Elaboration and Characterization of a Novel Buildings Material Impregnated with an Organic PCM for Thermal Inertia Improvement and Energy Saving

Lisa Boussaba[#1], Said Makhlouf[*2], Amina Foufa[#3], Gilles Lefebvre[+4]

[#] *Environment and Technology for Architecture and Patrimonium laboratory, Institute of Architecture, Saad DAHLEB University, Blida 09000, Algeria*

[1]`boussaba.lisa10@gmail.com`

[3]`aafoufa@gmail.com`

[*] *Laboratoire de Mécanique Structure et Energétique, Faculty of construction enginering, Mouloud MAMMERI University, Tizi-Ouzou 15000, Algeria*

[2]`saidmakhlouf@yahoo.com`

[+] *CERTES IUT Paris Est Créteil University, 61 av. General de Gaulle 94010 Créteil Cedex France*

[4]`gilles.lefebvre@u-pec.fr`

Abstract— **The following study focuses on the use of low cost, available and ecofriendly components for the elaboration of a novel composite phase change material (PCM) which may improve thermal inertia of buildings' elements. The goal is to improve the thermal comfort and to decrease the energy consumption rate. Paraffin with a melting temperature range close to the temperature range allowing human comfort is selected as a PCM. It is composed of microcrystalline wax and liquid paraffin; it is available in pharmacies and health facilities. The solid matrix is composed of natural clay powder and cellulose fibers. The cellulose fibers are obtained from the recycling of waste paper. Graphite is added to the matrix in order to improve the thermal conductivity of the composite-PCM. The PCM is introduced into its matrix following a single face immersion method of the matrix into the melted PCM.**

Keywords— **Paraffin, Composite-PCM, Thermal inertia, Thermal energy storage, Building application.**

I. INTRODUCTION

Nowadays, the building sector becomes one of the leader consumers of energy due to the excessive use of heating and air conditioning systems. The use of these consuming-energy systems is the only way to ensure thermal comfort in buildings; the increase of space and building thermal inertia is necessary to reduce the active heating, ventilation and air conditioning systems (HVAC) utilization. It is shown that it is an effective mean to conserve energy and to reduce peak energy demand for HVAC systems [1].

A good thermal inertia of buildings is essentially obtained by storing thermal energy inside an insulated envelope. The thermal energy may be stored as latent heat or sensible heat [2]. Thermal inertia based on latent heat thermal energy storage (LHTES) using Phase Change Materials (PCMs) is recognized early as an attractive mean to ensure thermal comfort in buildings [1]. So the use of these PCMs for LHTES in the building sector began in the mid-1940s.Without counting traditional arctic ice igloo constructions which are the first traditional constructions utilizing ice as a PCM. The first PCM house was designed by the architect Eleanor Raymond in collaboration with the mechanical engineer Maria Telkes in 1948 in Dover, Massachusetts, USA. It was one of the most ambitious ecotechnological experiments in the immediate post-war [3, 4].

Thermal storage with sensible heat storage technique is ensured using a storage medium. The heat capacity depends on the material type and the amount of material (the mass). Sensible heat thermal energy storage systems in buildings are very large and massive [5]; then, large heavy masonry walls have traditionally been used as passive storage elements in the past to ensure thermal comfort [6]. If we look to the traditional constructions such as Berber and Mozabite houses, we find that they are relatively thermally comfortable thanks to the thickness of their stone and earthen walls. The thermal energy is stored inside as sensible heat energy.

Several materials as adobe, stone and brick satisfy the requirements for sensible heat storage but this process is not always sufficient in order to stabilize the temperature swings because of the sensible temperature increasing of the storage mediums [6, 7]. Thereby, the use of LHTES using PCMs is more interesting because of its high storage density in a small temperature interval [8]. Excess heat in the ambient air is absorbed by the PCM during warmer periods and released during cooler ones at almost constant temperature, so it prevents large temperature fluctuations [9]. It is important to know that the integration of the PCMs in the buildings' envelope does not alter directly the net heat conducted

thought the envelope, but it alters the average room temperature [10].

Despite their good performance in controlling indoor temperatures and energy saving in buildings, the practical implementation of PCMs is hindered because of the lack of researches and equipment.

The present study is principally concerned with the elaboration of a porous building material impregnated with an organic PCM. Since the impregnation method offers a number of advantages which render them useful for LHTES in buildings elements [11] in one hand, and the process has the potential for achieving higher storage capacity than others in another hand [12].

Organic PCMs have a number of suitable properties as: chemical stability, safety, availability in broad temperature range and reasonable costs [13]. They are also compatible with various buildings materials [14]. The organic PCM used in this study is composed of microcrystalline wax and liquid paraffin. It is integrated in a porous matrix composed of natural clay powder and cellulose fibers. The cellulose fibers are obtained from recycling of waste paper and are integrated in the matrix in order to improve its porosity. It is known that wastes from industrial or agricultural productions lead the formation of pores when they are incorporated in building materials [15]. The graphite is added into the matrix in order to improve its thermal conductivity. Graphite is known for its high thermal conductivity which varies from 24 to 470 W/mK [16].

The thermal and physico-chemical characterizations have been done. Differential Scanning Calorimetery (DSC) and Thermo Gravimetric Analysis (TGA) are used for a thermal characterization; Scanning Electron Microscopy (SEM) allows observing the microstructure of the composite. Both Fourier Transformed Infrared Spectroscopy (FT-IR) and X-ray Diffraction (XRD) are used for a chemical characterization.

II. EXPERIMENTAL

A. Materials

Paraffin composed of microcrystalline wax and liquid paraffin is used as a PCM for the LHTES. Its melting temperature range turns around 32.5 °C. This PCM may be purchased in pharmacies.

The matrix which contains the PCM is synthesized in the laboratory. It is made of clay powder, cellulose fibers for porosity improvement and graphite for improving its thermal conductivity.

The natural clay powder and the graphite size particle distribution curves are shown in Fig. 1 and Fig. 2 respectively. Table I lists the particle size distribution parameters of the natural clay powder and the graphite used.

B. Preparation of the cellulose fibers

In order to prepare the matrix, cellulose fibers are obtained by soaking recovered cartons of molded cellulose into the water after being rinsed with distilled water. The purpose of soaking is to separate each fiber from another. The obtained

paste is then dried in an oven for 24 hours at 105 °C. Finally, it is grinded using an electric shredder.
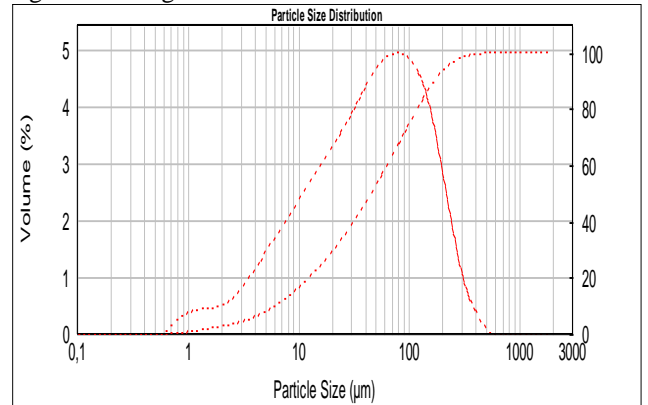

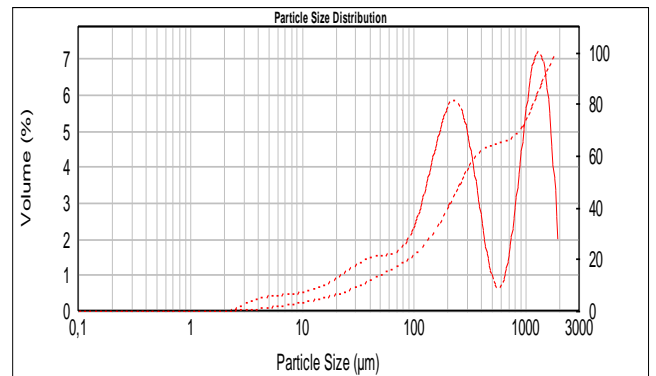Fig. 1 Particle size distribution curve of the natural clay powder

Fig. 2 Particle size distribution curve of the graphite powder

TABLE I
PARTICLE SIZE DISTRIBUTION OF CLAY AND GRAPHITE POWDERS

Samples	d(0.1) ʮm	d(0.5) ʮm	d(0.9) ʮm	S/g (m²/g)
Clay powder Numerical values	6.164	45.675	170.949	0.426
Graphite numerical values	34.338	264.504	1446.513	0.0821

Annotation: d (0.1), d (0.5) and d (0.9) refer to the corresponding particle size when the cumulative distribution reaches 10%, 50%, 90% respectively
When s/g is the specific area of particles on weight basis.

C. Preparation of the matrix and the composite-PCM

The matrix is composed of natural clay powder, cellulose fibers and graphite. The composite-PCM is prepared by introducing the PCM in its melted state into the porous matrix.

The processes of the elaboration of both the matrix and the composite-PCM are straightforward.

First, the natural clay powder, cellulose fibers and graphite are mixed together. Subsequently, distilled water is added to the matrix until the ratio (water/dry component) is equal to 1.

The resulted paste is left in the open air for 2 hours. After this, it is poured in a rectangular mold and an uniaxial force is applied. The obtained pellets of (40x40x12) mm dimension are dried in an oven at 105 °C for 24 hours. Finally, they are cooled at the room temperature in a glass tight box to prevent the penetration of the moisture.

The composite-PCM is prepared following the immersion process [17, 18]. Only one face of the experimented pellets is poured into the melted PCM for 30 minutes. There is one surface contact (liquid/solid) [18].

The PCM is maintained on a water bath at a temperature of 50 °C when the impregnation process is being operating. Pellets are impregnated with PCM thanks to the capillary and surface tension forces.

Six samples are prepared with different weight fractions of the components. When the impregnation process is finished; thermal treatment is carried out on a filter paper at 50 °C for 30 minute into an oven. The purpose is to test the ability of each sample to retain the PCM in its melted state. Table II lists the PCM absorption rate of each sample before and after thermal treatment.

TABLE II
PCM ABSORPTION RATES OF THE SAMPLES BEFORE AND AFTER THERMAL TREATMENT

Samples	Comp 1	Comp 2	Comp 3	Comp 4	Comp 5	Comp 6
PCM absorption rate: before thermal treatment (wt %)	49.70	58.88	65.60	43.50	47.43	82.57
PCM absorption rate: After thermal treatment (wt %)	49.60	58.79	65.41	43.50	47.40	82.25

D. Analysis methods

Fourier Transformed Infrared Spectroscopy (FT-IR), (JASCO FT/IR-4100 spectrophotometer) is used to study the chemical compatibility between the different components of the experimented material. The IR spectra of the different KBr pellets are recorded in a transmission mode with a frequency range between 400~4000 cm^{-1}.

X-Ray Diffraction (XRD) is done using (D2-PHASER BRUKER X-Ray Diffractometer) to characterize the crystalline phase of the composite-PCM under Cu-Ka radiation and $Ʌ$= 1.541874 Å conditions.

The Scanning Electron Microscopy (SEM) is performed to observe the morphology and the microstructure of the experimented composite before and after its immersion in the liquid PCM. (PHILLIPS ESEM XL 30 model) is used with 20 KV of acceleration voltage.

The Differential Scanning Calorimetry (DSC) of both the PCM and the composite-PCM is carried out with a heating rate of 5 °C/min and a cooling rate of 10°C/min in the temperature range of (-10°C~60 °C). (DSC Q100 of TA instrument) is used.

The Thermo Gravimetric Analysis (TGA) allowed evaluating the thermal stability of the composite-PCM. The test is performed using (PerkinElmer Simultaneous Thermal Analyzer STA 6000) with a heating rate of 10 °C/min from room temperature (20 °C) to 600 °C.

III. RESULTS AND DISCUSSION

A. FT-IR analysis

FT-IR is performed to study the chemical compatibility between the different components of the composite-PCM. Fig.3 shows the FT-IR spectra of each: the PCM, the cellulose fibers and the composite-PCM. From the PCM spectrum, the peak at 2922 cm^{-1} and 2855 cm^{-1} are the specific absorption bands of alkanes (C_nH_{2N+2}). The characteristic absorb peak at 1630 cm^{-1} is belonging to the CH_2 group when the band at 1380 cm^{-1} is related to the methyl group which is a hydrophobic group. This result is confirmed by Peterson [19].

The spectrum of the cellulose fibers ($C_6H_{10}O_5$) [20] shows the –CH_2 bending peak at 1432 cm^{-1}. The peak at 1641 cm^{-1} is attributed to the C-O bending and the other peaks at 1100cm^{-1} and 1500 cm^{-1} are reported to several C-H stretching vibrations. The result is confirmed by Hinterstoisser [21].

As seen in Fig.3, the spectrum of the composite-PCM contains all the characteristic peaks of its components. So, all spectra show the characteristic peaks of O-H and characteristic bands of C-H. No new peaks are reported on the spectrum of the composite-PCM. As a conclusion, there is only a physical interaction between the different components of the composite-PCM. The PCM is absorbed and retained thanks to the capillary and surface tension forces without any chemical interaction.
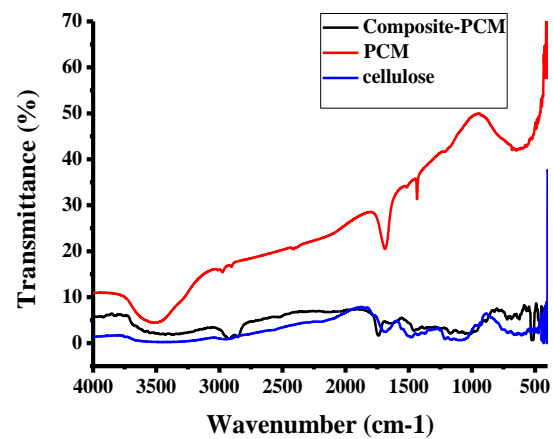

Fig. 3 FT-IR spectra of PCM, cellulose fibers and the composite-PCM

B. X-Ray Diffraction analysis (XRD)

Fig.4 shows the XRD patterns of each: the composite-PCM

and the PCM. The results show that both the PCM and the composite-PCM have the same peaks representing crystalline and non-crystalline materials. The peaks representing crystalline material are reported at mostly regular intervals. So it appears at around 22°, 26°, and 30 °. The peaks exhibited at 26° shift to a greater angle. The XRD patterns show that the peaks become less distinct at above 30°.

As a conclusion, since no shift in the characteristic peaks of the PCM and the composite-PCM is observed, there is no chemical reaction in the composite-PCM. The combination between the PCM and its matrix is only physical. This result is confirmed by Ruilong [22]. The greatest peaks exhibited at 26° can mean closer crystallographic packing which can be related to the fact that the materials expand when heated [19]. The peaks become less important above 30° because of the presence of non-crystalline materials due to the melting of the PCM when the temperature exceeds its characteristic melting point.
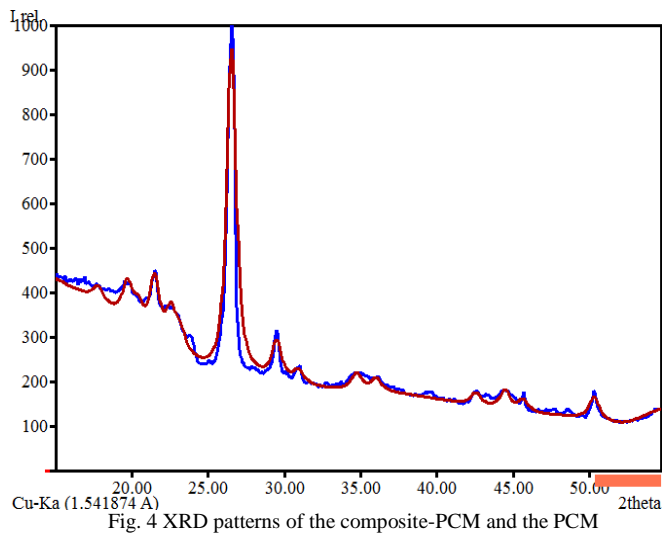

Fig. 4 XRD patterns of the composite-PCM and the PCM

C. Scanning Electron Microscopy (SEM)

Fig.5 shows the ESEM micrographs of the experimented matrix before its immersion in the liquid PCM and those of the composite-PCM after its immersion in the PCM. The microstructures are observed under different magnifications.

Fig. 5(a) (x 250 magnification) and fig. 5(c) (x 500 magnification) show the rough and accidental microstructure of the composite (the matrix) before its immersion in the PCM. This matrix presents non-smooth microstructure. As seen in fig. 5(b) (x250 magnification) and fig. 5(d) (x 500 magnification), the PCM is uniformly absorbed and successfully confined in the microstructure of the matrix.

It can be concluded that the rough and the porous microstructure of the matrix allows to absorb the PCM and to retain it without seepages and leakages thanks to its capillary and surface tension forces.
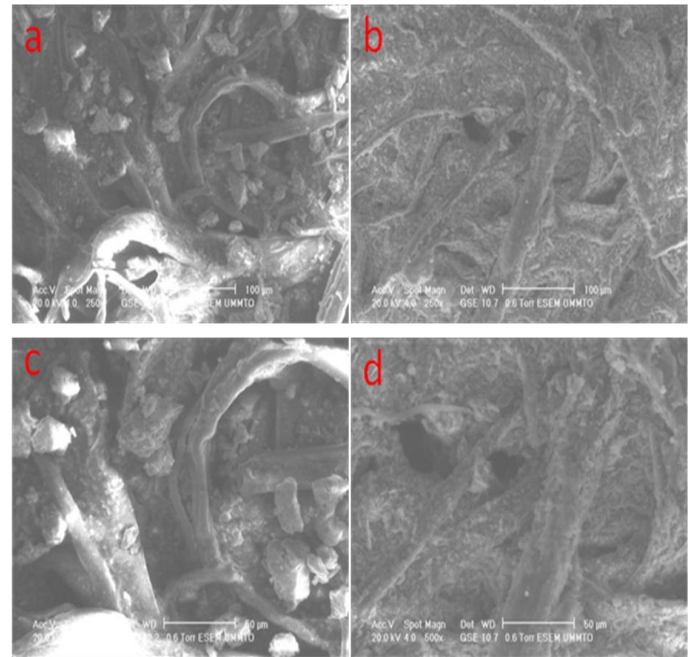

Fig. 5 ESEM micrographs of: a, c): the composite before its immersion in the PCM, b, d): the composite-PCM after the immersion process

D. Differential Scanning Calorimetry (DSC)

Fig.6 and Fig. 7 show the DSC curves of each: the PCM and the composite-PCM. The DSC test is performed on "Comp 6" because of its best absorption rate of the PCM.

Fig. 6 shows the respective melting cycles curves of the PCM and the composite-PCM while Fig. 7 shows their crystallization cycles curves. As can be seen from Fig. 6, the PCM melts at the temperature of 32.5 °C with a latent heat of fusion of 107.18 J/g. The composite-PCM curve displays the melting temperature at 37.5 °C while the latent heat of fusion is 45.12 J/g.

The crystallization curves of the PCM and the composite-PCM reported at Fig.6 shows their solidification temperatures at 29.5 °C and 35 °C respectively. The respective latent heat of solidification values of the two samples are 168.73 J/g and 60.75 J/g.

The thermal properties of the tested samples are reported in Table III. Table IV compares the obtained results to others found in the literature. The DSC result shows that the experimented composite-PCM has the potential to be a good candidate for an application of thermal energy storage in buildings.

TABLE III
THE THERMAL PROPERTIES OF THE PCM AND THE COMPOSITE-PCM

Samples	Melting points (°C)	Latent Heat of fusions (J/g)	Freezing points (°C)	Latent Heat of Freezing (J/g)
PCM	32.5	107.18	29.5	168.73
Composite-PCM	37.5	45.12	35	60.75

| Samples	Melting point (°C)	Latent Heat of fusion (J/g)	Freezing point (°C)	Latent Heat of Freezing (J/g)	Ref
Wallboard impregnated with Butyl-Stearate.	20.9	25.5	17.8	28.4	[14]
Concrete block immersed in PCM.	21.7	8.02	19.6	8.08	[23]
Autoclaved concrete blocks immersed in a PCM.	23.7	6.95	18.4	6.91	[23]
Wallboard impregnated with Dodecanol.	20	47	21	-	[14]
Composite clay/ cellulose fibers/ graphite impregnated with PCM	37.5	45.12	35	60.75	This study
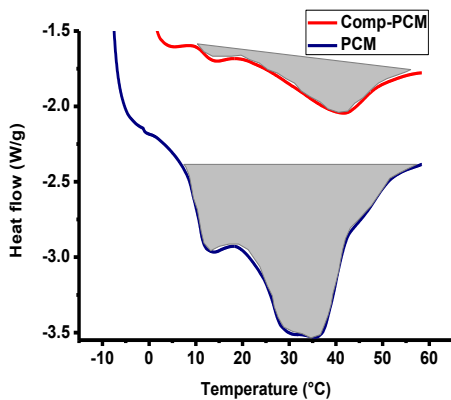
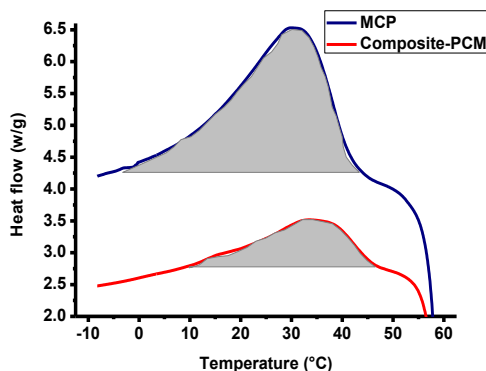Fig. 6 The DSC melting curves of the PCM and the composite-PCM

Fig. 7 The DSC freezing curves of the PCM and the Composite-PCM

E. Thermo Gravimetric Analysis of the composite-PCM

The TGA is performed in order to study the thermal reliability of the composite-PCM. Fig. 8 represents the TGA curve of the synthesized composite-PCM. As can be seen from Fig. 8, the curve displays mainly three stages of thermal degradation. The first stage of the weight loss of the composite-PCM begins effectively at 160 °C ± 10°C and completely decomposes at 280 °C ± 10°C. It corresponds to the thermal degradation of the PCM. The TGA curve shows a few weight loss of the composite-PCM at 100°C and it corresponds to the evaporation of the moisture.

The second step of the degradation occurs between 290 °C and 430 °C ± 10°C. It is related to the thermal degradation of the cellulose fibers. The final step takes place above 450 °C and it is reported to the thermal degradation of the natural clay. The TGA curve of the synthesized PCM shows that no weight loss is reported less than 100 °C. This result means that the composite-PCM is thermally stable in its working temperature range. There is no risk of thermal degradation of the composite-PCM in the working temperature range.
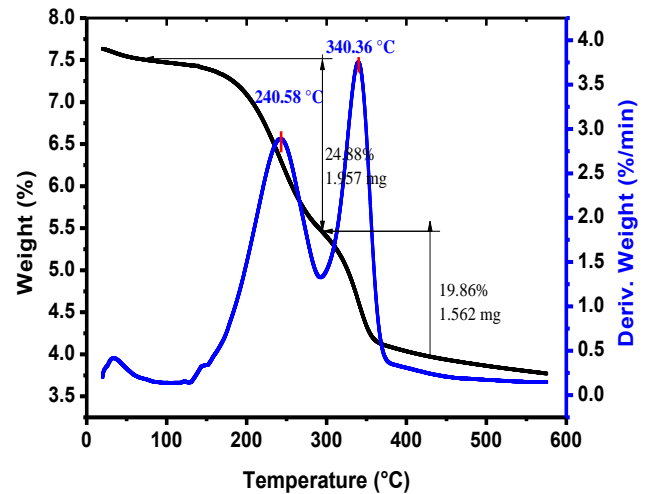

Fig. 8 TGA curve of the composite-PCM

IV. CONCLUSION

In this study, a composite phase change material is prepared for an application of thermal energy storage in buildings. The matrix is synthesized in the laboratory from natural clay, cellulose fibers and graphite. The PCM is incorporated in its matrix following the immersion method of the matrix in the PCM. The PCM is maintained in its melted state for 30min when the impregnation process is being operating. The maximum absorption rate of the PCM recorded before and after thermal treatment is 82.57 wt % and 82.25 wt % respectively. This result is obtained with the sample "Comp 6". The results of FT-IR and XRD reveal that there is only a physical combination between the different components of the composite-PCM. There is no chemical reaction. The result of SEM shows that the PCM is uniformly

distributed in the microstructure of its matrix and it is successfully retained thanks to the capillary and surface tension forces. The DSC analysis curves of the composite-PCM displays that the melting and freezing temperatures of the material turn around 37.5 °C and 35 °C respectively. The respective latent heats of fusion are 45.12 J/g and 60.75 J/g. The result of the TGA confirms that the experimented composite-PCM has a good thermal reliability above its working temperature range.

As a conclusion, the results of the characterization of the composite-PCM show that the material can be a potential candidate for an application of thermal energy storage in buildings.

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