the solid and liquid states. With calculations, it is possible to deduce the latent heat of fusion and solidification. To compare results, ranges of temperature used are the same than those used by the manufacturer and those obtained from literature.

Thermal conductivity $\lambda$ (W·m$^{-1}$·K$^{-1}$) is determined using expression (1), with $\Sigma \varphi$ (W/m$^2$) the heat flux measured, $e$ (m) the thickness’s sample and $\Delta T$ (K) the temperature variation:

$$\lambda = \frac{e \Sigma \varphi}{2 \Delta T}$$

To determine the specific heat $c$ (J·kg$^{-1}$·K$^{-1}$), the total heat stored $Q$ (J/kg) is first considered in expression (2), with $C_i$ (J·m$^2$·K$^{-1}$) the thermal capacity, $\Delta \varphi$ (W/m$^2$) the difference between the heat flux of the two faces, $dt$ (s) the acquisition’s period:
Then, expression (3) is used to deduce the specific heat \( c \) (J·kg\(^{-1}\)·K\(^{-1}\)), with \( \rho \) (kg/m\(^3\)) the density, \( e \) (m) the thickness and \( C_i \) the thermal capacity (J·m\(^{-2}\)·K\(^{-1}\)):

\[
c = \frac{c_L}{\rho e} \quad (3)
\]

Total heat storage capacity \( Q \) (J/kg) is given using expression (4) and represents the total amount of energy stored or released, with \( \Delta \varphi \) (W/m\(^2\)) the heat flux density, \( \rho \) (kg/m\(^3\)) the sample’s density, \( e \) (m) the thickness and \( dt \) (s) the acquisition period:

\[
Q = \frac{1}{\rho e} \int_{t_{\text{initial}}}^{t_{\text{final}}} \Delta \varphi dt \quad (4)
\]

Then, it is possible to determine the latent heat capacity \( L \) (J/kg) by expanding \( Q \) (J/kg) in expression (5), with \( c_{\text{mcp,S}} \) (J·kg\(^{-1}\)·K\(^{-1}\)) the specific heat at the solid state, \( c_{\text{mcp,L}} \) (J·kg\(^{-1}\)·K\(^{-1}\)) the specific heat at the liquid state, \( \Delta T_S \) the difference between \( T_{\text{fusion}} \) and \( T_{\text{initial}} \) (melting) or between \( T_{\text{solidification}} \) and \( T_{\text{initial}} \) (freezing), and \( \Delta T_L \) the difference between \( T_{\text{final}} \) and \( T_{\text{fusion}} \) (melting) or between \( T_{\text{initial}} \) and \( T_{\text{solidification}} \) (freezing):

\[
Q = Q_{\text{sens}} + L = \left( c_{\text{mcp,S}} \cdot \Delta T_S + c_{\text{mcp,L}} \cdot \Delta T_L \right) + L \quad (5)
\]

This method to determine thermophysical proprieties of a material has been used to characterize a composite PCM, a product developed by the DuPont de Nemours Society\textsuperscript{TM}. This product called Energain\textsuperscript{®} is a popular composite PCM wallboard constituted of 60% of microencapsulated paraffin included in a polymeric structure. The mixture is laminated by aluminium. It can be installed in any type of building envelope to improve thermal inertia [15]. The melting point of the paraffin microencapsulated is given by the manufacturer at 21.7 °C [15], a temperature included in the range of thermal comfort temperature. According to the CSTB [19-20], the composite PCM Energain\textsuperscript{®} is made up of a commercial paraffin, Rubitherm\textsuperscript{®} RT21 provided by Rubitherm GmbH [21]. Using the simple mathematical model presented before, typical data from manufacturers could be used to set-up a first theoretical approach to determine \( L \). However, it is impossible to deduce latent heat storage capacity using equation (5) because RT21 and Energain\textsuperscript{®} specific heat values are not available.

Sample’s dimensions of the composite PCM are 211 mm × 148 mm × 5.26 mm and the surface of the heat flux sensors are 210 mm × 140 mm. Sample’s mass has been determined in laboratory at 164.5 g, which gives a density of 1001.5 kg/m\(^3\).

Two configurations have been tested: one with the aluminium adhesive tape placed on the sample’s thickness (as provided by the manufacturer) and one without (hereafter Energain\textsuperscript{®} modified) to limit the edge effects.

The remainder of this paper presents the experimental investigation done at the LGCgE with comparisons to data from the manufacturer [15] and data from literature [16-18].

3. Results and discussion

3.1 Results depending on solid or liquid states

Tests have been done to measure the thermal conductivity and the specific heat for the solid state and the liquid state. Results are presented in the table 1. To measure the thermal conductivity, baths are adjusted to induce a temperature difference between the right and the left plates. For each state, tests have been done for higher or lower temperatures than the paraffin melting temperature of 21.7 °C given by the manufacturer [15]. Specific heat is calculated considering a range of temperature for the solid and the liquid state. Flux measurements have been determined with of precision of 4%. Considering a precision of about ± 0.3 °C for the
temperature measurement and using equation (1), thermal conductivity is determined with a precision of 10%.

Table 1. Results of thermal conductivities and specific heat for solid and liquid states

<table>
<thead>
<tr>
<th>Laboratory</th>
<th>LGCgE</th>
<th>LGCgE</th>
<th>[16]</th>
<th>[17]</th>
<th>DuPont™ [15]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product tested</td>
<td>Energain®</td>
<td>Energain® modified</td>
<td>Energain®</td>
<td>Energain®</td>
<td>Energain®</td>
</tr>
<tr>
<td>Density [kg/m³]</td>
<td>1001.5</td>
<td>1001.5</td>
<td>1019.0</td>
<td>900.0</td>
<td>855.5</td>
</tr>
<tr>
<td>Conductivity solid [W·m⁻¹·K⁻¹]</td>
<td>0.14</td>
<td>0.15</td>
<td>0.22</td>
<td>0.22</td>
<td>0.18</td>
</tr>
<tr>
<td>Conductivity liquid [W·m⁻¹·K⁻¹]</td>
<td>0.17</td>
<td>0.13</td>
<td>0.18</td>
<td>0.18</td>
<td>0.14</td>
</tr>
<tr>
<td>Solid specific heat [kJ·kg⁻¹·K⁻¹]</td>
<td>4.5 [7:15 °C]</td>
<td>3.9 [7:15 °C]</td>
<td>4.0* [2:6 °C]</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Range of temperature</td>
<td>2.3 [34:42 °C]</td>
<td>2.2 [27:35 °C]</td>
<td>4.0* T&gt;32 °C</td>
<td>2.4 T&gt;32 °C</td>
<td>NA</td>
</tr>
<tr>
<td>Liquid specific heat [kJ·kg⁻¹·K⁻¹]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Range of temperature</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*: evaluated

As shown in table 1, literature’s values, LGCgE’s values, and manufacturer values differ. First, values of density differ strongly between sources. This is an important result to consider because upcoming experimental and numerical calculations depend on it. For the thermal conductivity of Energain®, an inversion is observed between manufacturer values and LGCgE’s values. During tests, the value of the temperature difference between the plates and the mean temperature of the test do not affect results and reproducibility is ensured despite differences with the manufacturer and literature. Aluminium adhesive tape placed on the material thickness seems to affect material thermal behavior because thermal conductivity values are different without it. Differences on values indicate that the flux could not be unidirectional in the two experimental cases presented because the thermal mass panel is laminated by aluminium protective foils which can disturb heat flow patterns. However, it is impossible to test panels without it because leaks could occur with the PCM mixture, a phenomenon which explains the PCM microencapsulation for building envelope, as discussed by numerous authors [1-5] [9].

As detailed in table 1, specific heat’s value is different from solid state to liquid state. Results for specific heat differ strongly between experimental results and publication of Kuznik et al. [16]. Temperature ranges considered can impact on results. As shown in table 1, differences appear with regards to literature [16] and [17], which shows that difficulties can exist to characterize the thermophysical behavior and proprieties of such a complex kind of materials. Considering those aspects, it appears interesting to evaluate the evolution of the specific heat along a melting cycle with a phase change transition.

3.2 Results with a phase change transition

Complex behavior of composite PCMs are due to the phase change transition for a product considered as a mixture, i.e. not a pure ideal body. In this part, tests are carried out to examine the evolution of the thermal behavior of the composite PCM during a phase change process.

First, specific heat has been evaluated along a melting cycle to explain the difference between values at solid and liquid states and to compare it to the literature [16-17]. Figure 2 represents
an evaluation of the specific heat value according to the temperature. Figure 2 shows that specific heat undergoes a change during phase change transition and presents a melting peak. Globally, during the phase change transition, values are clearly lower than those from literature [16-17] but phase change peak occurs in the three cases between 20 °C and 23 °C, a temperature range including the melting temperature of the paraffin of 21.7 °C [15]. As shown, specific heat’s values differ between publications and experimental tests but global evolution is similar. For the liquid state, tests have given similar values than those reported in the publication of Kuznik et al. [17], with a specific heat stabilized about 2.4 kJ·kg⁻¹·K⁻¹ around 30 °C. In publication [16], the liquid specific heat is different and has been evaluated at 4.0 kJ·kg⁻¹·K⁻¹.

![Figure 2: Experimental specific heat of the composite PCM during melting process (LCGgE, [16], [17])](image)

Concerning the evolution of the specific heat according to the temperature, specific heat value increases strongly from about 14°C. Those values are clearly lower than the melting temperature of the paraffin given by the manufacturer (21.7 °C) [15]. This phenomenon shows that phase change transition is not linear and it could be due to the composition of the material. As explained before, the composite material is not a pure ideal body and it makes difficult to evaluate and isolate thermophysical proprieties of the each material component: the paraffin microencapsulated, the copolymer, the core material which forms the mix paraffin/copolymer and globally the laminated sample.

Tests presented here only show a thermal analysis for a melting process (solid to liquid). During a freezing process (liquid to solid), the composite PCM presents a different behavior. The solidification occurs at a temperature lower than the specified melting temperature and freezing peak value is lower than the melting peak value. According to Kuznik and Virgone [17], the difference between the melting temperature and the freezing temperature characterizes the hysteresis of the material, i.e. the fact that the mixture is not a eutectic.

After having considered the complex behavior along a melting process, experiments have been done using: 1) a linear evolution from solid to liquid; b) a stabilization at a higher temperature than the melting point of the paraffin; and c) then an evolution liquid to solid. The composite PCM heat capacity has been measured using heating and cooling rates of 0.2 K/min, which are rates included between the literature’s rate and the manufacturer’s rate. The thermal analysis is given for a range of [14:30 °C] (as the manufacturer’s information), and for a range of [5-35 °C] (which is included between the literature range [17]). Table 2 presents the results and figure 3 gives a test example for the range [14-30 °C]. Like in the single phase tests, two configurations
have been tested, the composite PCM as provided by the manufacturer (Energain®) and a configuration without the aluminium tape (called Energain® modified).

Figure 3 shows that during phase change process solid to liquid or liquid to solid, heat fluxes present a peak, hereafter peak melting temperature and peak freezing temperature, respectively. The experimental device used at Artois University [13] determined a peak melting temperature of 20.0 °C for the range [14-30 °C] and a peak freezing temperature of 15.9 °C. Total heat and latent heat for heating and freezing modes have been calculated. Calculations of latent heat values are done using expressions (4) and (5) and considering specific heat values measured in the single phase tests.

Globally, total heat and latent heat values are lower than those obtained from the manufacturer [15] and those from literature [17]. A first explanation is provided here for the temperature range [14:30 °C] used by the manufacturer. As explained before, the specific heat value increases strongly from about 14 °C, which can be explained by some local heat storage at this low temperature. Moreover, temperature range [1-34 °C] used by Kuznik et al. [17] gives similar values than that of DuPont [15] concerning the latent heat whereas DuPont proposed it for a smaller temperature range of [14-30 °C].

Concerning results at LGCgE, tests done for the temperature range [14-30 °C] could present a limit in validity because tests begin at a temperature close to the beginning of the phase change process. However, figure 3 shows that peak melting temperature has passed before the stabilization around 14 °C. Another publication of Kuznik and Virgone [18] has established the melting point at 13.6 °C. This value has been considered in calculations of latent heat values. Heat storage quantities for the test with the temperature range [14-30 °C] are on average 28 % lower than those from the test with the temperature range [5-35 °C]. It could be due to the beginning of the phase change process. Consequently, it appears more judicious to consider results of the test for the temperature range [5-35 °C].

The differences observed among all these results reflect the fact that sometimes erratic thermal behavior of composite PCM makes it difficult to evaluate thermophysical proprieties of the material.
Table 2. Results with a phase change transition

<table>
<thead>
<tr>
<th>Laboratory</th>
<th>LGCgE</th>
<th>LGCgE</th>
<th>LGCgE</th>
<th>LGCgE</th>
<th>[17]</th>
<th>DuPont™ [15]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product tested</td>
<td>Energain®</td>
<td>Energain®</td>
<td>Energain® modified</td>
<td>Energain® modified</td>
<td>DSC</td>
<td>DSC</td>
</tr>
<tr>
<td>Method and range of temperature</td>
<td>0.2 K/min [14:30 °C]</td>
<td>0.2 K/min [5:35 °C]</td>
<td>0.2 K/min [14:30 °C]</td>
<td>0.2 K/min [5:35 °C]</td>
<td>0.05 K/min [1:34 °C]</td>
<td>1 K/min [14:30 °C]</td>
</tr>
<tr>
<td>Peak melting temperature [°C]</td>
<td>20.0</td>
<td>20.0</td>
<td>20.0</td>
<td>20.0</td>
<td>22.3</td>
<td>21.7 (paraffin)</td>
</tr>
<tr>
<td>Peak freezing temperature [°C]</td>
<td>15.9</td>
<td>15.4</td>
<td>14.8</td>
<td>14.1</td>
<td>17.8</td>
<td>NA</td>
</tr>
<tr>
<td>Total heat of heating [kJ/kg]</td>
<td>87.9</td>
<td>138.2</td>
<td>85.7</td>
<td>126.7</td>
<td>NA</td>
<td>&gt;170.0</td>
</tr>
<tr>
<td>Total heat of freezing [kJ/kg]</td>
<td>86.2</td>
<td>139.2</td>
<td>86.1</td>
<td>127.2</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Latent heat of heating [kJ/kg]</td>
<td>50.1</td>
<td>69.1</td>
<td>48.8</td>
<td>57.7</td>
<td>72.4</td>
<td>&gt;70.0</td>
</tr>
<tr>
<td>Latent heat of freezing [kJ/kg]</td>
<td>49.3</td>
<td>70.1</td>
<td>49.2</td>
<td>58.1</td>
<td>71.0</td>
<td>NA</td>
</tr>
</tbody>
</table>

Recently, in a new datasheet provided by the manufacturer [22], temperature ranges considered for the total heat storage capacity has changed to [0-30 °C] (compared to [14-30 °C]) and total heat storage capacity is now about 140 kJ/kg (compared to 170 kJ/kg). The total heat storage capacity provided by the manufacturer is now very close to that measured at LGCgE’s laboratory (139.2 kJ/kg for freezing and 138.2 kJ/kg for heating) in the test for Energain® with the temperature range [5-35 °C]. New manufacturer’s values for the latent heat is still being >70 kJ/kg. Similar values have been found in the test [5-35 °C] with Energain®.

In summary, it was found that experimental conditions – like the aluminium tape, the heating and cooling rates or the temperature ranges – affect results for properties evaluation. To evaluate the impact of the specific heat values considered for the calculation of L, various hypotheses have been considered and it forms part of a discussion presented in section 3.2.

### 3.2 Discussion

To evaluate the impact of the specific heat values considered on the latent heat estimated, two calculations have been carried out for a phase transition test with a temperature range of [5:35 °C]. One estimate is done considering a solid and liquid specific heat values equal to 2.3 kJ·kg⁻¹·K⁻¹, as measured at the LGCgE’s laboratory. The other estimate is done with a specific heat value of 4.0 kJ·kg⁻¹·K⁻¹, which is the value of publication [17]. Authors of publication [17] have presented a specific heat value of 2.4 kJ·kg⁻¹·K⁻¹ in another publication [16]. As explained for manufacturer’s data, differences in literature could be the result of difficulties to characterize. Results are illustrated in figure 4 and compared to the manufacturer values [15] [22] and to publication [17] which provided only results on latent heat.
As shown in figure 4, if no consideration is done about temperature range (which differs from 5 °C, but with the same ΔT), LGcG’s results on heat storage capacity are close to the last values provided by the manufacturer [22]. Otherwise, values of specific heat, which have a complex evolution according to temperature and to the phase change process, affect the quantities of latent heat estimated. The problem that arises is that the specific heat value is hard to determine while both phases coexist. The key cause for the difference is the difficulty to define a realistic baseline to isolate the latent heat component. As discussed earlier, composite PCMs begins to melt at relatively low temperatures (about 14 °C) although temperature melting peak has been evaluated around 20 °C. Therefore, a perfect knowledge of the relevant proprieties of the material appears essential to calculate the latent heat and thereby to estimate performances of phase change materials.

4. Conclusions

The method detailed in this paper has proposed experimental results for the thermophysical proprieties of a composite PCM material. The wallboard is constituted of 60 % of a phase change material (paraffin), with 40 % of a copolymer developed by the manufacturer. The experimental device used is based on heat flux and temperature measurements. Measurements have been done using a large size sample wallboard that could be used in real operating conditions. Thermal conductivities and specific heats have been measured depending on various temperatures between solid and liquid states and compare to literature’s results and to data provided by the manufacturer. During phase change process, total and latent heat storage capacities have been evaluated with the peak melting temperature.

With regard to literature, datasheets provided by the manufacturer and experiments, thermophysical characterization is complex for composite PCM, because of the intrinsic particularity of the phase change process itself and the composite nature of the samples. Although temperature melting peak is lying somewhere between 20 °C and 23 °C, composite PCM begins to melt at relatively low temperatures (about 14 °C in this case). This makes the evaluation of relevant thermophysical proprieties of the material very difficult, especially for
specific heat. Complexity can be illustrated by the method used by the manufacturer to present typical data of the product Energain®. Precise values concerning specific heat are not available and latent heat is just estimated as superior to 70 kJ/kg. Moreover, some values for the same material have changed according to publications. Consequently, lacks of typical data can make difficult the validations of numerical model to examine behavior of a composite PCM, especially for model using specific heat.

The methods itself has been found acceptable to characterize large samples of combined materials which may complement calorimetric method, such as DSC. However, the proposed method is also subject to some problems: the aluminium packaging could disturb heat flux by increasing edge effects, which deflect the unidirectional heat flux. This will be considered for further works. To remove it could be a solution, but leaking problems would occur.

Nevertheless, despite several differences with published data, overall results are similar to the latest information provided by the manufacturer concerning total and latent heat storage capacity for the temperature range [5:35 °C].

In conclusion, the complexity of the thermal process within the composite materials containing PCMs requires the development of methods with experimental characterization coupled with numerical models to be able to use those materials efficiently.

5. References


6. Acknowledgements

The t3e industrial research chair thank the LGCD for the collaboration on this project and the DuPont de Nemours Society™ for having provided the samples. The authors would finally like to thank the partners of t3e and the Natural Sciences and Engineering Council for funding the research group.