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Review

Review on the Integration of Phase Change Materials in Building Envelopes for Passive Latent Heat Storage

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Featured Application: Passive latent heat storage for building applications, thermal comfort.

Abstract: Latent heat thermal energy storage systems incorporate phase change materials (PCMs) as storage materials. The high energy density of PCMs, their ability to store at nearly constant temperature, and the diversity of available materials make latent heat storage systems particularly competitive technologies for reducing energy consumption in buildings. This work reviews recent experimental and numerical studies on the integration of PCMs in building envelopes for passive energy storage. The results of the different studies show that the use of PCMs can reduce the peak temperature and smooth the thermal load. The integration of PCMs can be done on the entire building envelope (walls, roofs, windows). Despite many advances, some aspects remain to be studied, notably the long-term stability of buildings incorporating PCMs, the issues of moisture and mass transfer, and the consideration of the actual use of the building. Based on this review, we have identified possible contributions to improve the efficiency of passive systems incorporating PCMs. Thus, fatty acids and their eutectic mixtures, combined with natural insulators, such as vegetable fibers, were chosen to make shape-stabilized PCMs composites. These composites can be integrated in buildings as a passive thermal energy storage material.

Keywords: passive energy storage; buildings; phase change materials; energy efficiency



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1. Introduction

The latest report of the Intergovernmental Panel on Climate Change (IPCC) paints a very damning picture. In the most optimistic scenario, the experts predict a temperature rise of more than 1.5 °C as early as 2030, against a warming of more than 4 °C according to the most pessimistic scenario [1]. It is clear that the ambitious objective set by the COP21 and the Paris Agreement to limit global warming to 1.5 °C will not be met. This increase in temperature is responsible for the frequent heat waves and temperature records recently observed in several regions of the world.

Faced with this situation, it is essential to take actions to limit greenhouse gas emissions in order to achieve a zero carbon footprint. The building sector, which accounts for 40% of greenhouse gas emissions, remains one of the first sectors of action to reduce energy consumption and thus limit greenhouse gas emissions [2].

To reduce this energy consumption, mainly used for heating and cooling, it is essential to improve the energy efficiency of buildings by insulation and by taking advantage of renewable energies, such as solar energy.

Thermal energy storage is an effective solution to achieve these objectives through its many advantages:

- the correction of the phase shift between demand and off-peak periods during which prices are more favorable,
- the time shift between production and consumption which allows the reduction of the dependence on fossil fuels by using renewable energies and the limitation of heat losses through storage.

The basic principle of thermal energy storage is the same regardless of the application. A thermal energy storage cycle is divided into three parts: charging, storage and discharging. During the production period, energy is used to charge the storage system. The stored energy can later be returned to the environment as a supplement or substitute for the heating or cooling system, thus reducing energy consumption. The different thermal energy storage techniques are classified according to the scale, the method used and the duration of the storage.

Depending on the duration of the storage, we distinguish short-term and long-term (seasonal) storage. Short-term storage is used on the scale of a few hours, whereas long-term storage is used for longer periods (weeks and months). In addition, short-term storage is used to correct daily (diurnal) or hourly temperature variations, while long-term storage is used to smooth out seasonal temperature fluctuations.

Thermal energy storage can also be classified according to the storage mechanism. Thermal storage can be done in essentially three ways: sensible heat storage, latent heat storage, and thermochemical storage. The difference between these three methods lies in the material used, the operating temperature and many other parameters.

Historically, sensible heat energy storage is the most used in buildings [3–6]. However, it requires large volumes of materials due to the low energy density. The use of phase change materials (PCMs) overcomes this constraint through the contribution of latent heat of phase change, which allows the design of more compact systems [7]. Due to the latent heat involved in the phase change processes, PCMs offer high thermal capacity, and more energy can be stored in the building envelope compared to traditional sensible materials.

The main advantages of latent heat storage over sensible heat are higher energy density (up to 14 times higher), nearly constant storage temperature and the wide variety of materials available.

However, PCMs are subjected to many problems due to their low thermal conductivity, supercooling, phase segregation, etc. [7].

Numerous experimental and numerical studies have shown that the integration of PCMs into building envelopes can improve thermal comfort (maintaining the temperature inside a building room between 15 and 35 °C) by reducing peaks and fluctuations in indoor temperature [6–11].

The objective of this work is to review the recent advances on passive latent heat energy storage and, more specifically, on numerical and experimental studies of different techniques for the integration of PCMs in buildings. To do so, the review is structured as follows: first, a brief description of thermal energy storage systems and different techniques for integrating PCMs into buildings are presented in Section 2. Section 4 is dedicated to the presentation of experimental and numerical studies of buildings incorporating PCMs. The experimental studies are divided into two groups: studies at the composite scale and studies at the wall and building scale. This part is ended by a discussion of the conclusions of the different studies in order to select the techniques and materials that will be studied further in the context of passive thermal energy storage in buildings.

2. Thermal Energy Storage Systems in Buildings

Thermal energy storage systems in buildings are classified into three categories: passive, active or hybrid. Generally, an energy storage system consists of a storage unit and a heat transfer fluid. In passive systems, the heat transfer fluid does not contribute significantly to the storage because of its low heat capacity (usually air) and the storage is done at

low temperatures between 20–60 °C. In contrast, in active systems, the heat transfer fluid contributes to the storage and the heat can be stored at both low and medium temperatures (between 40 and 95 °C) [11]. Another singular difference between passive and active storage is the system used to circulate the heat transfer fluid. In passive systems, the heat transfer fluid circulates naturally while a mechanical device (fan, pump) is used to circulate the heat transfer fluid in an active system. Hybrid systems combine the two previous storage modes.

Passive storage systems have been shown to effectively improve thermal comfort while minimizing the need for mechanical heating or cooling systems.

2.1. Materials for Passive Thermal Energy Storage

Capacity, charge and discharge rate, storage period, charge and discharge time, and cost are the most important criteria for the selection of storage materials [12]. As mentioned in the introduction, heat can be stored in a material by three mechanisms: sensible, latent, and thermochemical heat.

Sensible heat storage is the easiest way to store energy and involves applying a temperature gradient to a material for storing heat or cold. The amount of heat stored depends on three parameters: the mass of the material, the heat capacity of the material at constant pressure, and the range of temperature variation. The materials generally used for sensible storage are clay, hollow bricks, concrete or stone, which are widely used in the building industry.

Latent heat storage stores energy by taking advantage of phase change. The materials used for latent storage are known as PCMs. PCMs are classified according to several criteria, such as their nature (organic or inorganic), their origin (renewable or non-renewable), and their phase change temperature (low, medium, and high) or according to the nature of the phase change involved in the process (solid-solid, solid-liquid, liquid-gas). The solid-liquid phase change is, to date, the most widely used because of its high enthalpy and the absence of problems related to pressure [13]. Abhat et al. [14] proposed a classification of solid-liquid PCMs into three groups according to their nature: organic, inorganic, and eutectic. Organic PCMs include paraffin, fatty acids, sugar alcohol, and polyethylene glycol (PEG). Inorganic PCMs are salt hydrates, nitrates, and metallics having a high heat of fusion. Eutectic PCMs are mixtures of two or more PCMs and are classified as organic-organic, inorganic-inorganic or organic-inorganic.

Finally, the last storage mode uses thermochemical materials that store energy through an endothermic/exothermic reaction/process by generating easily separable reaction products [15].

The advantages and disadvantages of the different storage modes are presented in Table 1.

Table 1. Advantages and disadvantages of the different storage modes [8,16,17].

Storage Modes	Advantages	Disadvantages
Sensible	<ul style="list-style-type: none"> - Low price - Availability - Non-toxic - Simple and already commercialized technologies 	<ul style="list-style-type: none"> - Incompatibility to corrosion - Thermal instability during cycles - Low energy density
Latent	<ul style="list-style-type: none"> - High energy density - Quasi-constant storage temperature - No overheating 	<ul style="list-style-type: none"> - Low thermal conductivity - Presence of overpressure and phase segregation

Table 1. *Cont.*

Storage Modes	Advantages	Disadvantages
Thermochemical	- Efficiency	- Corrosion
	- Suitable for seasonal storage	- Risk of exhaustion of solid-gas chemical reactions
	- Large storage capacity	- Complex and not mature technology

Recently, PCMs have been studied extensively in order to lift the locks and allow a massive deployment of this technology in buildings. Thus, the systems that will be presented in this study will be those incorporating PCMs only. Table 2 provides a comparative summary of the advantages and disadvantages of the different types of PCMs.

Table 2. Advantages and disadvantages of the different types of PCMs [9,18–20].

PCM Types	Advantages	Disadvantages
Organic	<ul style="list-style-type: none"> - High enthalpy of fusion - Long-term thermal and chemical stability - Compatibility with most building materials 	<ul style="list-style-type: none"> - Incompatibility with some container materials, e.g., plastic - Flammability - Low thermal conductivity (about $0.2 \text{ W m}^{-1} \text{ K}^{-1}$)
Inorganic	<ul style="list-style-type: none"> - High storage density compared to organic PCMs - High thermal conductivity (almost double that of organic PCMs) - Low cost availability - Compatibility with plastic containers - Non-flammability 	<ul style="list-style-type: none"> - Corrosion - Significant volume expansion - Phase segregation
Eutectic	<ul style="list-style-type: none"> - Appropriate and adjustable transition temperature - High enthalpy of fusion - Congruence of phase change 	<ul style="list-style-type: none"> - High cost - Limited thermo-physical properties

Organic PCMs are the most widely used for thermal energy storage due to their suitable melting/solidification temperature, high storage density, chemical stability, and storage capacity [17].

2.2. Passive Storage Systems Incorporating PCMs

Basecq et al. [11] have identified three techniques for passive energy storage. The first method is to use the structural elements of the building, such as walls, roofs, and floor, to capture and store energy. The second method is to increase the storage capacity of the building by adding an additional storage system, such as a water tank or pebble bed system. The last method is to use the thermal capacity of the ground or the exterior envelope of the building. Only the systems of the first method are presented in this section.

2.2.1. Building Envelopes

Firstly, we will present the conventional building envelopes and the efforts put in place to limit the energy consumption of buildings. Then we will compare these systems with those integrating PCMs in order to discuss the interest of this integration in terms of energy performance of the building.

2.2.2. Conventional Building Envelopes

The building can be considered as a thermodynamic system with the building envelope as its boundary. The balance between energy production, consumption, and storage in buildings is influenced by internal and external loads, as well as the thermal resistance and thermal capacity of the envelope [20]. Therefore, improving the thermal performance of the building envelope is crucial to reduce energy consumption for heating and cooling.

Conventionally, the building structure itself is a means of energy storage. Thus, many passive storage systems rely on structural elements of the building such as walls, roofs, windows, and floors. This type of system can be accomplished on the surface of the structure, which is called surface activation. In this configuration, no specific storage system is used; rather, the intrinsic storage capacity of the building is exploited. It is possible to improve the surface activation system by inserting ducts or pipes in the materials composing the structure to allow a more efficient circulation of the heat transfer fluid [11].

It is also possible to improve the thermal performance of conventional buildings through suitable insulation. The purpose of this insulation layer is to limit heat loss. Building insulation materials can be classified into three categories: conventional, state-of-the-art, and natural. Conventional insulation materials like mineral wool, polystyrene, cellulose, and cork are produced by both chemical and mechanical processes and are commercially available. State-of-the-art insulators are mostly in the research and development stage, such as aerogel, vacuum insulation board, etc. Natural insulators are obtained from agriculture and forest residues, sheep wools [21], and biochar that is obtained from the pyrolysis of agricultural residues.

In most cases, the replacement of part of the conventional building materials by waste materials, such as coffee grounds, natural fibers, wood aggregates, and rubber waste particles, enable to decrease the thermal conductivity and density of the building composites leading to better insulators. Building materials and cement composites have thermal conductivities in the range of $0.120\text{--}0.975\text{ W m}^{-1}\text{ K}^{-1}$ [22].

However, the main disadvantage of insulation materials is the reduction of mechanical properties, such as compressive and tensile strength, which limits their percentage in building materials (between 2.5% and 10%) [23,24].

Lastly, the thermal capacity, energy efficiency, and comfort impact of the thermal storage unit (building, structure or storage unit) can be increased by using PCMs.

2.2.3. Building Envelopes Integrating PCMs

PCMs have the advantage to be easily incorporated into the building structure. PCM-based gypsum boards have been used in many studies to incorporate PCMs into building envelopes [25–27]. In fact, gypsum boards are cheap and widely used in many applications, making them very suitable for encapsulating PCMs [28].

Window shutters can also be used to embed PCMs in buildings [29–31]. Thus, the shutter containing the PCMs is placed on the outside of the windows. During the day, they are open and exposed to solar irradiation, heat is absorbed, and the PCM melts. At night, the shutter is closed and the heat from the PCM is released into the rooms.

Finally, another possibility is to incorporate the PCMs into concrete blocks or other building materials, which results in a structure with high thermal inertia. This technique allows the incorporation of PCMs throughout the building envelope (walls, roofs, floors) to store energy [32–36].

2.2.4. Trombe Walls

Originally developed by Edward Morse in 1881, this passive wall system is named after the French architect Felix Trombe who began applying it in the late 1950s [37]. Standard Trombe walls consist of a high thermal mass wall made of concrete, stone, brick, or earth, covered with glass, resulting in an air channel between the two components.

New Trombe wall configurations incorporating PCMs have been developed in recent years to boost their performance [38–41]. The PCM layer is usually placed on the wall

surface but can also be located inside the wall [42]. The use of PCMs in the Trombe wall reduces the annual energy consumption by 10–30%, depending on the climatic conditions [43,44]. This is because PCMs can increase the amount of stored thermal energy. Therefore, the Trombe wall will be able to heat the room much longer with PCMs than without PCMs.

In the next section, we will discuss the different techniques for incorporating PCMs into passive systems.

2.2.5. Incorporation of PCMs into Building Envelopes

The integration of PCMs into building envelopes improves thermal comfort by reducing peak and fluctuating indoor temperatures due to a storage density 5–10 times higher than that of standard walls [17]. Moreover, thanks to this high thermal inertia, the temperature peak is delayed in time, resulting in a reduction in peak temperature, which allows taking advantage of lower electricity costs.

PCMs can be incorporated into the entire building envelope: walls, roofs, windows, and floors. Four techniques for incorporating PCMs into building envelopes are presented in the literature: direct incorporation, impregnation, encapsulation, and shape-stabilized.

The distinction between the last two methods is not clear in the literature. Some authors [9,18,45] distinguish between encapsulation and shape stabilization, while Umair et al. [46] classify encapsulation in shape stabilization. In this section, we will distinguish between encapsulation and shape stabilization.

2.2.6. Direct Incorporation

This technique involves the direct incorporation of PCMs into building materials. Direct incorporation is considered the simplest and most economical way to incorporate PCMs into building walls [17]. The main disadvantage of this technique is the risk of leakage of the PCM over time and degradation of the mechanical properties of the building material [45].

2.2.7. Impregnation

In this method, the porous building material, such as gypsum board, brick or concrete block, is immersed in the molten PCM and absorbs it by capillarity [20]. Although more effective than the direct incorporation technique, it is still subject to the same risks of leakage and degradation of the mechanical properties of the building material.

2.2.8. Encapsulation

In this technique, the PCM is encapsulated before incorporation into the building materials to contain the liquid phase. The encapsulation material must meet certain criteria to be compatible with the materials of construction: (1) formation of a shell surrounding the PCM called the core; (2) prevention from the leakage of molten PCM; (3) no incorporation of impurities into the core/shell system, and (4) resistance to mechanical and thermal stresses [47]. Capsules are classified based on their size and shape, which are influenced by the synthesis process and the type of shell material used. They are referred to as nano-capsules or nano-spheres if the diameter of the capsules is between 0 and 1000 nm, micro-capsules if the diameter of the capsules is less than 1 mm or 1 cm, and macro-capsules when the capsules are larger than 1 mm or 1 cm [48].

2.2.9. Shape-Stabilized

Shape-Stabilized PCMs are obtained by impregnating PCMs into porous building materials. This technique stabilizes the PCMs and prevents leakage problems during the phase change process due to capillary force, surface tension, hydrogen bonding interaction, and other interactions between the porous matrix and the PCMs confined in the nanopores of the building materials [49].

In general, two main techniques are used to infiltrate liquid or solid PCMs into a porous support to fabricate shape-stabilized PCMs composites: the two-step impregnation method and the one-step in situ synthesis method.

The two-step technique involves impregnating liquid PCMs into the nanopores of the porous support. Various impregnation methods have been used to synthesize shape-stabilized PCMs. The preparation processes generally involve the following steps: (1) design and synthesis of the porous supports; (2) addition of the porous support to the PCM solution, which is absorbed into the porous supports, and (3) obtaining the final composite PCMs after complete evaporation of the solvent [49]. Depending on the impregnation process, this method can be divided into direct impregnation and vacuum impregnation. Jeong et al. [50] analyzed the impregnation rate of a PCM in vacuum and non-vacuum processing. It was found that the impregnation rate was close to 50% in the vacuum treatment compared to only 30% in the non-vacuum conditions.

In the one-step method, the PCMs are encapsulated in situ during the formation of an interconnected network of porous supports [49].

There are a wide variety of materials used for shape stabilization of PCMs, including polymers, porous materials, and nanomaterials. Umair et al. [46] classified these materials into five major groups: micro-encapsulation, polymer matrices, nanomaterials, porous materials, and solid-solid PCMs.

Table 3 summarizes the advantages and disadvantages of the different techniques for incorporating PCMs into buildings. Due to the simple and inexpensive manufacturing techniques, the very high impregnation rate compared to other techniques as well as the wide variety of support materials available, shape stabilization was chosen to impregnate PCMs in our future studies.

Table 3. Advantages and disadvantages of the different techniques for incorporating PCMs into buildings [9,18,47,49].

Techniques	Advantages	Disadvantages
Direct incorporation	<ul style="list-style-type: none"> - Easy technique - Economical technique 	<ul style="list-style-type: none"> - Reduction of mechanical properties - Impact on the hydration process - Leakage of PCM
Impregnation	<ul style="list-style-type: none"> - Easy technique - Economical technique 	<ul style="list-style-type: none"> - Long-term leakage of PCM - Incompatibility with building materials - Corrosion of reinforced steel when incorporated into concrete elements
Micro-encapsulation	<ul style="list-style-type: none"> - Improvement heat transfer - Reduction of volume variation of PCM - Possibility of incorporation into various materials - Reduction of phase separation and improvement cycle stability - Improvement of thermal reliability 	<ul style="list-style-type: none"> - Limitation of the volume of PCM that can be used - Complex and costly manufacturing process - Requirement for a non-permeable capsule to prevent leakage - Some production methods may have harmful by-products
Macro-encapsulation	<ul style="list-style-type: none"> - Improved environmental compatibility of materials - Improved handling of PCMs during production - Increase in the amount of PCMs used 	<ul style="list-style-type: none"> - Moisture transfer problem since the PCM is macro-encapsulated - More work to integrate into the building envelope. - Low thermal conductivity

Table 3. Cont.

Techniques	Advantages	Disadvantages
Shape-stabilized	- Simple and inexpensive techniques	- PCMs can diffuse to the surface and be progressively lost if the process is not optimized
	- Containment of the liquid phase	- More contact between the PCM and the environment, which can lead to corrosion or adverse reactions
	- Wide variety of support materials	
	- Increased thermal conductivity	
	- Possibility to encapsulate a large fraction of PCMs (10–100%)	

3. Studies of PCMs Incorporated in Passive Systems

3.1. Experimental Studies

In recent years, many experimental studies have been carried out to evaluate the performance of buildings incorporating building materials/PCMs composites. In this section, these studies are divided into two categories according to the scale involved (material or system).

3.1.1. At the Composite Scale

Cunha et al. [19] incorporated a paraffin PCM (RT22HC) into a mortar made from Portland cement. Four different compositions were tested from the fresh to the 28-day aged state: the reference mortar (0 wt% PCM) and three other mortars composed of 5 wt%, 10 wt% and 15 wt% PCM. The different mortar formulations were tested in terms of physical properties (workability, density, water absorption by capillarity and immersion), mechanical properties (compressive and tensile strength) and thermal behavior. The thermal test was conducted in a climatic chamber of 0.008 m³ simulating the summer (11–44 °C) and winter (12–29 °C) climatic conditions of a region in Portugal. The results show an improvement of the liquid binder ratio but a reduction for superplasticizer with the PCM fraction was observed. Moreover, the incorporation of 5 wt% of PCM leads to a reduction of the water absorption coefficient by capillarity of 34%. The mechanical properties varied little with the addition of PCM up to 20 wt% where reductions of 8% and 19% were observed for the compressive and tensile properties. On the other hand, the mortar with 20 wt% PCM exhibited the best thermal performance due to a reduced peak temperature of 5 °C and was delayed by 48 min in time.

In a similar study, Kulkarni and Muthadhi [51] analyzed and compared the thermal performance of direct incorporation of PCMs into mortar. Five different PCMs with phase change temperatures in the range of 17–33 °C were used in this study: two inorganic PCMs, HS24 and HS29, and three organic PCMs, OM29, which is a commercially available organic PCM, n-Butyl stearate (n-BS) and polyethylene glycol-600 (PEG-600). The cement in the mortar is partially replaced by the PCMs in proportions of 5 wt% to 15 wt%. To ensure proper retention of the liquid phase of the PCM in the mortar, a leakage test was conducted. The compression test showed a reduction in compressive strength with the addition of PCM. For inorganic PCMs, there was no effect on the mechanical strength at all ages up to 10 wt% incorporation rate compared to organic PCMs where a drastic reduction in mechanical properties is observed at all incorporation levels regardless of ages. All PCM compositions showed high thermal stability after 750 and 1000 cycles. Thermal conductivity measurement performed by the guarded hot plate method for several days shows an increase in thermal conductivity with age and a decrease with the addition of PCM. The formulation of 10 wt% inorganic PCM in the mortar was selected as optimal because it

does not affect the mechanical strength properties and has good thermal performance with a reduction in peak temperature of 3–5 °C.

Boussaba et al. [52] conducted an experimental and numerical study of the characteristics of a bio-sourced composite material by direct impregnation of a vegetable non-cocoa oil in an insulating material made of clay and cellulose fibers with an incorporation rate of 56% by volume of PCM. The temperatures, heat of fusion, and solidification of the composite material are measured by differential scanning calorimetry (DSC) and have values of 34.83 °C, 22.34 °C, and 60.41 J g⁻¹, 62.39 J g⁻¹, respectively. The results of chemical and thermal analysis showed good thermochemical stability of the composite material after more than 2000 cycles. However, the PCM impregnation reduces the mechanical properties of the composite material by a factor of two, which remain acceptable for non-building applications. The addition of recycled graphite increased the thermal conductivity by 415% (from 0.2 to 0.83 W m⁻¹ K⁻¹).

Dehmous et al. [33] developed a new thermal energy storage concrete consisting of lightweight aggregates impregnated with vegetable oil PCMs, of melting temperature between 23 and 26 °C, mixed in a cement mortar. Three types of mineral aggregates were used (bentonite, sepiolite and silica gel), as well as two impregnation methods, namely direct incorporation and vacuum impregnation. The best impregnation rates were obtained with silica gel (56%), but sepiolite (32%) should be preferred for regulatory reasons according to the mechanical tests. In fact, the regulations for masonry elements stipulate that the value of compressive strength should not be less than 15 MPa [53]. Despite a loss of mechanical strength, the authors demonstrated that composite mortars with a compressive strength greater than 7–10 MPa are feasible. In addition, the results showed an improvement of 24.4% and more than 13.5% for energy storage capacity and thermal conductivity, respectively.

Bake et al. [54] studied the effect of incorporating micro-encapsulated PCMs (MICRONAL[®] DS 5040X) with temperature between 22 and 23 °C with a heat of fusion of 95 J/g into gypsum board. The proportion of PCM is chosen lower than 30 wt% in order to guarantee the mechanical properties of the composites. Thus, four different compositions of gypsum boards are manufactured: reference gypsum board (0 wt% of PCM), gypsum with 5 wt% of PCM, gypsum with 10 wt% of PCM, and gypsum board with 15% of PCM. The incorporation of PCMs leads to a reduction in compressive strength but the value is still permissible given the recommendation for gypsum board in the building structure, which suggests a compressive strength greater than or equal to 2 MPa [55]. In addition, the thermal conductivity decreases with the addition of PCM that increases the insulation properties of the gypsum boards.

Li et al. [56] conducted an experimental study on the thermal performance of wall-boards containing a micro-encapsulated PCM (MPCM for micro-encapsulated PCM), PH-31, using two methods: DSC and a home-made experimental device. Three different techniques were used to obtain the enthalpy-temperature (H-T) curve: theoretical calculation from DSC data, a dynamic method, and the stepwise method. The sample analyzed is composed of gypsum with 20 wt% microencapsulated kerosene having a phase change temperature of 31 °C. The addition of MPCM decreases the thermal conductivity of the gypsum board due to the lower density and thermal conductivity of PCM, but increases the apparent heat capacity up to 2.71 times for a temperature range of 26–32 °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 [57–59]. Kirilovs et al. [60] investigated the specific heat capacity and thermal conductivity of a wallboard made from hemp shives mixed with a commercial organic PCM, S50 at 5 wt%. The addition of nano-capsules increased the heat capacity by 62% to 2.369 J g⁻¹ K⁻¹. The thermal conductivity of the samples is in the range of 64–74 mW m⁻¹ K⁻¹, which is consistent with the class of commercially available hemp insulation products.

To improve the thermal conductivity of building envelopes incorporating PCMs, additives, such as expanded graphite (EG for "expanded graphite"), montmorillonite, pen-

taerythritol, and melamine polyphosphate can be used [61]. Karaipekli and Sari [62] found that the thermal conductivities of fatty acid/expanded vermiculite composite PCMs were increased by 104–150% by the addition of 10 wt% expanded graphite. Wang et al. [63] have suggested that dopamine modification can solve the problem related to the measurement of the latent heat of expanded vermiculite (EVM)-based composite PCMs. Indeed, the measured latent heat were significantly lower than the calculated values during the phase change process. This mismatch is reduced by increasing the concentration of dopamine. The effect of the dopamine is the modification of the surface of EVM leading to an increase of the latent heat and the encapsulation capacity.

Rathore and Shukla [64] investigated the combined effect of loading expanded graphite (EG) and expanded vermiculite (EV for “expanded vermiculite”) on the thermo-physical and thermal regulator properties of commercially available low-cost PCM (OM37). Four samples with different compositions of EG, PCM and EV were prepared with 0, 3, 5, and 7% expanded graphite, respectively. The heat of fusion of the composite was reduced from 50% to 57% compared to pure PCM due to the increase in the mass percentage of expanded vermiculite and expanded graphite in the composite, which do not contribute to latent energy storage. Increases of 33.1%, 79.3%, and 114.4% in the thermal conductivity were observed for the composites containing 3%, 5%, and 7% EG compared to pure PCM. The prepared composites exhibited the same thermal characteristics after 1000 heating and cooling cycles. In addition, when incorporated into the wall panel, the composite containing 7% EG showed excellent ability to regulate the interior temperature.

Biochar has been used to fabricate stabilized shapes due to its interesting porous structure [65–67]. Zhang et al. [68] prepared a shape-stabilized composite material by impregnating a eutectic mixture of lauric-stearic acid (LA-SA) into carbonized corn cobs (CNCC). The latter, thanks to its porous structure, constitutes an excellent support material allowing the LA-SA eutectic mixture to be suitably encapsulated with a maximum impregnation rate of 77.9 wt%. DSC analysis showed that the LA-SA/CNCC composite melts at 35.1 °C with a heat of fusion of 148.3 J/g and solidifies at 29.7 °C with a heat of solidification of 144.2 J g⁻¹. Moreover, its stability after 200 cycles makes it a good candidate for an application in energy storage in buildings.

To minimize the degradation of the thermal regulation performance of PCMs composites, Liu et al. [69] proposed the multi-layer sandwich structure of Na₂SO₄·10H₂O, expanded vermiculite and magnesium oxychloride cement (MOC) with a melting temperature in the range of 20–40 °C. Compared with the MOC house-like model and ambient condition, the multi-layer sandwich PCM composite exhibited better results with time shift of 93 min and 84 min for heating and cooling, respectively.

Different techniques are available to integrate PCMs into building envelopes. However, between the high cost of micro-encapsulation and the leakage problems of impregnation and direct incorporation techniques, shape-stabilized PCMs are a good compromise. Moreover, the availability and the wide range of support materials considerably increase the field of application of shape-stabilized PCMs.

Numerous experimental studies have shown that it is possible to increase the thermal conductivity of PCMs by shape stabilization with suitable support materials [70]. Table 4 summarizes some studies using materials of natural origin to shape-stabilize PCMs. It appears that bio-sourced materials, in particular, insulating materials, are promising for the future.

Table 4. Various experimental studies using naturally occurring support materials for the fabrication of shape-stabilized PCMs.

Composites		Temperature of Fusion (°C)	Heat of Fusion (J g ⁻¹)	References
Support materials	PCM (wt%)			
Diatomite	Paraffin (47.4)	41.11	70.51	[71]
	PEG (50)	27.7	87.09	[72]
	Capric-lauric acid (CA-LA)	23.61	87.33	[73]
Kaolin	Lauric alcohol (24)	19.14	48.08	[74]
	Capric acid (17.5)	30.71	27.23	[75]
	PEG600 (21)	5.16	32.80	[75]
	Heptadecane (16.5)	22.08	34.63	[75]
	Stearic acid (75)	60.1	149.5	[76]
Expanded Vermiculite	n-octadecane (80)	26.1	142	[77]
	Lauric acid (70)	41.88	126.8	[78]
	CA-PA-SA (70)	19.3	117.6	[79]
	CA-LA (40)	19.09	61.03	[62]
	CA-PA (40)	23.51	72.05	
CA-SA (40)	25.64	71.53		
Expanded Graphite	Heptadecane (94.5)	13.8	195.9	[80]
	LA-MA-SA (92.3)	29.05	137.1	[81]
	PEG (90)	18.89	98.59	[82]
	SA (90)	52.74	169.9	[83]
Biochar	Heptadecane (25.7)	13.9	53.3	[80]
	Paraffin (60)	57.67	179.4	[84]
	LA-SA (77.9)	35.1	148.3	[68]
	Methyl palmitate (43-55)	26–27	108–138	[85]

Table 4. Cont.

Composites		Temperature of Fusion (°C)	Heat of Fusion (J g ⁻¹)	References
Wood flour	LA-SA (60.3)	33.1	98.2	[86]
	Paraffin (29.9)	26.18	20.62	[87]
	CA-PA (80)	22.30	28.16	[88]
Wood fibers	CA-SA (52)	23.38	92.1	[89]
Wood (other forms)	CA-PA (61.2)	23.4	94.4	[90]
	1-tetradecanol (65)	36.87	119.2	[91]
	PEG (45.58)	25.5	46.7	[92]
	MA (83.9)	55.7	179.1	[93]
	Paraffin (84)	60.3	181.9	[93]
	PEG (74.1)	55.8	132.6	[93]
	1-tetradecanol (60.04)	36.24	125.6	[94]
Vegetable fibers	Paraffin (87.2–91.3)	22.1–22.5	192.2–201.6	[95]
	MA-TD (40.5)	28.5–42.5	192	[96]

In addition to their biological origin, these materials have a very good porous structure, which justifies the very high value of the impregnation rate approaching 100%. Shape stabilization is therefore considered as a promising way to take advantage of the latent storage capacity of PCMs. The list of bio-sourced materials that can be used to shape-stabilize PCMs is very large, so we focus on insulating materials that are already in use or are promising for application in buildings (Table 5). These are vegetable fibers, such as flax or hemp. Another advantage of these materials is their ability to regulate humidity, which ensures good indoor air quality. Finally, the cost of these bio-sourced insulators is very attractive.

Fatty acids and their eutectic mixtures have melting temperatures suitable for thermal comfort application (15 to 30 °C, T) and are commonly used. In addition, they are renewable and have similar or better characteristics than paraffin waxes used in actual systems. Fatty acids of interest for the targeted application are reported in Table 6.

Table 5. Bio-sourced insulators considered in a future study as support materials for the fabrication of shape-stabilized PCMs.

Insulator	Density (kg m ⁻³)	Thermal Conductivity (W m ⁻¹ K ⁻¹)	Cost (€/kg)	References
Bamboo fibers	431–538	77–88	–	[21]
Hemp fibers	25–100	40–49	2–5	[97]
Flax fibers	20–100	35–45	5–25	[97]
Cotton stalk fibers	150–450	58–82	–	[98]
Chênevotte	100–140	80–122	0.8–1	[99]
Kapok	17.24	30–48.6	–	[96,100,101]
Fibres de coco	40–90	501.09–57.58	63	[102]

Table 6. Fatty acids of interest for the targeted application, CA: capric acid, LA: lauric acid, MA: myristic acid, PA: palmitic acid, SA: stearic acid [103,104].

PCM	Temperature of Fusion (°C)
CA	29.87
CA (72%)-LA (28%)	21.14
CA (84%)-MA (16%)	24.24
CA (87%)-PA (13%)	27.95
CA (93%)-SA (28%)	26.91
LA (71%)-MA (29%)	33.07
LA (79%)-PA (21%)	35.46

3.1.2. At the System Scale (Envelopes and Buildings)

PCMs can also be integrated into existing building envelopes through the insulation layers. Lee et al. [105] integrated paraffin with a melting temperature of 28–30 °C into cellulose wall insulation. Two experimental cells of quasi-cubic shape (5.09 m³) with a window size of 0.32 m² were constructed to evaluate the energy performance of insulation with PCMs. Molten PCM is sprayed on the cellulose insulation and the mixture is blown into the wall cavities. Only summer data was studied, as the objective was to reduce space cooling and shift the thermal load over time by measuring the indoor air temperatures on the inside and outside of each wall. The incorporation of paraffin in the insulation reduced the heat flux from 16.1% to 38.5%. The maximum heat flow is delayed from 1.5 to 3 h, which reduces the electricity bill. Analysis of the results for each wall individually showed that only the west-facing wall exhibited a significant reduction in maximum heat flow.

Erlbeck et al. [106] studied different forms of hydrated salt-based PCM macro-encapsulated in aluminum foil to test the influence on the convective heat transfer during phase change. The PCM used is a mixture of 50 wt% MgCl₂·6H₂O and 50 wt% CaCl₂·6H₂O with a melting temperature of about 21 °C. Several brick block samples containing four different shapes of PCM macro-capsules were fabricated: cubic, cylindrical, spherical and plate shapes, and then compared to reference brick blocks. The results showed that changing the design of a set of PCMs can adjust the thermal behavior without changing the mass of the PCM. The best results were obtained for the plate and cylindrical shape but the complex production process required outweighs the positive thermal effects obtained.

Vicente et Silva [107] conducted a study on three types of wall: a horizontally hollowed-out clay wall taken as reference, a wall with macro-capsules of PCM and a wall with macro-capsules of PCM plus an insulation layer (XPS) named M1, M2, and M3, respectively. The walls are made of horizontally hollowed-out clay bricks (0.009 cm³) with insertion of parallelepiped steel macro-capsules of two different thicknesses (2.8 cm and 0.75 mm) filled with RT18, an organic PCM with a melting temperature of 18 °C. The tests were

conducted in a climate chamber simulating the equivalent temperature profile for different cities in Portugal. The results showed a strong reduction of the temperature peak for M2 and M3 compared to the reference (M1), up to 50% and 80%, respectively. In addition to the reduction of the temperature maximum, the peak is delayed in time by 3 h for M3. These results provide clear evidence of the thermal regulation effect of macro-encapsulated PCM and the value of combining PCM with well-managed insulation layers to achieve energy savings.

Al-Yasiri and Szabó [108] conducted an experimental study to determine the optimal thickness of a roof incorporating PCM macro-capsules containing paraffin wax of melting temperature 44 °C under the hot climate of Iraq. Three different thicknesses of 10, 15, and 20 mm were studied based on energy indicators, such as ambient temperature, interior surface temperature, and average exterior surface temperature. The values obtained were compared to a reference roof without PCM. The roofs with PCM showed a reduction in maximum room temperature between 7.25 and 9 °C compared to the reference roof. Increasing the thickness from 10 to 15 mm reduced the room temperature by 2.3% compared to only 0.4% when the thickness was increased from 15 to 20 mm. The average decrease in room temperature fluctuation during the day and night is defined as the sum of the average decrease in room temperature during the day and the average increase in room temperature during the night. This parameter allows comparison of different storage devices. The best value is obtained for 15 mm of macro-encapsulated PCM. The reason is that the 20 mm is too thick to solidify passively during the night, which reduces its performance.

To solve the moisture transfer problem caused by macro-encapsulation, Sun et al. [109] proposed a method for encapsulating PCMs in pipes. The tests were conducted in a cubic dynamic wall simulator. n-Octadecane with a melting temperature between 27.5 and 38 °C is used as the PCM. The PCM is melted and then poured into a copper pipe and placed inside the wall cavity by using a wooden frame. Two pipes of different diameters, 1.9 cm and 1.27 cm, are used and placed at two different locations: medium depth and next to the wall. The maximum reduction in peak heat flux was 36.5% for a mass fraction of PCM of about 25% when the maximum wall surface temperature was 55 °C. When the PCM is encapsulated in the 1.27 cm pipes and placed next to the wallboard, the maximum reduction in peak heat flux was 22.45%. Based on these results, the authors conclude that the optimal position should be between the middle depth and the wallboard to complete the daily melting/solidification, and that the PCM should be encapsulated in smaller tubes with a larger surface/volume ratio so that the phase transition process can proceed easily.

In order to increase the apparent thermal capacity of buildings, it is possible to incorporate PCMs not only in the building envelope but also in the partition walls and windows. Bontemps et al. [110] conducted an experimental study in two small rooms separated by a hollow glass brick wall and filled with three different PCMs: fatty acid, paraffin, and salt hydrates with melting temperatures of 21.4 °C, 25 °C, and 27.5 °C, respectively, and compared with an identical cell without PCM. The maximum temperature of the test cell with PCM is lower than that without PCM. The temperature decrease varies between 3.5 and 4 °C for fatty acid, 2 and 3 °C for paraffin, and between 3.5 and 5 °C for salt hydrate. These results are difficult to compare because of the varying boundary conditions. For this reason, a 1D model based on the Kondo method [111] was developed with TRNSYS. The simulated PCM temperature follows the same dynamics as the experimental temperature. In fact, the result of the simulation compared with the experiences showed that the assumption of a plane liquid-solid interface of the model is not valid because the PCM melts mainly at the center.

Silva et al. [29] conducted an experimental campaign during summer on a south-facing window shutter containing PCMs. The test cell was located in Aveiro, Portugal, a region with a Mediterranean climate. The south-facing orientation is chosen because it is subjected to discomfort problems, such as indoor temperature asymmetry in winter and overheating in summer. The cell is divided into two internal compartments (of equal dimensions) by an internal partition. The front facade consists of four double-glazed

windows. The reference compartment is equipped with an aluminum shutter; the PCM compartment is equipped with the same shutter filled with paraffin (RT28HC[®]). The results showed a thermal regulation capacity of the internal temperature of about 18–22% for the compartment equipped with the PCM shutter. The maximum and minimum temperature peaks decreased by 6% and 11%, respectively. In addition, the minimum and maximum temperature peaks are delayed by 45 min and one hour, respectively, compared to the reference compartment.

The majority of studies in the literature focus on the short-term thermal stability of PCMs incorporated into buildings. In order to provide reliable data and to go beyond the development stage, it is essential to investigate the stability of building envelopes with integrated PCMs over longer periods in real environmental conditions of a building. To this end, Cabeza et al. [112] evaluated the thermal performance of a cubic concrete enclosure containing encapsulated PCMs ten years after its construction in a previous study by the same authors [113]. In this previous study, two cubic enclosures were constructed, one serving as a reference made with conventional concrete and the other containing 5 wt% of encapsulated PCMs. The results showed a more stable temperature and a delay in maximum heat flux for the enclosure containing PCMs. Although the experiments in 2005 and ten years later were both performed in summer, the weather conditions were not identical. Indeed, the solar radiation was similar, but the outdoor temperature was higher in 2016 than in 2005. As a result, the indoor temperature was also higher in 2016 than in 2005, which explains a difference in temperatures between conventional concrete and concrete incorporating with and without PCMs (between 1–3 °C in 2005 and 5–7 °C in 2016). These results showed that concrete with PCMs is much more effective under extreme conditions (very high temperatures). The compressive strength test performed in 2016 in the same way as in 2005 showed no significant variation, which allows to affirm that the concrete with PCMs shows no change or mechanical degradation.

3.1.3. Dynamic Numerical Simulations of Buildings Incorporating PCMs

Numerical modeling and simulation of PCMs embedded in building envelopes are very useful for building design and optimization. In most numerical studies, commercial software, such as EnergyPlus, TRNSYS, MATLAB, COMSOL, and ANSYS Fluent, are used to solve the energy equations and to perform numerical simulations under varying weather conditions [17]. The main objective of these simulations is to study and optimize the effect of the integration of PCMs in the walls of buildings, their position in the walls, their thermo-physical properties, such as melting temperature, thermal conductivity, and the effect of their thickness.

Frazzica et al. [114] studied composites based on standard mortar and two commercial micro-encapsulated paraffin PCMs with melting temperatures of 23 and 26 °C, respectively. Several percentages of PCMs were used and the performance of the resulting composites was experimentally tested. These experimental data were used to validate a numerical model developed on COMSOL Multiphysics. The numerical model is based on a one temperature formulation and considers that the PCM and the mortar constitute a homogeneous medium. A parametric study was conducted to propose a method to optimize the choice of the melting temperature of the PCM. Using the climatic conditions of Messina in Italy, the authors obtained an optimal temperature of 27 °C. The results also showed that the addition of 15 wt% of PCMs increases the thermal comfort conditions by about 15% compared to the reference case composed of pure mortar (without PCM) based on the American standard ASHRAE 2017 [115].

Zhou et al. [116] conducted a parametric study on the factors influencing the performance of PCM-based wallboard applied on the interior and exterior faces using the effective heat capacity method to describe the phase change. The exterior wall is subjected to a periodic boundary condition and solar radiation. Thermal properties, such as melting temperature, phase change range, enthalpy of fusion, thermal conductivity, and heat exchange coefficient, were optimized based on two criteria: interior surface temperature and

diurnal thermal energy storage. The optimal melting temperature of the PCM embedded in the interior wall is equal to the interior ambient temperature without taking into account the internal heat gains. The melting temperature of the exterior PCM wall depends on both the interior and exterior environments, although the impact of the exterior environment is reduced due to the exterior insulation. Walls containing PCM show the best results if the PCM melts completely over a full daily cycle. Moreover, the parametric study showed that the thermal conductivity of the PCM has a low impact on the results.

Thiele et al. [117] examined, through a numerical study, the effects of adding micro-encapsulated PCMs to concrete based on four criteria: PCM mass fraction, enthalpy of melting, phase change temperature, phase change range, and external temperature. The simulations were performed considering two walls: one heterogeneous and one homogeneous. The difference between the simulation of the heterogeneous and homogeneous walls is less than 2%, which shows that the heterogeneous composite can be treated as a homogeneous material with a volumetric thermal capacity and an effective thermal conductivity. The rest of the simulation was therefore performed with a homogeneous model. The main results are as follows:

- the addition of micro-encapsulated PCM and/or the increase of the PCM melting enthalpy reduced and delayed the thermal load of the building,
- the melting temperature of the PCM should be close to the indoor temperature regardless of the climatic conditions,
- the phase-change temperature range had limited effect on energy flux reduction and time shift.

The thermal performance and energy consumption of a prefabricated building with PCM was investigated using EnergyPlus software in five different climate regions in China: severe cold area, cold area, mild area, hot summer and warm winter area, hot summer and cold winter area [118]. The study focused on the optimization of the thermal properties of the PCM, its position in the building structure, and the orientation of the PCM added to the building envelope using the direct incorporation technique. The results showed that adding the PCM to the building envelope on the East or West side is more energy efficient compared to the other orientations. For different regions, based on a comprehensive evaluation of the relationship between energy savings rate and cost, increasing the thickness of PCM has a limited effect on improving the energy savings rate of buildings. The authors suggested to place the PCM on the interior side of the building regardless of the area, as the energy saving rate is 77.11% and 32.53% when PCM is located on the interior and exterior sides of the wall, respectively.

Al-Absi [119] reviewed the related literature that examines the application of PCMs in different positions inside the walls of buildings to determine their optimal position and influential parameters. It was found that the optimal positions of PCMs are highly dependent on parameters, such as climatic and weather conditions, and the purpose of the application, melting temperature and melting enthalpy of PCMs, amount of PCMs, thermal properties of wall materials, and wall orientation.

In order to improve the thermal inertia effect in buildings using shape-stabilized PCM wall panels, Wi, Chang et al. [120] analyzed the enthalpy-temperature function based on the thermal properties of 22 types of shape-stabilized PCMs and applied it to a dynamic energy simulation program. The modeled building has a wooden structure and is south-facing. Then, the PCMs were integrated into the internal and external face of a 20 mm thick wall. A preliminary study was carried out to determine where the PCM should be integrated. During cooling periods, the PCM should be placed on the outer layer of the wall and on the inner layer during heating periods because it is effective in storing and releasing the heat generated in the room during this period. On average, total energy consumption was reduced by 5% per year.

Recently, Li et al. [36] conducted an optimization process with COMSOL Multiphysics to find the best value for critical parameters such as: the location of the PCM layer, its thickness, the melting temperature of the PCM, and different loading conditions (month

and city). The authors used two performance indicators to evaluate the performance of the wall: the instantaneous fluctuation of the indoor temperature and the intensity of thermal discomfort, which is defined as the period during which the temperature is outside the chosen thermal comfort range between 22 and 28 °C. The optimal position is obtained for PCMs placed close to the inner layer of the wall. The analysis of several thicknesses ranging from 2.5 to 15 mm showed better results obtained for thicker layers due to the comparatively larger amount of PCMs. It was also found that the selection of the melting temperature of PCMs is highly dependent on the loading condition. Indeed, the authors recommend PCMs with a melting temperature between 26–30 °C for cooling and 20–24 °C for heating.

3.1.4. Discussion

At the experimental level, it can be seen that the majority of studies are focused on the development of composite materials and their characterization. Different materials and methods of incorporation have been used and the positive effect of PCMs on temperature regulation inside buildings has been demonstrated. However, among the analyzed articles, very few have moved to the application of PCMs at the building or wall scale. This last step is essential to evaluate the effect of PCMs at real scale. Some areas of uncertainty remain, namely the positioning of the PCM in the building envelope, and the melting temperature of the PCM to be chosen according to the climatic conditions, even if many studies have been carried out in this direction.

The literature also lacks studies on the stability of PCMs in building envelopes over the long term and the effect of aging. A very important aspect that remains to be investigated is the analysis of the hydric behavior of buildings incorporating PCMs necessary for the evaluation of air quality. Finally, as pointed out by Lamrani et al. [17], no study takes into consideration the internal loads and the existence of the occupant or his behavior (real use of the building).

Numerical studies carried out under different climatic conditions established criteria for the selection of PCMs as well as their location in the building envelopes. The conclusions of these studies showed that the PCM should be placed near the heat source. Thus, in hot climates, the PCM should be located next to the exterior envelope while in cooler climates, a location near the interior envelope is recommended.

The findings of the various numerical studies indicated the need to conduct an optimization study on the properties of the PCM to select its location as well as its quantity under various weather conditions.

4. Conclusions

In this work, recent experimental and numerical advances on the incorporation of PCMs in building envelopes have been reviewed. Passive thermal energy storage systems in buildings incorporating PCMs are presented as a promising solution for improving the energy efficiency of buildings. The various studies have shown the potential of PCMs to reduce peak temperature, temperature fluctuations, and improve thermal comfort. The PCMs targeted for passive storage must have a melting temperature in the comfort range (15 to 35 °C). Fatty acids and paraffinic compounds have been used in the majority of experimental studies. Techniques for incorporating PCMs into passive systems are classified into four categories: direct incorporation, impregnation, encapsulation, and shape-stabilized PCMs. Shape-stabilized PCMs are promising because of the high impregnation rate compared to other techniques and the wide variety of support materials. Most of the studies were devoted to the optimization of the selection of the PCM and its position in the building envelope according to the climatic conditions.

Despite numerous improvement, more studies are required regarding the mass and moisture transfer problem, the long-term stability of passive systems incorporating PCMs, the optimization of the properties of the PCMs and their location, and the consideration of the real use of the building in numerical simulations.

This literature review allowed us to screen the different PCMs, support materials, the different techniques of incorporation of PCMs in building envelopes, and the challenges to be taken up for a future study. In terms of PCMs, fatty acids and their eutectics have retained our attention because of their renewable nature and their interesting thermo-physical properties. These PCMs can be stabilized in shape by using natural insulators, such as vegetable fibers, already used in building insulation.

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