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Abstract: Due to growing consciousness regarding the environmental impact of fossil-based and non-sustainable materials in construction and building applications, there have been an increasing interest in bio-based and degradable materials in this industry. Due to their excellent chemical and thermo-physical properties for thermal energy storage, bio-based phase change materials (BPCMs) have started to attract attention worldwide for low to medium temperature applications. The ready availability, renewability, and low carbon footprint of BPCMs make them suitable for a large spectrum of applications. Up to now, most of the BPCMs have been incorporated into inorganic matrices with only a few attempts to set the BPCMs into bio-matrices. The current paper is the first comprehensive review on BPCMs incorporation in wood and wood-based materials, as renewable and sustainable materials in buildings, to enhance the thermal mass in the environmentally-friendly buildings. In the paper, the aspects of choosing BPCMs, bio-based matrices, phase change mechanisms and their combination, interpretation of life cycle analyses, and the eventual challenges of using these materials are presented and discussed.

Keywords: bio-based PCMs; bio-based matrices; buildings and constructions; energy storage applications; wood

1. Introduction

Due to an increase in global population and technological development, the demand for energy has experienced a significant growth over recent decades. In addition, environmental problems have also been one of the biggest concerns associated with the overuse of fossil resources for generating energy. In order to cope with growing energy demands, the energy storage and management methods are as important as finding new energy sources and techniques [1]. Energy consumption in residential buildings is one of the biggest energy demanding sectors that need to be managed and controlled [2]. Recent studies [3,4] reported that more than 40% of the energy generated in the world is consumed in buildings. This represents one-third of the annual greenhouse gases emitted to the environment. Therefore, energy consumption in residential buildings needs to be managed. In this regard, there is a need to find new solutions for keeping the indoor temperature consistent and for controlling the temperature fluctuations. These new solutions should involve environmentally-friendly strategies to avoid negative impact on the environment. To meet these demands, thermal energy storage in the form of latent heat energy storage in bio-based phase change materials (BPCMs) has a role to play. Due to their unique chemical, thermal, and physical properties, BPCMs are promising materials for fulfilling the above-mentioned requirements. Using BPCMs in buildings for thermal energy storage is a strategy to curb energy intermittency. These materials are widely used in buildings for thermal comfort, solar heating systems, thermal protection, air conditioning, etc. [4–6].
For better use of BPCMs, they need to be incorporated in the construction and building elements. Traditionally, phase change materials (PCMs) are incorporated into inorganic materials such as concrete and gypsum in the building elements. Recently, attention has been paid to natural, renewable, sustainable, and environmentally-friendly materials [7,8]. Wood and wood-based materials offer reliable properties, which readily meet the above-mentioned requirements. Some unique characteristics of wood and wood fibers such as renewability and sustainability, easy transformation, high mechanical strength, and proper chemical properties make them one of the best options for construction applications. Wood is widely used in constructions and buildings not only to decorate the interior spaces but also to construct frames, walls, roofs, and floors. Using bio-based materials as PCMs in combination with wood as matrices can address both managing energy consumption and environmental concerns about buildings [7–9].

PCMs incorporation into wood and wooden materials can provide production of reliable materials for utilization in constructions and buildings. Wood is a natural porous material and can be impregnated with PCMs and used in internal and external joineries to enhance thermal mass of the building, control temperature fluctuations in residential buildings, and enhances its thermal comfort [7,8,10].

There is an abundance of review papers covering various treatment and application aspects of inorganic and organic PCMs [11–24]. Most of the studies investigated PCMs incorporated in inorganic matrices. To the best knowledge of the authors, there is no comprehensive review on incorporation of BPCMs into bio-based containers for utilization in building applications. Therefore, the literature review is limited to only bio-based PCMs (BPCMs) and matrices and presents recent developments and research challenges.

2. Basics in the Phase Change Mechanism, Systems, and Analysis

In a specific range of temperature, PCMs store and release energy in terms of latent heat during the phase transition. This process occurs in three phases, i.e., solid-solid, solid-liquid, and liquid-gas [23]. In building envelopes, only a solid-liquid phase change can be considered [6,11,20,22,23]. When the material is heated up to a specific temperature, the hydrogen bonds and other attractive forces (van der Waals) in these materials become weak. The material will then absorb and store energy (heat) in an endothermic process where its phase state transients to another phase state. When the temperature drops down, the material releases the energy and, consequently, returns to its initial phase state [11,19].

2.1. Energy Conversion Mechanism

Ideally, phase transition is an isothermal process during which the temperature of the material remains almost unchanged. The isothermal process offers a reliable storage density with narrow temperature variations between storing and releasing heat [6,20,23,25]. Theoretically, the storage capacity of a latent heat system during phase transition with use of PCMs is given by the following equation [20,22,23,25]:

\[
Q = \int_{T_i}^{T_m} mc_p dT + m_{am} \Delta h_m + \int_{T_m}^{T_f} mc_p dT
\]

(1)

where \(Q\), \(T\), \(m\), \(c_p\), \(a_m\), and \(\Delta h_m\) are storage capacity, temperature, mass of the material, specific heat capacity of the material, fraction melted, and heat of melting per unit mass, respectively. Subscripts \(i\), \(m\), and \(f\), respectively, refer to initial, melting, and final states of the material. If thermo-physical properties of the material are constant, then Equation (1) is rewritten as [20,22,23,25]:

\[
Q = \int_{T_i}^{T_m} c_p(T_m - T_i) + a_m \Delta h_m + c_p(T_f - T_m)
\]

(2)

Figure 1 shows a schematic diagram of the heat storage mechanism of PCM. The process consists of three sections. The first and the last sections are sensible heat storage while the second part presents latent heat storage. The process starts from initial temperature at a certain time and absorbs heat.
Upon heating, the temperature of the material will increase and reach its melting temperature. During the melting process, the temperature remains stable and the heat will be stored in the material in the form of latent heat. By a further increase of the heat, the temperature reaches higher degrees and this extra heat is stored in the form of sensible heat. When releasing the absorbed heat, the process reverses.

The governing energy equation for sensible regions (phases one and three) and latent region (phase two) when the material transfers heat by conduction is expressed by the following equations [26–29]:

For sensible storage:
$$\rho c_p \frac{\partial T}{\partial t} = k \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right)$$  \hspace{1cm} (3)

For latent storage:
$$\rho \frac{\partial h_m}{\partial t} = k \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right)$$  \hspace{1cm} (4)

where \(\rho\) and \(k\) are the density and thermal conductivity of the material, respectively, \(t\) is time and \(x, y,\) and \(z\) are directions. Equation (3) indicates that the temperature of the material changes (sensible storage) while, for the latent heat storage, the temperature remains constant (isothermal process) and the energy is stored by variation in enthalpy (phase change enthalpy), as described by Equation (4).

### 2.2. Energy Storage System Mechanism

In building applications, the process of storing and releasing energy using PCMs can be used for both passive and active systems. In the passive systems, the PCM is incorporated into the building elements and, when the surrounding temperature reaches a melting temperature or above, the PCM will absorb the energy, and release it when the temperature falls down. In active systems, the energy is stored in PCMs in certain separate collectors during lower demands and will be released when the demands are high. This system is mainly used to store solar energy during the daytime when there is abundance of sun and release the absorbed energy during nights when there is more demand for energy [5].
2.3. Available Analytical Methods of Energy and Chemical Behavior of PCM

For thermal analysis of PCMs, differential scanning calorimetry (DSC), T-History methods, guarded hot plate, and thermo-gravimetric characterization methods have been used. DSC is the most commonly used approach to determine the PCMs’ thermo-physical characteristics including melting temperature and latent heat of fusion [6,11,14]. However, this method can only be used for analyzing small and uniform test samples of PCMs [6,11]. Using the T-history method makes it possible to investigate the melting temperature, degree of super cooling, heat of fusion, specific heat, and thermal conductivity of several PCMs simultaneously [6,11,14]. Another method known as a guarded hot plate is used to analyze thermal conductivity of energy saving systems using PCMs [6,11]. Thermo-gravimetric analysis (TGA) is used to evaluate the thermal stability of PCMs [13]. Scanning electron microscopy (SEM) [15] is applied to assess the morphology of the material and particle size distribution. Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) methods are available for investigating chemical stability and compatibility of the materials [15,18].

3. Organic PCM (OPCM) for Building Applications

Studies concerning the incorporation of OPCMs in construction materials concentrated on storing and releasing solar energy for indoor heating. This pattern is suitable for regions where there is enough sun during winter times when the demands for energy is high. However, in many cold weather countries with high interest in biomaterials such as Canada and Nordic countries, there are not many sunny days during the winter periods. Therefore, using OPCMs to control indoor temperature fluctuations in residential buildings seems more interesting than storing solar energy during the daytime and releasing it during nights.

As discussed by Kalnaes and Jelle [11], in cold climates, building constructions ensure passive housing standards, which consist of using a large amount of insulation materials to reduce heating loads exchange between indoor and outdoor temperatures. The authors reported that, when the inside thermal mass of a building with incorporated PCMs increases, the exceeding energy will be stored and released when the indoor temperature drops down. This process results in temperature fluctuations control, which uses the energy more efficiently.

Various parameters should be considered when selecting a suitable PCM for building applications. This includes physical, thermal, chemical, and kinetic characteristics. In addition to these parameters, there are other aspects such as cost, availability, safety, compatibility, and reliability that need to be taken into account [1,4,11–13,15,19,22,23]. A key problem in choosing an appropriate PCM is the working temperature and latent heat of fusion. A suitable candidate PCM should fit the working temperature range and have a large latent heat of fusion.

The basic requirements for a PCM are categorized as follows.

Physical requirements: suitable phase change temperature, large latent heat of fusion, reproducible phase change or cycling stability, little super cooling, no phase separation, and good thermal conductivity.

Technical requirements: low vapor pressure, small volume change during phase transition, chemical stability of PCM, compatibility of PCM with other materials, and a safety constraint.

In terms of physical characteristics, a suitable PCM for building applications should have a phase transition temperature in the range of human comfort temperatures (i.e., around or less than 25 °C internal temperature) [1,2,5]. According to the American Society of Heating, Cooling, and Air-conditioning Engineers (ASHRAE), the room temperature for summer and winter conditions are suggested to be in the range of 23.5–25.5 °C and 21.0–23.0 °C, respectively [22]. In these temperature ranges, a super cooling phenomenon always occurs. Therefore, considering OPCMs for this range is more rational compared to inorganics, which suffer from super cooling.

In terms of technical requirements, a material with low vapor pressure and small volume change during phase transition is preferred. Otherwise, a large container is required. A liquid-gas mechanism needs a huge container to keep the material when it changes to its gas state and it is difficult.
to prevent material leakage [13]. Solid-solid PCMs are not commercialized yet and need further developments. Therefore, the solid-liquid mechanism is the only possible option for construction and building applications.

OPCMs are divided into paraffins and non-paraffins [30] (Figure 2). Compared to inorganic PCMs, OPCMs have little super cooling and phase segregation and are suitable for absorption in various building materials [4,11,19–21]. Paraffins and polyethylene glycols are not bio-based but are frequently used as reference materials and, thus, are included in the review. The non-paraffin BPCMs are alcohols, fatty acids, and esters. Most of these materials are derived from raw materials such as vegetable oils and animal fat (soybean oil, coconut oil, palm oil, and beef tallow) [22,31–33]. These materials have high latent heat, no super cooling and phase separation, are less flammable, and are thermally and chemically stable for loads of cycles [22,31–33].

Figure 2. Diagram of organic PCMs’ classification and the possible bio-based containers.

3.1. Paraffins

Paraffins (saturated hydrocarbons with \( C_nH_{2n+2} \) formula) and commercial paraffin waxes \( (CH_3(CH_2)_nCH_3) \) are crude oil-based products that have been extensively used to store solar energy by latent heat energy storage techniques [19,21,22,30]. Paraffins possess a high latent heat storage capacity, are non-toxic, non-reactive, non-corrosive to metals, and inexpensive. They have stable properties and good thermal and chemical reliability after loads of cycles and less likely to suffer from phase segregation and super cooling [19,22]. However, these materials have a moderate thermal energy storage density, but the most important drawback of these materials is the low thermal conductivity [19,21,22]. Paraffins can cover a wide range of temperature depending on the carbon number. The longer the average length of the hydrocarbon chain, the higher the melting temperature would be [20,21]. Paraffins with carbon chains less than 15 carbons are liquids. By increasing the number of carbon chains, the melting temperature and heat of fusion increase [21,23].

3.2. Polyethylene Glycols

Polyethylene glycol (PEG), called polyoxyethylene (POE) or polyethylene oxide, is derived from dimethyl ether chain [22]. PEGs are organic but not bio-based as they are derived from crude oil. Due to its chemical form and characteristics, PEG is soluble in water and organic solvents [22].
PEGs are provided in grades such as 400, 600, 1000, 3400, 10,000, 20,000, 35,000, 100,000, and 1,000,000 [22]. They have been widely used and investigated as potential materials for use as PCMs due to their chemical and thermal stability and due to being non-flammable, non-toxic, and non-corrosive [21,22]. These materials have large heat of fusion varying from 117 to 174 kJ/kg, high degree of crystallinity, and a melting temperature in the range of 4–70 °C depending on molecular weight [21,22]. An increase in molecular weight of a PEG leads to an increase in the heat of fusion and melting temperature [21,22].

3.3. Polyols

Polyols are divided into sugar alcohols, poly-alcohols, and glycols and are considered as medium temperature (90–200 °C) PCMs [22].

Kaizawa et al. [34] studied some materials including sugar alcohol for use as PCM finding erythritol with a large latent heat of fusion of 344 kJ/kg. A melting point of 117 °C is a promising PCM material for medium-to-high temperature applications.

Alcohols possess excellent characteristics as PCM. However, the problem with this type of BPCM is the super cooling at lower temperatures that limits their usage in the suitable range for building applications. Another problem is the volume expansion during phase transition, which requires a large matrix volume [22,35,36].

Some sugar alcohols, e.g., D-mannitol, myo-inositol, and galactitol were studied as potential PCMs. The reported results indicated that myo-inositol experienced some chemical instability. However, it was discussed that this did not affect thermal characteristics during cycles [37]. Galactitol showed poor cycling stability and D-mannitol reacted with oxygen and was not chemically stable [37].

3.4. Fatty Acids

Fatty acids with a general formula $\text{CH}_3(\text{CH}_2)_{2n}\text{COOH}$ are derived from animal and vegetable sources. Most used fatty acids are categorized in six groups, i.e., caprylic, capric, lauric, myristic, palmic, and stearic [19,20].

Fatty acids benefit from the unique and superior characteristics such as congruent melting, good chemical and thermal stabilities, non-toxic, bio-degradable, and a melting temperature range suitable for building applications if mixed together or esterified [19–21]. Fatty acids have recently attracted researcher’s attention as potential BPCMs for low-to-medium energy storage applications [38,39].

Reviews by Yuan et al. [38] and Rozanna et al. [39] have focused on fatty acids and their binary mixtures as BPCMs for thermal energy storage. Yuan et al. [38] reported that the research has concentrated on saturated fatty acids but only their thermal behavior was investigated. The study concluded that it is difficult to find a pure fatty acid with a phase transition temperature in the range of a comfortable temperature. Rozanna et al. [39] focused on the application of fatty acids and their derivatives concluding that it is difficult to find any pure fatty acid suitable for passive thermal storage in buildings. However, their mixtures and esters are very promising as BPCMs for building applications.

Feldman et al. [40,41] investigated the potential use of fatty acid derivatives including butyl stearate, vinyl stearate, mixtures of ethoxylated linear alcohols [40], and methyl palmitate and methyl stearate [41] as PCMs. The former study reported melting temperatures of these materials between 10 to 43 °C with latent heat between 100 to 140 kJ/kg [40] and between 23–27 °C with latent heat of fusion of 180 kJ/kg in the latter study [41]. It was concluded that the mixtures and esters are promising for use as PCMs in building applications. Although the melting temperature of pure fatty acids is rather high, if mixed or esterified, the thermal characteristics of the new products can fulfil the requirements of the targeted applications.

Hasan [42,43] investigated stearic and palmitic acids as BPCM in the range of 65–69 °C [42] and 57–62 °C [43]. The studies stated that both fatty acids are suitable BPCMs for thermal energy storage in domestic solar water heating systems due to their favorable phase transition temperatures for
solar heating applications and large latent heat of fusion. Sari and Kaygusuz [44,45] studied thermal performance and phase change stability of stearic [44] and myristic acid [45] as BPCMs for thermal energy storage, and showed that these materials are suitable for solar water heating applications. Cedeno et al. [46] studied thermal characteristics of pure fatty acids including palmitic, stearic, and oleic acids and their binary and ternary mixtures. They defined phase transition and latent heat of fusion for these materials and revealed that oleic acid showed a solid-solid phase transition before a solid-liquid transition. Moreover, it was found that the melting temperature differed between the binary and ternary fatty acid mixtures [46].

Lin et al. [47] used a mixture of palmitic acid, polyvinyl butyral, and expanded graphite as a PCM. Thermal and chemical structures and behavior of the PCM were studied using FTIR, XRD, SEM, DSC, and TGA methods. The authors reported that the three materials integrated in a stable chemical and crystalline mixture despite physical and chemical interactions were not observed. The onset temperature of the pure palmitic acid was found at 62.9 and 60.1 °C during charging and discharging processes, respectively. However, the phase transition temperatures of the mixture was slightly lower (56–59 °C), i.e., temperatures mostly suitable for solar energy storage applications.

Sharma et al. [48] studied thermal and chemical stability and reliability of three OPCM including paraffin wax, palmitic acids, and myristic acids for 1500 melting/freezing cycles. Using DSC and FTIR, the authors reported that there were gradual changes in thermo-physical properties of the tested PCMs. However, a significant and reliable thermal and chemical stability was reported. The study also reported a decrease in melting temperature for two fatty acids after 500 thermal cycles compared to paraffin, which showed an increase in the melting temperature.

3.5. Organic-Organic Eutectics and Esters

Eutectic systems are melting compositions of two or more materials. Although these compositions have different melting and freezing temperatures, it is expected that eutectics melt and freeze without phase separation because the intimate mixture of crystals leaves little opportunity for the components to separate [4,11,20].

Fatty acid esters are an important group of BPCMs. Pure fatty acids suffer from certain drawbacks such as bad odor, corrosivity, and a high sublimation rate. In order to tackle these drawbacks and take advantage of the attractive properties of these materials, some transformations of the fatty acids are required. The most studied transformation is the esterification process to achieve desired thermal and physical properties [21]. This process consists of replacing the hydroxyl group with an alkyl group to obtain an ester [22]. The majority of BPCMs suitable for use in building passive applications are the ones involving fatty acid compositions and esters [5].

Nikolic et al. [49] studied fatty acid esters including methyl stearate, methyl palmitate, cetyl stearate, cetyl palmitate, and their binary mixtures. The mixtures showed a phase-transition temperature close to room temperature and were suitable for passive solar thermal storage. These materials were incorporated in gypsum wallboards and bricks by the impregnation technique and showed stability for a large number of thermal cycles with no changes after 18 months in service. The thermal storage capacity of the gypsum and bricks impregnated by PCM was about 10 times higher than that of ordinary materials without PCM. The thermal characterization showed some small extra peaks in addition to the main sharp peaks in the thermograms, which indicates the presence of certain incongruent melting and freezing with eutectic mixtures during the phase transition process.

Sari [50] studied eutectic mixtures of lauric acid (LA)-myristic acid (MA), lauric acid (LA)-palmitic acid (PA), and myristic acid (MA)-stearic acid (SA) as BPCMs. It was found that these mixtures have reasonable thermal properties and reliability in terms of both melting temperature and latent heat of fusion for passive solar energy storage. The melting temperature of the binary mixtures was found to be lower than that of pure acids. Another study [51] found no deterioration in thermal properties of stearic acid esters as PCM after 1000 cycles. Four types of mannitol-fatty acids were synthesized and evaluated [52] to reveal that the phase transition temperature and latent heat of fusion of these
materials vary between 42–65 °C and 145–202 J/g, respectively, which enable them as promising PCMs for active energy storage systems. The above studies concluded that the possibility of incongruent melting and freezing of the esters might be lower than that of eutectic mixtures.

For thermal energy storage for a working temperature in the range of 30–50 °C, high chain fatty acid esters of myristyl alcohol [53,54] and 1-hexadecanol [55] were proposed. These materials have interesting thermal storage potential and thermal reliability. Xu et al. [56] synthesized a fatty acid ester by making use of methyl palmitate (MP) and methyl stearate (MS) as PCMs for building applications with a melting temperature of 25–40 °C. These PCMs showed a possible incongruent melting for the mass ratio of MP/MS of 70/30, 60/40, 50/50, and 40/60. However, after 360 thermal cycles, there was still a reasonable thermal and chemical reliability. Other attempts in synthesis of eutectic PCMs focused on improvement of thermal performance. Mixtures of capric acid (CA) and lauric acid (LA) [57] for low temperature thermal energy storage were evaluated and it was found that an addition of pentadecane can enhance the thermal reliability and storage potential [58].

Mixtures of fatty acids and PEGs have been investigated and certain improvements compared to pure fatty acids or PEGs were obtained. A study reported that it is possible to obtain a homogeneous mixture of fatty acids and PEGs by mixing them in a liquid state and then freezing the mixture [22]. In this regard, various mixtures of PEG and fatty acids as PCMs to store energy in the form of latent heat were investigated [59]. The results indicated that the melting temperature range of this type of mixture and eutectic PCMs is mainly from 30 to 72 °C. The mixtures have higher latent heat of fusion when compared to that of pure fatty acids and PEGs.

Karaipekli and Sari [60] have studied mixtures of fatty acids for working temperatures in the range of 18–25 °C. Composition of capric, lauric, palmitic, and stearic acids has been incorporated in expanded vermiculate by vacuum impregnation. The melting temperature of the composite was in the range of 19–25 °C and was suitable for building applications. No phase separation was reported. The mixture was thermally and chemically stable after 5000 cycles. Sharma et al. [61] studied similar eutectics based on capric, lauric, myristic, palmitic, and stearic acids for building applications. The study reported melting temperatures of the eutectics in the range of 20–30 °C. Ke et al. [62] prepared four binary fatty acid eutectics of capric-lauric, capric-myristic, capric-palmitic, and capric-stearic acids and produced composite phase change nanofibers of the above eutectics and polyethylene terephthalate (PET). The results showed that the novel eutectic composites are suitable for building applications. Hawes et al. [63] used various OPCMs for latent heat storage in building materials and found that butyl stearate was a potential candidate. However, fire and fume generation are yet to be addressed.

3.6. Selection Criteria

Although paraffins have excellent properties as PCMs, they are derived from fossil resources. In this regard, fatty acids, fatty acid eutectics, and esters are more suitable for using in buildings and constructions. They are of plant and animal origin, i.e., of renewable and sustainable nature. Due to their unique properties and potential as PCMs, fatty acids and their homologue esters have recently attracted attention worldwide for application in buildings for lower temperature conditions. Fatty acids, fatty acid eutectic mixtures, and esters have high latent heat of fusion, good chemical stability, and remain stable after a large number of phase change cycles. However, these types of PCMs are more expensive when compared to paraffins. Some pure fatty acids, esters, and eutectics of esters with a melting temperature suitable for a building application are shown in Tables 1–4.

### Table 1. Properties of two pure fatty acids suitable for the building application [23,38,39].

<table>
<thead>
<tr>
<th>BPCM</th>
<th>Melting T (°C)</th>
<th>Freezing T (°C)</th>
<th>Latent Heat of Fusion (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caprylic acid</td>
<td>16</td>
<td>144</td>
<td></td>
</tr>
<tr>
<td>Capric acid (CA)</td>
<td>32</td>
<td>25</td>
<td>150</td>
</tr>
</tbody>
</table>

Table 2. Properties of eutectic mixtures of fatty acids suitable for the building application [2,4,22,38,39].

<table>
<thead>
<tr>
<th>BPCM</th>
<th>Proportion</th>
<th>Melting T (°C)</th>
<th>Freezing T (°C)</th>
<th>Latent Heat of Fusion (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CA:LA</td>
<td>67:33</td>
<td>22.8</td>
<td>-</td>
<td>154.16</td>
</tr>
<tr>
<td>CA:LA</td>
<td>64:36</td>
<td>19.62</td>
<td>-</td>
<td>149.95</td>
</tr>
<tr>
<td>CA:LA</td>
<td>70:30</td>
<td>21.09</td>
<td>-</td>
<td>124</td>
</tr>
<tr>
<td>CA:LA</td>
<td>45:55</td>
<td>21</td>
<td>-</td>
<td>143</td>
</tr>
<tr>
<td>CA:MA</td>
<td>74:26</td>
<td>22.16</td>
<td>21.18</td>
<td>154.83</td>
</tr>
<tr>
<td>CA:MA</td>
<td>70:30</td>
<td>21.79</td>
<td>-</td>
<td>123.62</td>
</tr>
<tr>
<td>CA:PA</td>
<td>76.5:23.5</td>
<td>21.85</td>
<td>-</td>
<td>173.16</td>
</tr>
<tr>
<td>CA:SA</td>
<td>83:17</td>
<td>25.39</td>
<td>25.2</td>
<td>188.15</td>
</tr>
<tr>
<td>CA:SA</td>
<td>70:30</td>
<td>23.4</td>
<td>-</td>
<td>104.9</td>
</tr>
</tbody>
</table>

Table 3. Properties of some fatty acid esters suitable for the building application [2,4–6,22,39,40,51].

<table>
<thead>
<tr>
<th>BPCM</th>
<th>Melting T (°C)</th>
<th>Freezing T (°C)</th>
<th>Latent Heat of Fusion (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butyl stearate</td>
<td>19–24</td>
<td>-</td>
<td>130–140</td>
</tr>
<tr>
<td>Dimethyl sabacate</td>
<td>21</td>
<td>-</td>
<td>120–135</td>
</tr>
<tr>
<td>Isopropyl stearate</td>
<td>22.12</td>
<td>21.99</td>
<td>113</td>
</tr>
<tr>
<td>Vinyl stearate</td>
<td>27</td>
<td>29</td>
<td>122</td>
</tr>
<tr>
<td>Propyl palmitate</td>
<td>19</td>
<td>-</td>
<td>186</td>
</tr>
</tbody>
</table>

Table 4. Properties of eutectic mixtures of fatty acid esters suitable for the building application [2,4,41,49].

<table>
<thead>
<tr>
<th>BPCM</th>
<th>Proportion</th>
<th>Melting T (°C)</th>
<th>Freezing T (°C)</th>
<th>Latent Heat of Fusion (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emerest 2325 (butyl stearate + butyl palmitate)</td>
<td>49:48</td>
<td>17–21</td>
<td>-</td>
<td>138–140</td>
</tr>
<tr>
<td>Emerest 2326 (butyl stearate + butyl palmitate)</td>
<td>50:48</td>
<td>18–22</td>
<td>-</td>
<td>140</td>
</tr>
<tr>
<td>Methyl palmitate + Methyl stearate</td>
<td>93:7</td>
<td>23</td>
<td>22</td>
<td>180</td>
</tr>
<tr>
<td>Methyl palmitate + Methyl stearate</td>
<td>95:5</td>
<td>26</td>
<td>23</td>
<td>180</td>
</tr>
<tr>
<td>Methyl palmitate + Methyl stearate</td>
<td>86:14</td>
<td>23.9</td>
<td>23.8</td>
<td>220</td>
</tr>
<tr>
<td>Methyl stearate + cetyl stearate</td>
<td>91:9</td>
<td>22.2</td>
<td>21.8</td>
<td>180</td>
</tr>
<tr>
<td>Methyl stearate + cetyl palmitate</td>
<td>91:9</td>
<td>28.2</td>
<td>27.9</td>
<td>189</td>
</tr>
</tbody>
</table>

Apparently, there is no ideal single pure fatty acid to fulfill all requirements for building applications. Eutectic mixture of fatty acids, fatty acid esters, and their mixtures have similar thermal characteristics, but eutectics and mixtures are more likely to suffer from a phase separation and, hence, have no congruent melting. The most important disadvantages of BPCMs are their low thermal conductivity and leakage problems.

4. BPCM Containment

4.1. Microencapsulation

Incorporation of BPCMs into building materials without encapsulation often leads to leakage. Microencapsulation is a technique where a molecule or a material in solid or liquid form is coated with another material. In this technique, a PCM is the core of a matrix to produce capsules of various shapes [2,15,21,22]. The capsules are produced in microscales in solid form and are then incorporated in another material or container, e.g., wood, for use in building elements [6,8]. The main purpose of this technique is to have better control on the PCMs in the application phase. Microencapsulated
PCMs are easier to handle and less exposed to the environment in a container. The main problem with microencapsulated PCMs is the heat transfer since most of the coating materials have low thermal conductivity. Organics, inorganics, and mixtures can be used as shell materials to encapsulate the PCMs. Inorganic shell materials possess high conductivity. On the other hand, bio-based shell materials are renewable and more available.

Various techniques and methods have been employed to take advantage of the microencapsulation. Coacervation [64,65], interfacial polymerization [65–67], coatings [68], and spray drying [64] are the most used techniques. In order to cope with stresses and volume changes during the phase transition, the capsules need to possess strength and flexibility at the same time [8].

Organic materials, which are used as shells to microencapsulate BPCMs, are mainly resins, e.g., melamine-formaldehyde (MF) resin [69,70], urea-formaldehyde (UF) resin [71], poly (urea-urethane) [72], polyurea [73,74], and acrylic resin [68]. The advantage of using organic shells is that they offer structural flexibility and sufficient endurance for changing the volume during a phase transition for repeated cycles [16]. However, this type of shell material suffers from poor chemical and thermal stability [16].

4.2. Nano-encapsulation

Nano-encapsulation is another approach that has been extensively investigated due to its advantages over the other encapsulation methods, e.g., its high surface area/volume ratio that facilitates the thermal transfer and high stability [75,76]. In order to nano-encapsulate PCMs, several synthesis approaches have been developed. Liu et al. [77], Shchukina et al. [76], and Rodríguez-Cumplido [78] have summarized the most important methods for preparing nano-capsules, which include emulsion and mini-emulsion polymerizations, in-situ polymerization, interfacial polymerization, and the sol-gel technique. Most of the studies on the nano-encapsulation used n-alkanes as PCM, e.g., n-octadecane and poly (methyl methacrylate) (PMMA) as a shell. Among the investigated synthesis approaches, mini-emulsion is considered a superior technique for nano-capsulation of various materials [79]. High conductive additives such as silica [80], titania [81], alumina [82], and zinc oxide [83,84] nanoparticles have been incorporated into organic polymer shell materials to enhance the thermal conductivity and stability. Du et al. [85] included a phosphorus-based flame retardant as a crosslinking agent in the PMMA shell containing n-octadecane during the mini-emulsion polymerization process and reported an improvement in the flame-retardant properties of the nano PCMs. In addition, the incorporation of phosphorus-based flame retardant into the nano PCMs resulted in significant suppression of heat and smoke releases, and increased the residual weight and limiting oxygen index value of the composite. Recently, Yuan et al. [86] proposed a chemical reduction method to synthesize nano capsules with LA as the core and silver as the shell to increase the heat transfer performance. The obtained nano-capsules reached 95.29 J/g thermal storage capacity with an encapsulation ratio of 67.21%. The thermal reliability of the composites was found satisfactory after 2000 cycles while the thermal conductivity of the nano-capsules was 333% more than that of the LA. Matteis et al. [87] used PEG600 as PCM encapsulated in a silica shell and compared its performance to that of a simple incorporation into a gypsum plasterboard for indoor plastered surfaces of referential residential buildings. Compared with a building without PCM, savings of 4.3% and 1.1% of heating and cooling energy were predicted.

Recently, new multifunctional, phase changing nano-capsules were investigated for thermal management and storage systems to improve the phase change performance of the existing systems. Zhou et al. [88] reported the use of n-octadecane and n-butyl stearate as binary core PCM and polyacrylate supplemented with titanium dioxide nanoparticles as hybrid shell material with a high latent heat storage performance and an encapsulated efficiency of 61.5%. The study reported that the nano-capsules possessed good thermal stability and ultraviolet absorption properties due to a combination of a compact polyacrylate–TiO$_2$ hybrid shell. Imran Hussain et al. [89] investigated a binary system comprising oleic acid and PEG as a core with the SiO$_2$/SnO$_2$ shell as shape-stabilized
PCMs for cold thermal energy storage and reported encapsulation efficiency of 52.12% with good solidification characteristics and a lower degree of supercooling.

4.3. Shape Stabilization Using Organic Polymer Matrices

As mentioned above, encapsulation methods have a certain limitation, e.g., high preparation cost [16,90]. Moreover, the encapsulation techniques cannot enhance the thermal conductivity of PCMs [18,91]. Shape-stabilized PCM (SPCM) or form-stable composite PCM is another technique to contain the main PCMs. The advantage of the SPCM technique is that the used materials remain in their solid state even at temperatures higher than their melting points [16,92]. Umair et al. [16] reported that the micro-encapsulation technique is also a subdivision of the shape stabilization method. The shape stabilization technique can employ both organic and inorganic materials. When using organic polymer matrix as PCM’s shape stabilization material, some factors need to be considered. Among these factors, chemical compatibility and thermal stability of polymers play an important role [16]. One of the prerequisites for selection of the matrix is that it should be congruent with the organic PCMs [18]. Various polymers are used as supporting material, e.g., low density polyethylene [93], styrene maleic anhydride copolymer (SMA) [94], polymethyl methacrylate [95,96], polyurethane [97], polypyrrole [98], high density polyethylene [99], polyvinyl alcohol [100–102], and a biodegradable polymer such as cellulose, chitosan, and agarose [103]. In a recent comprehensive review, Prajapati and Kandasubramanian [104] provided insights into various biopolymers utilized as capsules to overcome the leakage issues. They concluded that the low thermal conductivity resulting from using the biopolymer-framework based PCMs could be overcome by integrating hybrid nanofillers.

Among the cited matrices, polymethyl methacrylate (PMMA) has been extensively used as supporting material for preparing SPCMs. This polymer is easy to handle and process, non-toxic, has enough strength, and is cost-effective [18]. Wang and Meng [96] investigated PMMA as SPCM for capric acid (CA)-lauric acid (LA), capric acid (CA)-myristic acid (MA), capric acid (CA)-stearic acid (SA), and lauric acid (LA)-myristic acid (MA). The shape stabilization of the mixtures was performed by using a self-polymerization method. The DSC results indicated that the studied PCMs and PMMA are compatible with no chemical reaction. The phase transition temperatures of CA-LA/PMMA, CA-MA/PMMA, CA-SA/PMMA, and LA-MA/PMMA composites were 21.11, 25.16, 26.38, and 34.81 °C, i.e., suitable indoor temperatures for human comfort. The latent heat of fusion for the studied mixtures was 76.3, 96.32, 59.29, and 80.75 kJ/kg [96] and, thus, compared to PCMs without shape stabilization, the PMMA seems to reduce the latent heat of fusion of the PCMs.

Series of encapsulated palmitic acid (PA), lauric acid (LA), stearic acid (SA), and myristic acid (MA) blended with a styrene maleic anhydride copolymer (SMA) were studied [105]. The resulting products showed good thermo-physical and chemical properties with no leakage.

Bio-based materials are also used as biodegradable supporting polymers in shape stabilization of some fatty acids and polyethylene glycols. Among these materials, gelatinized potato starch and cellulose were used as matrices in shape stabilization of PEG. The results indicated a strong intermolecular interaction between PEG and supporting materials leading to lower enthalpy value of the phase transition [106,107]. Similarly, a strong intermolecular interaction between PEG and cellulose as well as agarose and chitosan used as supporting materials were observed, while the melting temperature and latent heat of fusion experienced certain changes, but no leakage [99]. Cellulose-based composites have been investigated as potential supporting materials to shape stabilized fatty acids. Cao et al. [108] used carboxyl methyl cellulose fibers to stabilize fatty acid eutectics by using an absorbing technique. It was reported that the PCM was absorbed into the supporting material (porous structure) and a reliable thermal stability was achieved. Another study [109] used gelatin Arabic gum to encapsulate coco fatty acid obtained from coconut oil. This process could also be considered as a shape stabilization using biodegradable supporting material. The relatively low cost and abundance of coconut oil as well as the melting temperature range (22–30 °C) makes this material
an interesting PCM suitable for building applications. Moreover, studies indicated that the coco fatty acid is chemically stable and is not affected by the encapsulation process [109].

4.4. Shape Stabilization Using Inorganic Porous Materials

Porous materials have recently become attractive as supporting materials to shape stabilized OPCMs [16]. These materials have low density, a large surface area, and a wide pore size distribution, which allows them to store PCMs in the pores by capillary forces and hydrogen bonding [16,110]. The advantages of using this technique is prevention of PCM leakage and enhanced thermal conductivity of the composite. Carbon-based materials have extensively been used as supporting materials, e.g., expanded graphite (EG), graphene oxide (GO), carbon nanotube (CNT), graphene nanofibers, graphene nanoplates, and activated carbon. All of them benefit from high thermal conductivity and flexibility [16,18,111]. These materials are able to encapsulate OPCMs, but this ability depends strongly on their pore sizes and structure. In addition to fossil-based porous matrices, some porous bio-based materials such as wood and charcoal can also be used to encapsulate PCMs. One important aspect of the combination of a bio-based matrix and BPCMs is the interaction between the pore surface and PCM. If the interaction is strong, an elevated phase change temperature will be observed and vice versa. In the case when an organic bio-based material (e.g., a fatty acid) is encapsulated in a porous matrix, there is a strong interaction between pores and the PCM [18,112,113].

Sari and Karaipakli [114] studied the encapsulation of palmitic acid (PA) with expanded graphite for medium temperature utilization. Similarly, Wang et al. [115] incorporated sebacic acid into pores of expanded graphite and reported an enhanced thermal reliability and thermal conductivity compared to the pure fatty acid PCMs. Other combinations studied stearic acid/graphene oxide [116], palmitic acid/graphene nanoplates [117], and myristic acid/graphite nanoplates [118], which confirmed the improved thermal reliability and conductivity compared to pure BPCMs. Expanded graphite as supporting material not only prevents leakage of PCMs but also enhances the thermal conductivity [18].

Sheng et al. [119] used a cotton-derived carbon sponge as a bio-based organic supporting material for shape stabilization of OPCMs. The carbon sponge was produced by carbonization of cotton biomass and consisted of cotton-derived carbon fibers forming an interconnecting porous network. The obtained material was vacuum-impregnated with paraffin as PCM. The studied supporting material prevented leakage of the PCM, enhanced the thermal conductivity, and proved its properties as a shape-stabilizing matrix of PCMs for solar energy storage applications.

4.5. Incorporation of PCM in Lignocellulose Materials

Due to its renewable nature and availability, wood is extensively used in construction and buildings in the European and Nordic countries, Canada, the US, and Australia. Most of these countries need to manage energy used to heat up residential buildings especially during the winter. Wood is a porous material, which can be used as a matrix to encapsulate PCMs by the impregnation process (Figure 3). However, due to the complexity of the wood structure, the process of incorporating PCMs is challenging and some factors such as climate, building architecture, user’s behavior, and thermo-physical properties of the PCMs should be considered [8].

![Figure 3. Schematic diagram of preparing PCM/wood composite](image-url)
Liang et al. [120] investigated wood-flour as an impregnable matrix to encapsulate lauric acid (LA), myristic acid (MA), hexadecanoic acid (HA), and stearic acid (SA). It was revealed that the wood pores were filled and retained the acids by physical interaction while no leakage was observed. However, the studied combinations/composites showed a low phase transition temperature and low latent heat of fusion compared to pure fatty acid (41 to 59 °C and 87 to 201 J/g, respectively).

Mathis et al. [8] investigated the potential use of red oak and sugar maple for micro-encapsulation of BPCM (Nextek29). The PCM used in the study originated from agricultural resources, but its composition is unknown. The reported results indicated a 77% enhancement in thermal storage capacity of impregnated red oak when compared to the untreated one. For a flooring application, wood impregnated with PCM receives and stores solar energy in the working temperature range between 28 and 31 °C. The authors reported lower thermal mass for sugar maple than for red oak. Another study [7] incorporated BPCM consisting of a blend of lauric and capric acids in decorative wood-based panels (medium density fiberboards (MDF)). Initially, the PCMs were encapsulated in plastic poaches and then incorporated in grooved MDF panels. It was concluded that the wood panels filled with PCM have a suitable phase transition temperature and latent heat of fusion of 22.2 °C and 57.1 J/g, respectively. The finding is interesting since it fits well the building application of PCM for passive systems.

Yang et al. [121] studied delignified and carbonized wood samples, which were impregnated with lauric acid (LA). The composite was performed as a lightweight high porous material with a significant encapsulation ratio of more than 80% and a latent heat of fusion 178 J/g. Li et al. [122] studied the potential use of paraffin/high density polyethylene/wood-flour composite as a stable PCM form and as a thermal storage layer of an electric floor heating system. The resulting composite gained a proper phase change temperature for the building application of 20 to 30 °C, high latent heat of fusion, thermal conductivity, and good shape retention that positioned the composite as a promising PCM for the building application. Other studies [123,124] investigated a self-luminous wood composite for both thermal and light energy storage. In these studies, poplar wood was delignified and impregnated with tetradecanol as PCM. The obtained composite had 146 J/g latent heat of fusion and a 37 °C phase change temperature, which makes the composite suitable for building applications. Figure 3 shows incorporation of PCMs in wood for energy storage in buildings.

The schematic picture of a composite material made of lignocellulose fibers impregnated with a BPCM is shown in Figure 4. Fibers can be treated to improve their hydrophobicity, fire resistance, and durability against micro-organisms. Figure 5 shows a light microscopy picture of a single fiber (mechanical pulp) impregnated with oleic acid where the fiber serves as an encapsulation cell for the BPCM. The composite can be improved further by adding a conductive polymer to encapsulate the fibers.
Ma et al. [125] investigated delignified cedar wood impregnated with capric acid-palmitic acid (PA) eutectic as a thermal energy storage system. The thermal analysis of the composite showed 94 J/g latent heat of fusion and a 23 °C phase change temperature. Furthermore, the thermal conductivity and reliability of the composite was found to be higher than that of the pure eutectic PCM.

Jamekhorshidi et al. [126] prepared a wood-polymer composite combined with micro-encapsulated PCM for application in buildings as a lightweight material. An industrial high-density polyethylene PCM (Cotene™) and pine sawdust were hot-pressed. The resulting composite showed reasonable thermal properties and a phase transition temperature with no leakage. Barreneche et al. [127] studied a coated PCM/wood composite for passive energy storage in building envelopes. The studied composite consisted of black alder wood impregnated with RT21 and RT27 paraffins as PCMs. The impregnated wood was coated with polystyrene to enhance the structural stability of the composite. The phase transition temperatures were 20–21 °C for RT21 and 25–27 °C for RT27 paraffin. The composites are recommended for applications in the temperate region climate.

Guo et al. [128] studied incorporation of micro-encapsulated dodecanol as PCM into wood flour/high density polyethylene composite. Pre-polymer modified by polyethylene glycol was used as a matrix material to micro-encapsulate the PCM. The composite was prepared by hot-compression, and showed melting and freezing temperatures of 27.2 and 11.3 °C. In another study, Guo et al. [129] used paraffin as PCM, which was stabilized by expanded graphite and wood-flour. The use of expanded graphite considerably enhanced the thermal conductivity of the composite. The composite’s melting temperature was found to be between 20 to 30 °C, which made it suitable for building applications.

5. Practical Challenges for Application of BPCM in Buildings

Although the BPCMs are promising for controlling the indoor temperature fluctuations in buildings, they possess a low thermal conductivity, which is approximately 0.2 W/mK. This limits their application [3,19,22]. The low thermal conductivity affects the response time to temperature variations, which results in a slow and inefficient heat exchange rate between the PCM and the surrounding medium [3]. Some applied strategies consist of including highly conductive materials (e.g., graphite) in the matrices or in the PCM as microparticles or nanoparticles. Examples of matrices containing conductive materials include stainless steel, copper, aluminum-based matrices [130,131], porous graphite matrix [130,132,133], nanographite [134], carbon fibers [135,136], carbon nanofibers [137,138], and carbon nanotubes [138]. Sharma et al. [22] discussed that the inclusion of nanoparticles is better than microparticles and does not affect the melting point of PCM. However, due to their high-volume fraction, the addition of microparticles/nanoparticles to the matrix/PCM always results in reducing the energy density of PCM.

Parameshwaran et al. [139] investigated the effect of addition of silver nitrate nanoparticles into OPCM of polyvinyl pyrrolidone (PVP) 40,000 and found that the addition did not affect PCM’s
chemical behavior and characteristics. The nanoparticles improved the thermal conductivity of PCM from 0.284 to 0.765 W/mK accompanied with some changes in the melting and freezing temperatures. Wang et al. [140] used β-aluminum nitride powder as an additive to PEG to improve the thermal conductivity from 0.3847 to 0.7661 W/mK with no change in melting and freezing temperatures. Yang et al. [141] used carbonized wood poplar impregnated with tetra-decanol as PCM to prepare a high thermal conductive composite. Compared to pure tetra-decanol, the carbonized wood enhanced the conductivity of the composite by 114%. Li et al. [142] investigated the addition of 8.8% (wt) MicroMist graphite to micro-encapsulated paraffin/high density polyethylene/wood-flour composite. An enhancement in the thermal conductivity of 17.7% was observed with no negative impact on the mechanical and chemical behavior of the composite. Singh et al. [143] also found that the low thermal conductivity is a major drawback when using OPCM for low temperature applications. The authors studied carbon powder mixed with polyethylene glycol (PEG-1000) and it was inserted within aluminum and graphite fins. The thermal conductivity was increased by 40 and 33 times, respectively.

Another challenge related to energy management in building is the concept related to energy poverty. As discussed by da Cunha and de Aguiar [144], the energy consumption of the production and exploitation of buildings is related to a wide range of costs including extraction and production of the construction components from raw materials as well as building and maintenance costs during the time of exploitation. The authors introduced the concept of energy poverty related to economical limitations when less than 10% of the monthly income cannot be paid for thermal comfort in the buildings. However, Madad et al. [145] demonstrated that the use of PCM decreases the energy cost in buildings.

Apparently, the lignocellulose materials deserve research attention due to their unique characteristics as renewability, being lightweight, and porosity. As outlined in the review, the incorporated PCMs into lignocellulose lightweight envelopes, e.g., wood fibers (Figure 3), can increase the thermal inertia of these envelopes and reduce the indoor temperature fluctuations. However, the biological nature of lignocellulose materials determines their susceptibility to biodegradation by several biotic factors including bacteria, fungi, and insects. The above is valid even for the fatty acids used as PCM since they are derived from animal and vegetable sources. Flammability is also a challenge since it is often considered the most serious disadvantage of organic products in built environments. Although the BPCMs are intended for use in indoor environments, biological durability as well as fire resistance are important challenges that need to be addressed if plant fibers, wood, or wood-based composites are used as matrices for PCMs in building applications. Since very limited attempts [121,123–125] have been made to incorporate BPCMs into wood-based products, there are no studies investigating the long-term biological durability and fire resistance of the combinations of BPCMs and lignocellulose materials as matrices.

Most of the PCMs are susceptible to leakage when integrated into building envelopes, which seriously limits their application. Although suitable for encapsulation of BPCMs, the lignocellulose in any form can hardly prevent the leakage during exploitation [104]. Studies indicated that the leakage of PCM during the transition phase could be avoided by embedding them into suitable supporting materials. It is probable that an additional coating of the impregnated lignocellulose matrices will be necessary to eliminate the leakage. It is further discussed by Frigione et al. [146] that leakage and incompatibility of PCM can negatively affect the mechanical and durability properties of the construction components. Mathis et al. [147] studied the use of a BPCM in wood-based panels for energy storage in a cold climate. Plastic bags with a commercial BPCM (Puretemp® 23, unspecified composition) with a melting temperature of 23 °C were inserted in wood-based panels, i.e., a lignocellulose container. The authors concluded that the combination of a wood-based container and BPCM improved the energy efficiency and performance of the entire wooden construction in a cold climate, which resulted in energy savings during the winter and improved thermal comfort during the summer.
The comprehensive interest of all renewable materials to address the climate changes and cover the increasing demand for clean energy has led to enhanced research and developments of BPCM materials. The outstanding ability of the BPCMs to maintain internal temperatures and ensure a large energy storage density within a relatively narrow temperature range is expected to result in an accelerated demand of these materials. Consequently, a decrease in the availability and increase of the cost of the BPCM is predicted.

6. Life Cycle Assessments

Life cycle assessments (LCAs) have been applied for buildings or building systems [148–151] to demonstrate the environmental impact and the suitability of the materials. However, LCA of PCMs, which are considered as a material or included in a building, are restricted to a small number of studies. A review [152] has summarized nine publications on LCAs of PCMs for building applications. These studies focused on paraffin (organic PCM but originating from fossil sources), salt hydrates, and esters of stearic acid [153,154] incorporated in alveolar bricks and concrete [155,156], rammed earth matrix [157,158], tiles [159], and ventilated double skin facades [160]. It is concluded that the esters (i.e., BPCMs) have lower impact on the environment in the production stage when compared to the salt hydrates. Inclusion of salt hydrates and esters resulted in 9% and 10.5% impact reduction compared to the crude oil-based paraffin [154].

The system boundaries that have been employed in LCA studies of PCMs in buildings have been frequently selected for manufacturing and disposal stages [154,155] with an addition of the operation stage [159] or plant cultivation, manufacture, and transport stages [161]. A study which compares raw, waste palm oils and paraffin [161] demonstrated that palm oil production generated the most negative impact on the resources, ecosystem, and human health (15.5, 170, and 103.9 mPt), which is significantly higher than the values of paraffin (37.6, 4.2, and 9.2 mPt). The above is explained by the high CO$_2$ emissions as well as land and water consumption needed for the plant cultivation. On the other hand, when the polluter that pays a principle is applied, the waste palm oil showed the lowest impact of the three studied PCMs. Thus, the environmental advantages of BPCMs are not self-evident and their selection for building applications should be done in consideration of LCA.

LCA of PCMs is often combined with life cycle cost assessment [162]. Two BPCMs [163], i.e., dodecanoic acid produced from palm oil and ethyl hexadecanoate generated from algae and used in a solar heating application, were assessed in terms of embodied energy and CO$_2$ emissions. Dodecanoic acid showed ca. three years payback time for both energy and carbon emissions and proved to be viable as BPCM. On the other hand, the high embodied energy of ethyl hexadecanoate showed a payback time of more than 30 years for use in domestic thermal buffering applications. Another study [164] employed life cycle cost analysis to demonstrate that the payback time of an unspecified BPCM varied from 7.5 to 14.5 years when applied with and without insulation in a test dwelling.

The results of the LCAs for a product can differ in dependence on the employed tools. A study [165] compared the suitability of streamlined LCA (SLCA) based on Bilan Produit tool and a full LCA to reveal their robustness when a wood-based panel with an incorporated BPCM (mixture of 64% capric acid and 36% lauric acid) was studied. The BPCM had the highest impact regarding the non-renewable energy and resource consumption impact categories. Middle density and high density fibreboards of the panel were contributed to acidification, eutrophication, and aquatic eco-toxicity.

It can be concluded that a limited number of PCMs, particularly those of bio-origin, have been subjected to a life cycle and cost assessment. The results vary because various PCMs and material characteristics, system boundaries, and LCA tools have been employed. Nevertheless, LCA is a valuable tool for selecting BPCMs with low environmental impact for building applications.

7. Conclusions

This review focuses on the incorporation of BPCMs in lignocellulose materials for thermal energy storage in building applications. Due to to their sustainability and renewability, the combination of
BPCMs and wood-based matrices will result in fully bio-based materials for energy management. The review presents and discusses various aspects of some promising BPCMs, energy characteristics, and wood-based materials as matrices. Summarizing the findings in the reviewed articles, the following conclusions can be drawn.

1. Among the investigated OPCMs, fatty acids, their derivatives, and their eutectic mixtures are the most promising bio-based materials that can be used as PCMs. They have been extensively investigated for solar energy applications but have not been explored for controlling indoor temperature fluctuations.

2. BPCMs benefit from some properties such as non-corrosivity, high latent heat of fusion, suitable melting temperature, non-toxicity, reasonable thermal and chemical stability, and lack of any environmental impact.

3. In cold temperate regions (e.g., Canada, North-European countries) with few sunny days in the winter, using PCMs for controlling the indoor temperature intermittency is rather interesting than for storing solar energy. However, only a few pure fatty acids have phase change temperatures in the range of human comfort (i.e., 18–25 °C). A further functionalization of the fatty acids is a prerequisite for the application in a building sector.

4. Most of the PCMs are incorporated in wallboard and ceiling board gypsum while only a few studies investigated the possibility of incorporating BPCMs into wood and wood-based materials. Using wood as a matrix appears as a significant improvement of the thermal mass of a “green” building.

5. Encapsulation and shape stabilization are the most used approaches for incorporating PCMs. Recently, special attention has been paid to shape stabilization using porous materials and fibers. This method is cheaper and have no side effect compared to encapsulation that reduces thermal performance of the PCM.

6. The main limiting factor of using BPCMs is their low thermal conductivity, which can be improved by inclusion of metallic, carbon-based nanoparticles as well as by using carbon and a graphite-based scaffold for encapsulation.

7. Wood and wood-based materials, e.g., delignified wood and carbonized wood, wood-flour, and wood fibers are interesting biomaterials for cost-effective and shape-stabilized BPCMs. Utilization of these materials will result in lightweight construction materials and enhancement in the thermal mass of buildings.

8. Use of BPCM can introduce a negative impact on the environment and, thus, LCA appears as a compulsory tool for selecting BPCM with a low impact for building applications.

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References
Energies 2020, 13, 3065


42. Hasan, A. Thermal energy storage system with stearic acid as phase change material. Energy Convers. Manag. 1994, 35, 843–856. [CrossRef]


Energies 2020, 13, 3065


60. Sharma, A.; Shukla, A.; Chen, C.; Dwivedi, S. Development of phase change materials for building applications. *Energy Build.* 2013, 64, 403–407. [CrossRef]


78. Rodríguez-Cumplido, F.; Gelves, E.P.; Chejne-Jana, F. Recent developments in the synthesis of microencapsulated and nanoencapsulated phase change materials. *J. Energy Storage* 2019, 24, 100821. [CrossRef]


95. Wang, L.; Meng, D. Fatty acid eutectic/poly(methyl methacrylate) composite as form-stable phase change material for thermal energy storage. *Appl. Energy* 2010, 87, 2660–2665. [CrossRef]


102. Sari, A.; Akcay, M.; Soylak, M. Polymer–stearic acid blends as form–stable phase change material for thermal energy storage. *Energy Sources* 2005, 27, 1535–1546. [CrossRef]


108. Cao, L.; Tang, Y.; Fang, G. Preparation and properties of shape-stabilized phase change materials based on fatty acid eutectics and cellulose composites for thermal energy storage. *Energy* 2015, 80, 98–103. [CrossRef]

109. Özo˘nr, Y.; Mazman, M.; Paksoy, H.; Evliya, H. Microencapsulation of coco fatty acid mixture for thermal energy storage with phase change material. *Int. J. Energy Res.* 2006, 30, 741–749. [CrossRef]


121. Yang, Z.; Deng, Y.; Li, J. Preparation of porous carbonized woods impregnated with lauric acid as shape-stable composite phase change materials. *Appl. Therm. Eng.* 2019, 150, 967–976. [CrossRef]

122. Li, J.; Xue, P.; He, H.; Ding, W.; Han, J. Preparation and application effects of a novel form-stable phase change material as the thermal storage layer of an electric floor heating system. *Energy Build.* 2009, 41, 871–880. [CrossRef]


132. Py, X.; Olives, R.; Mauran, S. Paraffin/porous-graphite-matrix composite as a high and constant power thermal storage material. Int. J. Heat Mass Transf. 2001, 44, 2727–2737. [CrossRef]


147. Kovacic, I.; Zoller, V. Building life cycle optimization tools for early design phases. Energy 2015, 92, 409–419. [CrossRef]


