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Investigation of eco-friendly and economic shape-stabilized composites for building walls and thermal comfort

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Abstract: The objective of this study is to investigate the potential of natural fibers as support materials for PCMs for buildings application using shape-stabilization. The material selection software Ansys Granta has allowed a preliminary selection of four natural fibers (fir fibers, hemp fibers, hemp shives and flax mulch) based on physical, thermal, geographical and economic criteria. The candidates fibers are impregnated with capric acid and lauric acid and their performances are compared, allowing the selection of the fiber with the highest impregnation rate. Hemp shives with maximum impregnation rate of about 50 wt% with LA and a good thermal stability under 150 °C has shown the best performances and has been selected as support material. Afterwards, it has been impregnated with 5 different pure fatty acids and 7 eutectic mixtures in order to identify the best composite. Most of the composites developed have latent heat higher than 50 J g^{-1}, which is very promising for energy storage in buildings application. Taking into account the thermal requirements, which are high latent heat, low undercooling and temperature of fusion ranging from 15 to 45 °C, lauric acid hemp shives composites has been selected as potential materials for buildings application with promising performances (enthalpy of fusion of 79.31 J g^{-1} at 50 wt% of impregnation rate).

1 Introduction

Building is one of the most energy-intensive sector in the world, accounting for 40% of the total energy consumption and 33% of greenhouse gas emissions [1]. A large part of the energy demand in buildings is used to prevent temperature changes in the indoor space, or to regulate the thermal conditions of the indoor space within the comfort range. In order to reduce the environmental impact of buildings, a new regulation for buildings namely RE2020 in replacement of the RT2012 has been set by the French government [2]. The RE2020 has three main objectives: to prioritize energy sobriety and decarbonization; to reduce the carbon impact of building construction; to guarantee the comfort in hot weather, as heat waves are expected to become increasingly frequent.

Latent heat thermal energy storage (LHTES) is an efficient technique to increase the thermal capacity, energy efficiency and comfort impact of buildings due to the integration of phase change materials (PCMs) [3–8] and could contribute to the previous objectives. Shape-stabilized PCMs are presented as a promising technique to incorporate PCMs in buildings envelopes [9,10]. This technique consists in impregnating a porous support with a PCM in order to stabilize the PCM and limit the risk of leakage. The shape-stabilization technique is simple, inexpensive, possesses high impregnation rates compared to other techniques and is compatible with a wide variety of support materials including polymers, porous materials and nanomaterials. These shape-stabilized composites would ensure insulation like the conventional insulating construction materials but would also contribute to keep indoor temperature for thermal comfort.

Depending on the building user, the comfort temperature may be different (currently ranging from 18 to 25 °C according to the relative humidity, sunlight etc.). The composites considered in this study should be integrated into an insulating wall, itself in building envelopes. The latters, having low conductivities, are unfavorable to thermal transfers. In addition, thermal losses can occur in building walls. Thus, we have voluntarily increased the maximum melting temperature of the PCMs that will be integrated in these walls to overcome these drawbacks (PCMs melting temperature should therefore be between 15 °C and 45 °C).

Renewable materials, such as natural fibers, are considered as promising carbon sequestration resources with beneficial effects on the planet’s ecosystems, living environment and energy efficiency [11–13]. In addition, their porous structure is suitable for shape-stabilization. They are also compatible with the construction materials and several formulation of concrete has been proposed in the literature [14–17]. Ma et al. [18] impregnated capric-palmitic acid (CA-PA) eutectic mixture in delignified wood to create a form stable PCM using vacuum impregnation method with an impregnation rate of 61.2 wt% without leakage. The composite presented high thermal stability and reliability, a phase transition temperature of 23.4 °C and a high latent heat of 94.4 J g^{-1}. Sheng et al. [19] fabricated a composite PCMs as-supported by carbon fiber bundles by a simple vacuum impregnation. The porous and honeycomb-shaped carbon fibers were prepared by the direct carbonization of biomass sisal fibers and impregnated with a petroleum derivative (paraffin) with two fusion (25 °C and 60 °C) and solidification pics (25 °C and 57.6 °C). The composite PCMs showed very high latent heat (192.2 J g^{-1} at a carbon ratio of 12.8 wt%), good shape stability, favourable thermal reliability and cyclability.

Despite the mentioned studies, natural fibers PCM composites especially fatty acids and their eutectic mixtures have been poorly studied considering the wide variety of natural fibers. A literature review conducted by Sawadogo et al. [20] has allowed the establishment of a list of potential candidates for shape-stabilization (**Table 1**). The novelty of this study is an extensive investigation and the fabrication of eco-friendly and economic shape-stabilized PCMs, impregnated within natural fibers,for building application.

To achieve that, a first investigation using Ansys Granta, a material selection software, with selection criteria such as availability, cost and renewable nature has allowed the identification of four natural fibers as potential candidates for shape-stabilization: fir fibers, hemp fibers, hemp shives and flax mulch. In addition, these fibers fulfil physical requirements such as high water absorbency, porous structure and low thermal conductivity. In fact, the low thermal conductivity will allow a continuous release of heat from the PCMs over a long period whereas high water absorbency and porous structure would ensure good impregnation rate. The impregnation technique depends on several criteria such as the residence time and the condition of the impregnation (under vacuum or atmospheric pressure). For this reason, a preliminary study has been conducted with hemp shives impregnated with capric acid in order to establish a suitable experimental protocol for this study. Afterwards, the natural fibers selected as potential candidates are impregnated with capric acid and lauric acid following the experimental protocol set up and their performances are compared allowing the selection of an adequate natural support material. The criteria of comparison are impregnation rate and mass degradation. After this first step, hemp shives showed the best results and has been selected as support material. The second step of the study is dedicated to the selection of the PCM for the fabrication of the final composite. Therefore, hemp shives have been impregnated with 5 pure fatty acids and 7 eutectic mixtures. The resulting hemp shives/PCM composites are compared in terms of impregnation rate, energy storage capacity and temperature of fusion in order to select the best composite for buildings walls.

Table 1. Natural fibers as potential candidate support materials for the fabrication of shape-stabilized PCMs.

Natural fibers	Density (kg m^{-3})	Thermal conductivity (W m^{-1} K^{-1})	Cost (€ kg^{-1})	References
Bamboo fibers	431-538	0.077-0.088	-	[21]
Hemp fibers	25-100	0.040-0.049	2-5	[22]
Flax fibers	20-100	0.035-0.045	5-25	[22]
Cotton stalk fibers	150-450	0.058-0.082	-	[23]
Hemp shives	100-140	0.080-0.012	0.8-1	[24]
Kapok	17	0.030-0.049	-	[25–27]
Coco fibers	40-90	0.050-0.058	63	[28]

2 Preliminary selection of the materials

Two series of experiments are carried out successively: the first one aims at selecting the support material, thus several types of fibers are investigated, the second one aims at selecting the PCM to impregnate the fiber retained after the first experimental series.

2.1 Selection of the fibers

The material selection software Ansys Granta has been used for the selection of the natural fibers. Ansys Granta is a material selection software based on a set of criteria such as physical-chemical, thermo-mechanical and environmental properties, manufacturing processes and raw material costs. The large number of materials available in its huge database is an important feature in the selection process. In this study, the natural fibers are selected based on physical, thermal, economic and geographical criteria of several families of materials. The materials are selected based on four criteria: i. bio-based, ii. produced in European continent, iii. with high water absorption and porous structure to obtain good impregnation rate and moisture regulation capability and iv. with low thermal conductivity to replace converenntional insulation in building walls.

The material category "natural fibers" in Ansys Granta allowed the accomplishment of the first selection criterion. The natural fibers within the database of the software and their location are presented in **Fig. 1** (see the geographical origins of all the fibers selected in red and green in **Fig. 1**). The second criterion leads to the elimination of the majority of the natural fibers in the software (see red color in **Fig. 1**). At this stage, only hemp fibers, hemp shives, flax mulch and fir pellets are satisfying the first two criteria.

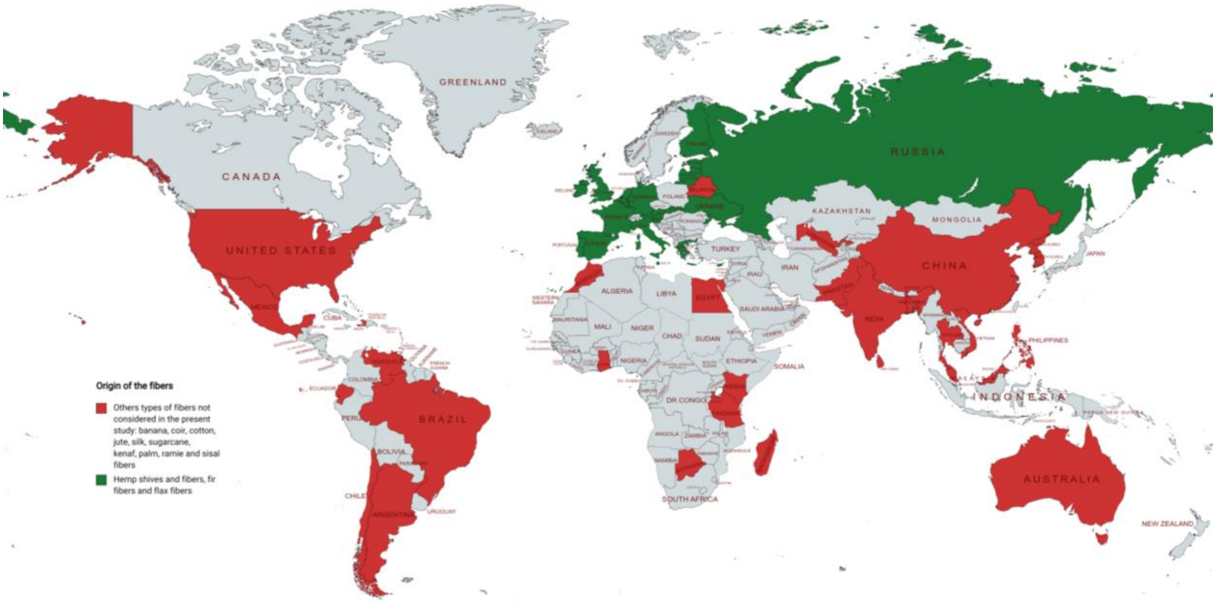

Fig. 1. Type of fibers and their origin provided by Ansys Granta Software.

The water absorbency of the selected fibers are presented in **Table 2**. All the selected fibers possessed a water absorbency higher than 200 wt% meaning that they can absorb more water than twice the weight of the dry fibers making them suitable for the impregnation process with expected high impregnation rates with fatty acids. The microporosity and the pores diameters of the fibers are also indicators of the absorption capacity of a material and necessary to make the composite, so that the fibers encapsulate the PCM and prevent its leakage during fusion. Scanning electron microscopy (SEM) images of flax mulch and hemp shives in the literature justify their use in PCM impregnation process [29] due to their very porous structure. Indeed, the pores diameters of hemp shives are between 15 and 40 µm and those of flax mulch between 5 and 20 µm. For fir pellets and hemp fibers, there are no information on their microstructure in the literature.

Table 2. Properties, origin and cost of the selected fibers for this study.

	Fir pellets	Hemp fibers	Hemp shives	Flax mulch
Water absorbency (wt%)	200 [a]	230 [29]	300-400 [30]	300 [a]
Density (kg m^{-3})	250	50	100	80
Thermal conductivity (W m^{-1} K^{-1})	0.14	0.05	0.11	0.04
Origin	Denmark, France, Belgium, Germany, UK	France, Hungary, Italy, Russia, Ukraine	France, Hungary, Italy, Russia, Ukraine	Belgium, France, Russia, UK

[a] datas from Ansys Granta

Finally, in view of application of the composite in a building wall concrete, fibers with low thermal conductivity are sought. This would allow a continuous release of heat from the PCMs over a long period. On the other hand, the fibers should not be completely insulating, otherwise they would not transmit the heat generated by the solidification of the PCM. The thermal conductivity of each material was therefore checked and presented in **Table 2**. As it can be seen, all the natural fibers can be considered as insulators with thermal conductivity in the range 0.04-0.14 W m^{-1} K^{-1}. Therefore, all four materials are selected for this study (**Fig. 2**).

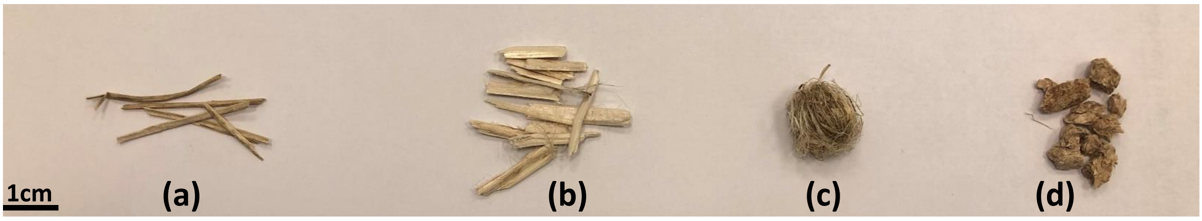

Fig. 2. Natural fibers considered in the study: flax mulch (a), hemp shives (b), hemp fibers (c) and fir pellets (d).

The selected fibers are impregnated with two pure fatty acids, capric acid and lauric acid, in order to compare the impregnation rate, an important criterion in the selection of the support material. The two fatty acids are chosen because their temperatures of fusion fit the thermal requirements for thermal comfort temperature. Next, the fibers with the best impregnation rates will undergo a mass degradation assessment to ensure that they do not suffer from any degradation within the temperature range of the buildings.

2.2 Selection of the PCM

After the selection of the best support materials, the panel of PCMs has been extended in order to select the best composite (natural fiber and PCM). Fatty acids such as capric acid (CA), lauric acid (LA), myristic acid (MA), palmitic acid (PA) and stearic acid (SA) have been extensively studied in recent years and their potential in passive latent heat storage systems was demonstrated [18,31–33]. Therefore, in addition to CA and LA already considered in the first part, MA, PA and SA has been added to the list of potential PCM of interest. General information of the pure fatty acids are presented in **Table 3**. However, among the fatty acids, only few possess a temperature of fusion in the targetted temperature range (15-45 °C, **Table 4**). This condition is necessary to ensure efficient and rapid passive charge and discharge of the PCM in a diurnal cycle. Fortunately, it is possible to tune the temperature of fusion of the PCMs to meet this climatic requirement by fabricating eutectics mixtures. Fatty acid eutectic mixture is a composition of two or more fatty acids with eutectic mass ratio [34], each of which melts and solidifies at the same eutectic temperature, being always inferior to the temperature of fusion of the pure PCMs constituting the mixture [35,36]. Fatty acid mixtures with eutectic mass ratio have the lowest temperature of fusion and the best thermal reliability compared to the other mixtures obtained with the same fatty acids at different proportions.

Table 3 . General information about the studied pure PCMs.

PCMs	Acronym	CAS Number	Formula	Supplier	Purity*
Capric acid	CA	334-48-5	$C_{10}H_{20}O_2$	Sigma aldrich	99 wt%
Lauric acid	LA	143-07-7	$C_{12}H_{24}O_2$	Sigma aldrich	≥98 wt%
Myristic acid	MA	544-63-8	$C_{14}H_{28}O_2$	Sigma aldrich	99 wt%
Palmitic acid	PA	57-10-3	$C_{16}H_{32}O_2$	Sigma aldrich	99 wt%
Stearic acid	SA	57-11-4	$C_{18}H_{36}O_2$	Sigma aldrich	99 wt%

Table 4. Thermal conductivity and temperature of fusion of pure fatty acids acids *[33]*.

Acronym	Fusion Temperature (°C)	Thermal Conductivity (W m^{-1} K^{-1})
CA	29.6 - 33.2	0.21
LA	41 - 45.3	0.15 - 0.37
MA	49 - 56.1	0.17 - 0.39
PA	58.9 - 64	0.3
SA	53.8 - 70.8	0.159 - 0.35

Therefore, six eutectic mixtures made of a combination of the aforementioned pure fatty acids have been fabricated. The eutectic mixtures of the fatty acids, their mass composition and temperature of fusion are gathered in **Table 5**. As can be seen, the temperature of fusion of all the selected eutectic mixtures falls in the thermal comfort temperature range.

Table 5. Fatty acids eutectic mixtures.

Eutectic mixture	Acronym	Mass composition (wt%)	Temperature of fusion (°C)
Capric acid-lauric acid	CA-LA	73-27	21.7
Capric acid-myristic acid	CA-MA	83-17	24.1
Capric acid-stearic acid	CA-SA	91-9	26.0
Capric acid-palmitic acid	CA-PA	88-12	26.1
Lauric acid-myristic acid	LA-MA	73-27	33.6
Lauric acid-palmitic acid	LA-PA	79-21	34.6
Lauric acid-stearic acid	LA-SA	87-13	40.2

3 Experimental protocol

3.1 Techniques of characterization

3.1.1 Scanning electron microscopy (SEM)

The characterization of the morphology and microstructure of the samples is essential to understand the impregnation mechanism. The microstructure of hemp shives and hemp shives/CA composites was successively observed by scanning electron microscope (SEM) (QUANTA 200 environmental field effect gun, FEI, FRANCE) in environmental mode. This mode avoids any preliminary treatment of the samples and is very adapted to non-conductive samples such as hemp shives. The observations were performed at low pressure (typically 2 mbar) and a voltage of 15 KV.

3.1.2 Differential scanning calorimetry (DSC) and Thermogravimetry Analysis (TGA)

A DSC3+/TGA differential scanning calorimeter/thermo-gravimetric analyser device provided by METTLER TOLEDO is used to measure the heat flow released by the materials tested as well as the mass change during the tests. TGA is performed to verify the mass degradation and the thermal stability of the natural fiber/PCMs composites in the building application's temperature range.

The DSC allows the estimation of the fusion/solidification temperatures and enthalpies of the different samples: PCMs and natural fibers/PCMs composites. The DSC was calibrated using four calibration standards (gold, zinc, aluminium and indium) to ensure precise certainty on the temperature range considered. The purity of all the calibration standards is about 99.999 wt%. Prior to the measurements, a blank run is performed to correct the baseline. The measurements are performed over a cycle with a heating/cooling rate of 0.5 °C min^{-1} in a range of temperatures from 10 to 80 °C (superior to the highest temperature of fusion of the sample) for the heating phase, and from 80 to 10 °C for the cooling phase. The low heating/cooling rate is selected in order to avoid thermal gradient inside the sample and because of the insulating behaviour of the fibers that may cause a slow down of the heat transfer. For the same reasons, the isothermal steps are hold for 15 min to reach an eliquibrium. For each sample (PCMs and natural fibers), a mass between 10 and 20 mg are weighed and placed in 70 µL alumina crucibles. The experiment was carried out by purging the sample cell with Argon at a flow rate of 25 mL min^{-1}. The integrated software of METTLER TOLEDO is used to calculate the latent heats of fusion and solidification by numerical integration of the area under the peaks that represent the solid-liquid and the liquid-solid phase transitions. The onset temperature is chosen as temperature of fusion for the fusion peak whereas the endset is selected as solidification temperature for the solidification peak. These two values are chosen because they are not influenced by the heating rate unlike the peak temperature. The maximum uncertainty for the enthalpy calculation is 15% and 1.5 °C for the temperature. In addition, for all measurements (DSC and TGA), the tests are repeated three times for each sample to verify repeatability and reproducibility.

The thermogravimetric analysis (TGA) is performed with the same device. TGA allows analyzing the mass degradation of the composite in the building temperature's range by quantifying the mass variation of the material according to the temperature. CA, hemp shives only and hemp shives/CA composites samples are analyzed in a temperature range of 25-500 °C with a heating rate of 10°C min^{-1}.

The thermal cycling test is conducted only on the hemp shives/CA samples. The vacuum and non-vacuum impregnation techniques are compared in terms of stability over 50 cycles between the temperature range 20-70 °C.

3.2 Impregnation process

The impregnation process is used to fabricate the natural fiber/PCM composites. First, the selected natural fibers are weighed (m_1) and mixed with PCM. The precision (Δm) of the balance is about 10^{-4} g. The mixture is placed in an oven at 10 °C above the highest temperature of fusion of all the PCMs (80 °C). The molten PCM is absorbed into the pores of the natural fibers by mean of capillary and surface tension forces [31]. The amount of liquid PCM is chosen to recover the fibers to ensure effective impregnation. The weight ratio depends on the nature of the fibers but in general, a ratio was 1:10 chosen for the majority of fibers. After impregnation, the excess liquid PCM was removed by filtration. The impregnated natural fibers were placed on a filter paper and kept in the oven at 80 °C to remove the PCM on the surface of the fibers. The filter paper is changed continuously until no leakage is observed (after 3 days). The final mass of the composite (m_2) is weighed and the mass ratio of PCM in the composite is calculated using equation (1). The uncertainty (ΔR) on the mass ratio is calculated by the error propagation law (equation (2)).

$$R = \frac{m_2 - m_1}{m_2} * 100 \tag{1}$$

$$\frac{\Delta R}{R} = \left(\frac{2}{m_2 - m_1} + \frac{1}{m_2}\right) * \Delta m \quad (2)$$

The impregnation process depends on several criteria such as the residence time and the conditions of the impregnation (under vacuum or atmospheric pressure). Jeong et al. [37] analyzed the impregnation rate of a PCM in vacuum and non-vacuum processing and found that the impregnation rate was close to 50 wt% in the vacuum treatment compared to only 30 wt% in the non-vacuum conditions.

3.2.1 Vacuum vs non-vacuum impregnation

To establish the experimental protocol, first the vacuum and non-vacuum impregnation techniques are compared. The vacuum level is set at 100 mbar [38] in order to remove the air inside the fibers and enabled the liquid PCMs to diffuse into the fibers. The impregnation is governed by the capillary force and therefore, the vacuum level depends on the surface tension, the radius and the wettability of the fiber [39]. For this first study, we selected hemp shives as support material and CA as PCM to set the adequate operating conditions for the impregnation process. The two impregnation modes are compared in terms of long-term stability over thermal cycling (DSC). In fact, the composite should store and release energy over a long period without any leakage or decrease in thermal performances. The thermal cycling test is important to evaluate the long-term stability of the PCM composite. This test investigates the thermal reliability of the bio-composite PCM after several repetitive phase change cycles. The samples obtained by the two methods are thermally cycled over 50 cycles in a temperature range between 20 and 70 °C (**Fig. 3**).

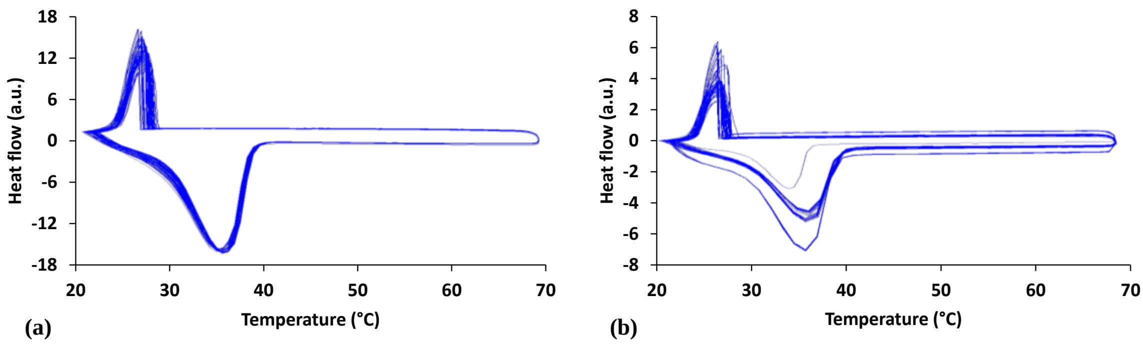

Fig. 3. 50 cycles DSC of CA/hemp shives composites impregnated under vacuum (a) and under atmospheric pressure (b).

When the impregnation is performed at atmospheric pressure, the PCM is not absorbed inside the nanopores. Therefore, there is leakage during the heating phase, affecting thermal properties (phase change temperatures and enthalpies). The thermograms obtained in DSC with hemp shives/CA composites impregnated under vacuum show a quasiperfect superposition of the 50 cycles that allows visualizing their stability under cycles. The final protocol had to consider this result and all other composites were vacuum impregnated.

This proves that the composite reacts in the same way to all the cycles, so it does not degrade with cycling, and there does not seem to be any leakage of the PCM from the fibers. All the thermograms obtained for the remaining composites show similar quasi-perfect superpositions.

3.2.2 Residence time

The residence time is one of the factors that influences the impregnation rate of PCMs in a support material. In this part, the effect of residence time on the impregnation rate of CA within hemp shives has been investigated. The hemp shives are impregnated with CA and filtered after 1, 4, 5, 6, 7 and 10 days. The impregnation rate at each time is measured and presented in **Fig. 4**. After 1 day, the impregnation rate was 30 wt% and increased by 50 wt% after 5 days to reach a value of 48 wt%. After 5 days, the impregnation rate does not increase a lot and a plateau of about 50 wt% is reached. At the end of the 10 days, the maximum impregnation rate was 53 wt%. Since the impregnation rate increased only by less than 10 wt% between day 5 and day 10, it can be stated that an impregnation rate of 5 days is a good compromise.

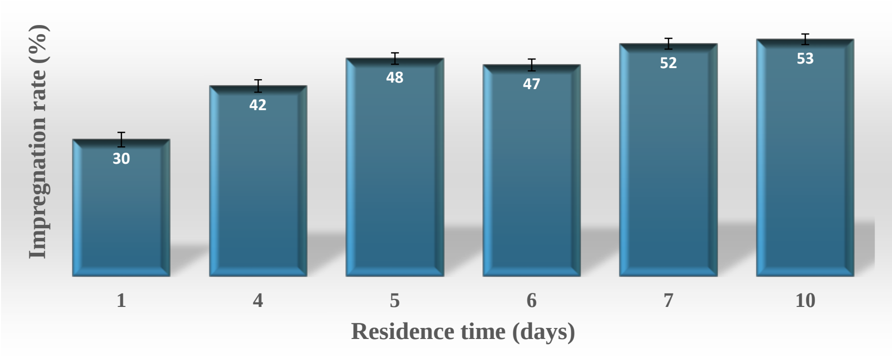

Fig. 4. Impregnation rate of hemp shives in CA as a function of time.

Based on the preliminary study, all the remaining tests are conducted under vacuum with a residence time of 5 days.

In order to ensure the effectiveness of the impregnation process, the impregnated hemp shives/ CA has been observed by SEM. The cross section images of hemp shives/CA composite obtained by SEM is presented in **Fig. 5**. The interior of the pores is more visible in the cross-section of the fiber, which allows the observation of PCM in hemp shives. From the SEM observations, we observe that CA successfully occupies the pores of the hemp shives after the impregnation process. The experimental protocol is thus validated and applied for all subsequent investigated composites made of natural fibers and bio-based PCMs.

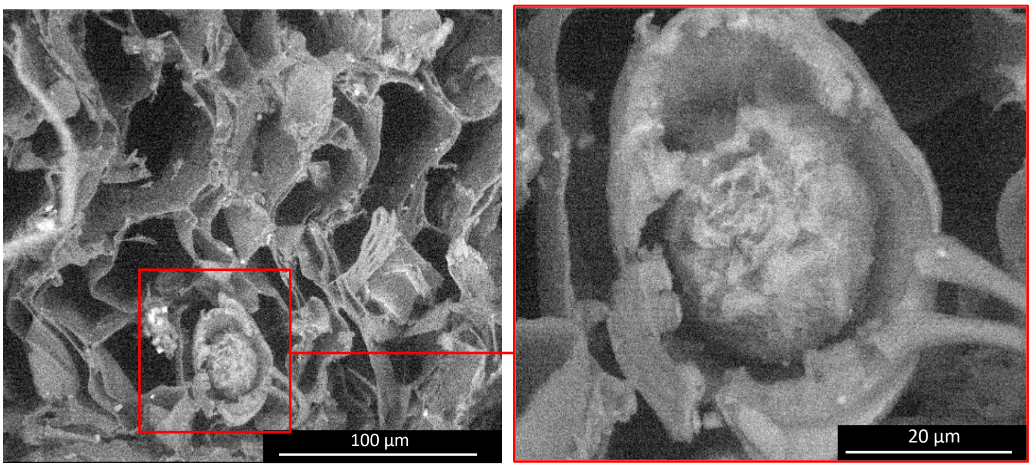

Fig. 5. SEM observations of hemp shives/CA composite

4 Results and selection of PCMs natural fibers composites

4.1 Selection of the support material

4.1.1 Impregnation rate

The impregnation rate of capric acid and lauric acid in the selected natural fibers are presented in **Table 6**. The best impregnation rates are obtained for hemp shives and flax mulch with a maximum of 50 wt% and 51 wt% respectively for hemp shives/LA and flax mulch/CA whereas the impregnation rate for hemp fibers and fir is much lower (about 8 wt%) . This is explained by the microstructure of the material [40]. In fact, the porosity of materials such as hemp shives is very large and allows then better impregnation compared to fibers with relatively poor porosity, pore size and density. This porosity affects the absorption capacity of the material. This is consistent with the absorption capacity values of about 200 wt%, 300 wt% and 400 wt% for fir, flax mulch and hemp shives respectively given in **Table 2**. Based on these results, hemp fibers and fir are eliminated from the list of potential natural support materials impregnation rate. The rest of the study is conducted for the two remaining materials: hemp shives and flax mulch.

Table 6. Impregnation rate of the studied natural fibers.

Impregnation rate (wt%)	Capric acid	Lauric acid
Hemp fibers	5	0
Hemp shives	48	50
Fir pellets	1	8
Flax mulch	51	43

4.1.2 Mass degradation

The results of the TGA performed for hemp shives and flax mulch are presented in **Fig. 6**. The mass degradation of the pure fatty acids (CA and LA) are also illustrated in order to allow comparison. The degradation of CA started at 150 °C against 200 °C for LA. The mass degradation curve of the hemp shives and flax mulch are almost similar. The degradation of flax much occurs between 200 and 350 °C with 60 wt% of mass loss. For hemp shives, 60 wt% of the initial mass is lost between 200 and 325 °C. The TGA curve of the composites is a combination of the TGA curve of each component (natural fiber and PCM) represented by two inflexions in the TGA curve. The results showed that the composite is stable up to 150 °C and therefore suitable for application in buildings.

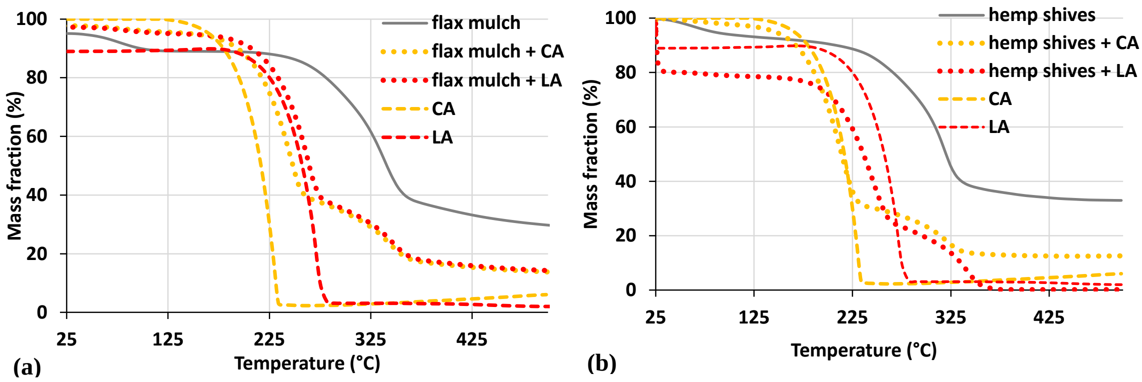

Fig. 6. TGA of CA, LA/flax mulch (a) and hemp shives (b) composites

Finally, both, flax mulch and hemp shives could satisfy the requirements. As hemp shives have a slightly higher density and thermal conductivity and as they are already used in buildings through hemp concrete, they are selected as natural support material for the rest of the study .

4.2 Selection of the PCM

The results of the previous section have shown that hemp shives are efficient natural support materials. The impregnation performances of hemp shives being only investigated for two PCMs, the impregnation rate of hemp shives in different fatty acids and their eutectic mixtures have been experimentally assessed. Five pure fatty acids (CA, LA, MA, PA, SA) and seven eutectic mixtures (CA-LA, CA-MA, CA-PA, CA-SA, LA-MA, LA-PA and LA-SA) are tested.

4.2.1 Impregnation rate

The impregnation rates of hemp shives with the PCMs are presented in **Fig. 7**. As observed, the maximum impregnation rate is about 50 wt%. This maximum value is obtained for LA and LA eutectic mixtures showing that hemp shives have better affinity with LA compared to the other fatty acids. CA, MA and PA have similar behaviors with impregnation rates of 48, 48 and 45 wt% respectively. The lowest impregnation rate is obtained for SA with a value of 40%.

The impregnation rate of eutectic mixtures is a combination of that of the components. This explains the relatively high impregnation rate of LA eutectic mixtures and especially when the amount of LA in the mixture is high. Another illustration is the lowest impregnation rate value of CA-SA, which is made of a pure fatty acid (SA) with the lowest impregnation rates. The resulting eutectic compound possesses the lowest impregnation rate of all the studied PCMs.

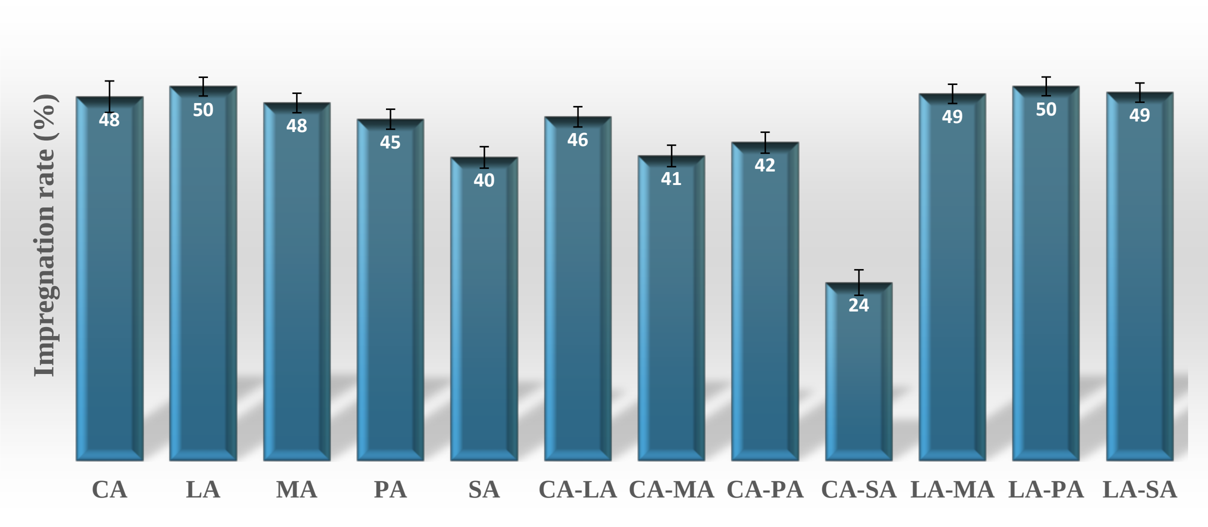

Fig. 7. Impregnation rate of hemp shives in fatty acids and their eutectic mixtures.

4.2.2 Mass degradation

TGA analysis has been conducted in order to study the mass degradation of all composites selected and also allows ensuring the presence of PCMs in hemp shives. **Fig. 8 (a)** presents the mass degradation curve of pure fatty acids and the eutectic mixtures used in this study. The temperature of degradation of the materials increases with the temperature of fusion. In other words, the higher the temperature of fusion, the higher is the temperature degradation. Therefore, the lowest and highest temperatures of degradation are obtained for CA-LA and the LA-SA with values of 150 °C and 230 °C respectively.

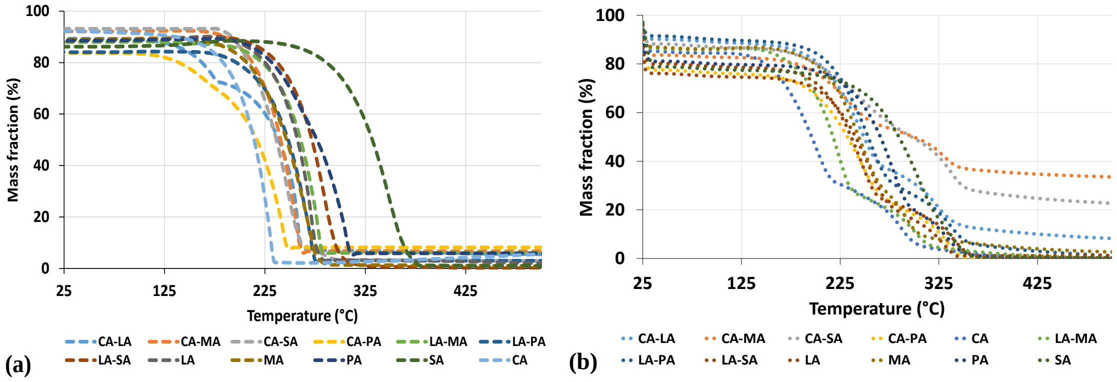

Fig. 8. TGA of PCMs (a) and PCMs/hemp shives composites (b).

The TGA curves of PCMs/hemp shives composites are plotted in **Fig. 8 (b)** and showed two inflexions points corresponding to the degradation temperature of each component of the composite (natural fiber and PCM). This result indicated that the PCMs are successfully impregnated with hemp shives. In addition, the lowest degradation temperature being 150 °C, it can be stated that all the PCMs hemp shives composites are stable up to 150 °C and therefore suitable for application in buildings.

4.2.3 Energy storage performances

In addition to the impregnation rate, the fusion and solidification properties of the composite are of real interest. These properties will govern the thermal performances of the overall thermal energy storage system that is the building envelope in our case. If a composite possesses a high impregnation rate but a low heat of fusion, it is clear that another composite with low impregnation rate but a higher heat of fusion will be preferred since we are interested in the thermal properties of the composites. Therefore, the heat of fusion and solidification of the composites are plotted in **Fig. 9 (a)**. The heat of fusion of the composites are between 33.64 and 94.3 J g^{-1}. The heats of solidification are slightly lower than that of fusion and are between 24.5 and 93.7 J g^{-1}. The highest values for both quantities are obtained for SA with 94.29 and 93.7 J g^{-1} for heat of fusion and solidification respectively. In contrary, the lowest are obtained for CA-SA with values of 33.6 and 24.5 J g^{-1} for heat of fusion and solidification respectively.

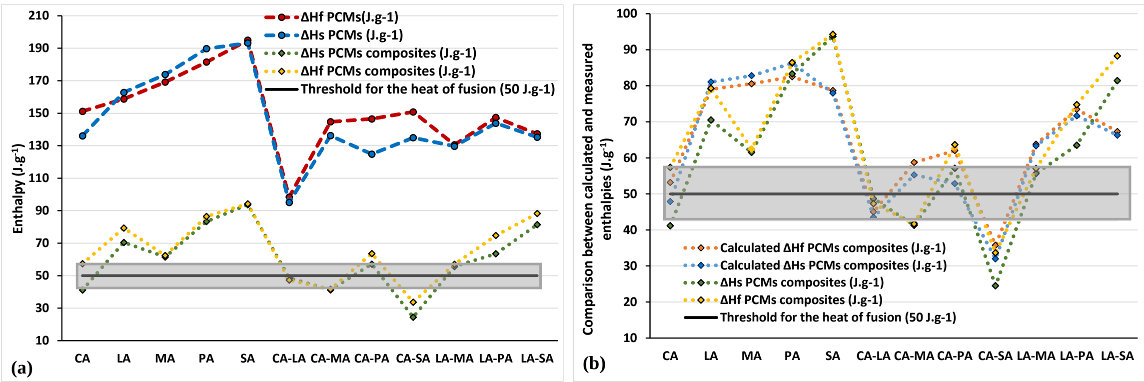

Fig. 9. (a) Enthalpy of fusion and solidification of PCMs and PCM hemp shives composites, (b) Comparison between calculated and measured enthalpies. The gray box represents the uncertainty on the threshold enthalpy (50 J g^{-1}) based on the precision of the device (15%).

As can be seen, the enthalpy of fusion and solidification for all composites are lower compared to that of pure or eutectic fatty acid eutectic mixtures. This reduction is caused by the reduction of the mass ratio of PCM in the composite and the reduction of the crystallinity of the PCM. It is possible to assess that by comparing the theoretical enthalpy and the measured one. The theoretical enthalpy is calculated by multiplying the enthalpy of the fatty acid alone by the impregnation rate (R) as presented in equation (3).

$$\Delta H_{calculated} = R * \Delta H_{calculated} \qquad (3)$$

Fig. 9 (b) compares the calculated and measured enthalpies of fusion/solidification. In general, the two values are close but the calculated values are higher than the measured one. In order to better represent the discrepancies, the absolute and relative differences between calculated and measured enthalpies are plotted in **Fig. 10**. The differences ranges from 0.26 to 21 J g^{-1}, and 2.93 to 21.3 J g^{-1} for heat of fusion and solidification respectively. These differences correspond to relative errors between 0.31-41% and 3.51-34% for enthalpies of fusion and solidification respectively. The maximum relative difference are obtained for MA and CA-MA composites. For the remaining composites, the differences for the enthalpy of fusion is between 0 and 15%, which is within the uncertainty range of the DSC device (15% for enthalpy calculation). However, the difference is still very large especially for the solidification enthalpy that exceeds the uncertainty of the device for some composites. This difference may be explained by the statistical behaviour of the impregnation process (all the particles will not absorb the same amount of PCM) and the error induced by the sampling. In fact, the impregnation rate is measured on a sample of few grams whereas the DSC measurements are obtained on samples of 10-20 mg. The mismatch between calculated and measured enthalpy could be considerably improved by the utilization of DSC with high size samples.

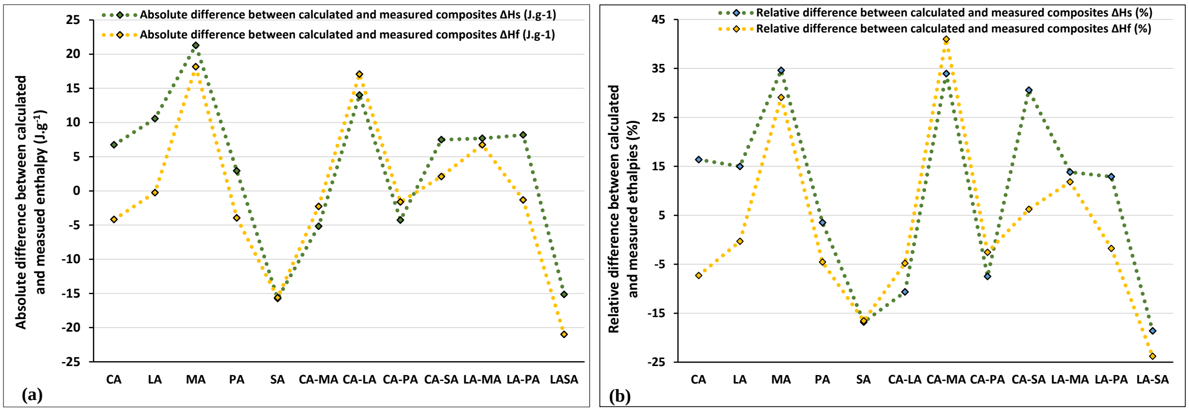

Fig. 10. (a) Absolute and (b) relative differences between measured and calculated enthalpies.

Except from CA-SA, CA-LA and CA-MA, all the composites have a latent heat of fusion superior to 50 J g^{-1}, which is higher than most of the composites with natural fibers [38,41–43]. These latent heat values are very promising for energy storage in buildings.

In addition to a high value of latent heat, the temperature of fusion of the composites should be in the temperature range (15-45 °C) in order to be eligible to building application and thermal comfort. The temperatures of fusion of the composites are presented in **Fig. 11**. Except from pure MA PA and SA, all the pure PCMs and the fabricated composites possess a temperature of fusion corresponding to the aimed thermal requirements.

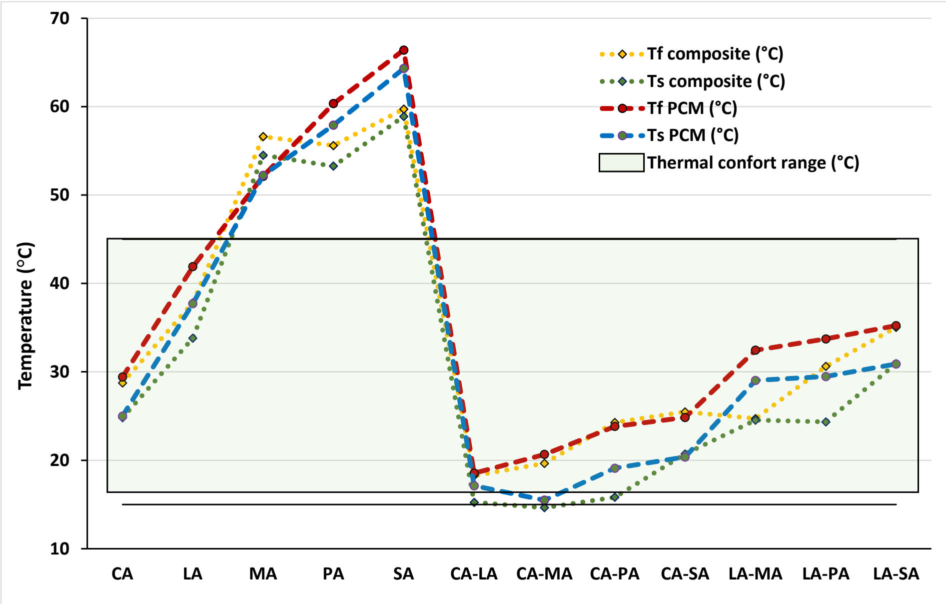

Fig. 11. Temperature of fusion/solidification of PCMs and hemp shives PCMs composites.

Fig. 12 shows the absolute and relative differences between the PCMs and PCMs/composites fusion and solidification temperatures. The differences range from 0.045 to 8°C corresponding to a relative difference between 0.14 and 25%. The fusion and solidification temperatures of the composites are lower than that of the PCMs alone. This difference is explained by the insulating nature of the hemp shives that can induce a delay in the heat conduction resulting to lower temperature compared to those of pure PCMs. In addition, this decrease in phase change temperatures can be due to weak attractive interactions between fatty acid molecules and inner surface wall of the porous material [44].

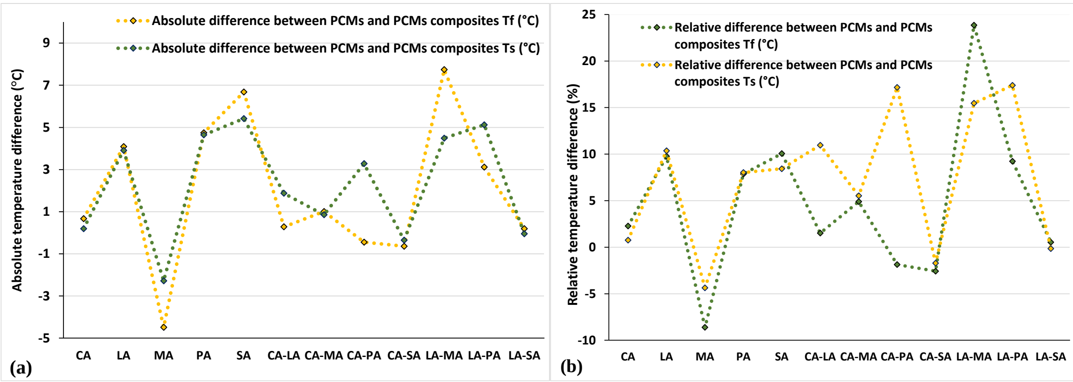

Fig. 12. (a) Absolute and (b) relative differences between the PCM and PCMs/composites fusion and solidification temperatures.

4.2.4 Undercooling

The performance of energy storage systems incorporating PCMs is typically evaluated in terms of charge/discharge cycles. The latter and the associated performances are strongly influenced by the nature of the PCMs and their properties as previously mentioned but also by their undercooling.

Undercooling is a metastable state in which a liquid remains in a liquid state at a temperature inferior to its melting temperature. The integration of composites in buildings walls will allow for an increase in thermal inertia and short term passive energy storage. The latter allows managing the diurnal sunshine variation. For this type of storage, the phenomenon of undercooling must be as low as possible (5 °C maximum) in order to discharge the thermal energy fastly in the desired temperature range and to facilitate the charge/discharge cycles.

The undercooling level of PCMs and hemp shives PCMs composites are presented in **Fig. 13**. Apart from CA-PA, all the PCMs possess an undercooling degree below 5°C making them suitable for thermal energy storage. The same tendency is observed for hemp shives PCMs composites at the exception of CA-MA, CA-PA, CA-SA and LA-PA. The latter are eliminated from the list of potential candidates because of high undercooling. CA-SA is also eliminated because of its undercooling degree close to 5 °C but mainly because of its low impregnation rate (24%, **Fig. 7**).

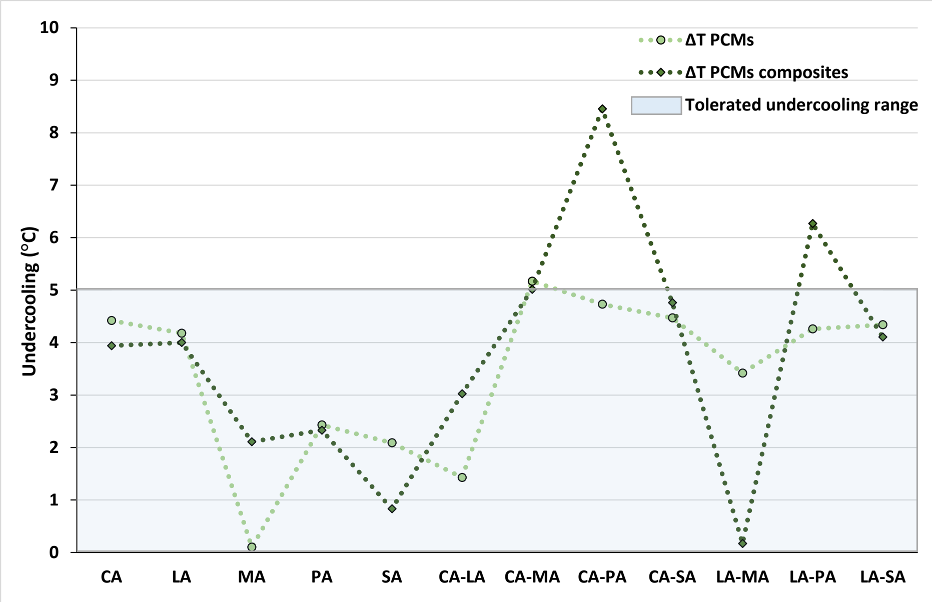

Fig. 13. Undercooling level of PCMs and PCMs composites.

Finally, taking into account the thermal requirements, which are a high latent heat, undercooling below 5 °C and temperature of fusion between 15 and 45 °C, only CA, LA, LA-MA and LA-SA composites are selected as potential materials for buildings application. However due to the complexity of fabrication of eutectic mixtures for large scale applications, LA-MA and LA-SA are also eliminated and the final composites selected are CA and LA hemp shives composites.

4.3 Discussion

The selection process has allowed the selection of hemp shives as support material for the fabrication of shape-stabilized composites. In addition to his high impregnation rate, this support material is very cheap (less than 1€ kg^{-1}) and possesses a relatively low thermal conductivity. The thermal conductivity of hemp shives is compared with some natural insulators in buildings (**Table 1**). Despite a higher conductivity compared with conventional insulators, hemp shives impregnated with PCMs can be an interesting alternative due to expected higher energy density and acceptable thermal conductivity. Another advantage of hemp shives is their hygroscopic behaviour, which can help to regulate the humidity in buildings.

Regarding the composites selection, CA and LA hemp shives composites have been selected as potential composites for building applications because they fulfil all physical, thermal, geographical and economic criteria. In addition, the composites made with pure fatty acid are easy to manufacture compared to those made with eutectic mixtures. This is of great importance for building scale applications.

Among the two composites, hemp shives/LA is the best compromise because of higher impregnation rate (50 wt%) and higher enthalpy of fusion and solidification (79.3 and 70.4 J g^{-1} respectively) compare to CA. In addition, LA is more than two times cheaper than CA respectively 36.4 and 75.1 € kg^{-1} at a purity of 99% [33]. The fusion/solidification temperatures and enthalpy of LA hemp shives composites are still very promising for energy storage in buildings compared to shape-stabilized PCMs studied by other references (**Table 7**). The composite exhibits competitive latent heats of fusion and solidification with low undercooling.

Table 7. Comparison of the phase change properties of the prepared hemp shives/LA composite with some bio-based PCM composites

PCM composites	Temperature of fusion (°C)	Solidification temperature (°C)	Heat of fusion (J g^{-1})	Heat of solidification (J g^{-1})	Reference
Delignified wood/CA-PA	23.4 ± 0.3	14.5 ± 0.2	94.4 ± 1.0	91.4 ± 0.6	[18]
Carbon fibers/paraffin	22.5-60	22.5-57.6	192.2	191.1	[19]
Kapok fibers/MA-Tetradecanol	24-42.3	10.5-29.7	76.8	77.4	[38]
Hemp shives/LA	37.8	33.8	79.3	70.4	**This study**

Fatty acids in general and LA in particular have shown a good affinity with hemp shives. The reason is probably due to the roughness of the hemp shives as presented in figure 1 that improve the probability of nucleation [45]. This roughness may have a positive impact on the fusion/solidification cycles of composite. This hypothesis should be properly studied, especially at the hemp shives/LA interface for better understanding of the underlying phenomenon and how it affects the thermal properties of the composites. The characterization of the LA/hemp shives interface can be done using microscopy and chemical analysis XPS and will be the purpose of further investigations. In addition, a quantitative analysis of the heteregeneous nucleation of fatty acids at the surface of the hemp shives, based on infrared thermography, will be conducted to assess the influence of the roughness of the hemp shives in the nucleation process.

The mismatch between calculated and measured heat of fusion has been explained by the statistical behaviour of the impregnation and the limitation of the size of sample for DSC measurement. This limitation can be alleviated by using a large volume calorimeter like Calvet that allow samples of few grams and possesses 3D heat and temperature sensors. Another possibility is to reduce the heating and cooling rate because fibers slow down heat transfer due to their insulating nature.

Finally, the fabricated PCMs hemp shives composites could be easily integrated in buildings through hemp concrete. In fact, hemp concrete is very wide spread in France and has a regulatory frame work for its use and formulation in the construction sector [46]. Therefore, the fabricated CA and LA hemps shives composite could be mixed with lime and water in various proportions to fabricate a PCM hemp concrete. The new PCM hemp concrete material is expected to possess excellent hygrothermal properties and suitable for LHTES application in building envelopes.

5 Conclusion

In this study, the potential of natural fibers as support materials for PCMs for buildings application was investigated. The material selection software Ansys Granta has allowed the a preliminary selection of four natural fibers namely fir fibers, hemp fibers, hemp shives and flax mulch based on physical, thermal, geographical and economic criteria. First, the selected fibers are impregnated with two pure PCMs (CA and LA) and compared in terms of impregnation rate in order to selected the best support material for shape-stabilization. The results indicated poor performances for fir and hemp fibers with impregnation rates of 1 and 8 wt% respectively. In contrast, hemp shives and flax mulch presented better results with impregnation rate of 50 wt% and 51 wt% respectively. Therefore, only hemp shives and flax mulch are selected for the rest of the study and two others (hemp and fir fibers) were eliminated. TGA curves of PCMs/hemp shives and flax mulch composites showed a no mass degradation under 150°C, thus suitable for buildings application. As hemp shives are already used in buildings through hemp concrete, which is a normalized insulating material and presently slighltly higher density and thermal conductivity, they have been selected as natural support material since they presented highest impregnation rates with good thermal stability.

After the selection of the support material, it has been impregnated with 5 pure fatty acids and 7 eutectics mixtures in order to select the suitable PCM for the fabrication of a composite with optimized performances. The comparison of the different impregnation rates has shown that hemp shives are more compatible with LA and LA eutectic mixtures. The lowest impregnation rate are obtained for CA-SA. In addition, the lowest degradation temperature being 150 °C, it can be stated that all the PCMs hemp shives composites are stable below 150 °C and therefore suitable for application in buildings. Except from CA-SA, CA-MA and CA-LA, all the composites have latent heat higher than 50 J g^{-1}, which is higher than most of the composites with natural fibers. Taking into account the thermal requirements, which are high latent heat, low undercooling temperature of fusion between 15 and 45 °C, and facility to manufacture, LA hemp shives composite (enthalpy of fusion of 79.3 J g^{-1} at 50 wt% of impregnation rate) has been selected as potential materials for buildings application.

In order to develop competitive and efficient envelopes with good insulation, hygroscopic, energy storage capacity with the incorporation of PCMs, it is necessary to conduct a multiscale analysis. First, at the material level in order to characterize and select a suitable composite. Then, once the composite selected, it must be integrated in envelopes and compared to conventional walls. Finally, the solution must be tested at the building scale and its performances in terms of energy saving must be evaluated. This investigation was a part of the first step. It has allowed the selection of hemp shives/LA composite that showed a highpotential for building application. Future works will be emphasized on the development of hemp concrete incorporating PCM. The hygrothermal properties of the material will be characterized and its thermal performances evaluated under various climatic conditions at different scales (from the material to the envelope one).

Author Contributions

Conceptualization, all authors; methodology, all authors; formal analysis, all authors; investigation, all authors; resources, all authors; data curation, all authors; writing—original draft preparation, M.S.; writing—review and editing, all authors; visualization, all authors; supervision, A.V., A.G., R.B., M.D., and A.H.; project administration, R.B. and M.D.; funding acquisition, R.B., M.D. All authors have read and agreed to the published version of the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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