Review on Application of Phase Change Materials for Thermal Energy Storage

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Abstract: Phase change materials, as a novel energy storage material, have been attracting the scientists’ and engineers’ attention and research interest for the past several decades. This paper would exhibit the hitherto outcomes of thermal energy storage (TES) applications concerned with PCMs. Via these phenomenal PCMs applications, people have witnessed the improvement of accountability and efficiency of thermal energy storage (TES). As the popularization of TES in people’s daily life and industrial field, it is a burgeoning growth of investigation and investment in PCMs-relative research to stimulate PCMs applicable systems innovation.

Keywords: Phase change materials (PCMs); Thermal Energy Storage (TES); PCMs Applications; TES Applications
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1. Introduction

The thermal energy storage (TES), like a sage, has been standing aside from human civilization for millions and thousands of years and waiting to be found patiently. As the most senior energy form presumably, TES has been influencing to people’s life profoundly, to illustrate, the popularity of ice in Persia over three hundred years ago[1], without even being recognized appropriately until recently, for the past thirty years during which scientists and engineers have been striving for the optimal achievement of TES balancing industrial and environmental development. In particular, from the aspect of ice’s transforming role in the modern industry, the significance of ice towards human beings has elevated from the temperature regulator to thermal energy container remarkably renowned as Ice Storage [2]. In the aim of doing that, the technology of thermal energy storage by phase change materials (PCMs) is the core breakthrough of latent heat storage (LHS) [3]–[5], a subordinated energy storing system of TES [3], [4], [6]–[8], steadfastly attracting scientists’ and relative-field researchers’ attention many
years as a prosperous proposition to bridge the mismatches between the energy supply and demand [1], [9], [10].

The intrinsic essence of PCMs, specified by their corresponding principle, classification, and characteristics, has been summarized systematically in followed articles emphasizing various aspects abovementioned. More explicitly, S. Mondal, A. S. Fleischer and C. Amaral have defined the PCMs as a thermal energy storing medium comprehensively in their articles [11]–[13]. Meanwhile, the related calculations and formulas have been deduced in A. Sharma and G.A. Lane’s papers [14]–[16]. Furthermore, there are other in-depth interpretations and understanding about the stratification and traits of PCMs respectively [17]–[26], [27]–[31]. Whereas, this paper would focus on the pragmatically applied area where PCMs have been synthesized to be a critical element of thermal energy relative systems. For instance, modern lightweight construction, due to the lack of thermal mass, is supposed to be supplanted by more “thermal-smart” PCMs to alleviate the ambient temperature adverse effect on buildings [32].

In the contract with past-year research and reviews on phase change materials (PMCs), this paper elucidates the enhancement of PCMs by the different type encapsulation and shape-stabilization at the beginning exclusively. Apart from that, the article also expounds on the principles of distinguished application systems that are integrated and functionalized by the PCMs substantially. The rational conclusions about these applications would be specialized in the last section of this paper.

2. Enhancement of Phase Change Materials

To reach the practical requirement of TES systems, most PCMs are no long satisifiable being answerable of various circumstances resulting from the considerably inferior thermal conductivity. Therefore, how to enhance thermal performance, such as heat transferring efficiency and volumetric changes along with temperature raise, has been the core concern for researchers for the past thirty years [33], [34]. Meanwhile, how to eliminate, at least to an acceptable extent, the cooccurred but adverse effect during the enhancement of PCMs is also what researchers should be aware of scrupulously [35].

(I) PCMs Encapsulation

The encapsulation technique, as a renowned and fully developed method of PCMs enhancement, makes it possible to put advanced fabricated PCMs into practice [36]–[39] by aggrandizing heat transfer efficiency and containing the reactivity of PCMs [40], [41]. The principle of PCMs encapsulation is a procedure, without the chemical reaction between PCMs and container materials [42], [43], of coating container-materials particles with diameters within 1 mm range on the periphery of targeted PCMs [44]. As the phenomenal evolution of encapsulated techniques, the utilized area has been expanding from virtually building material to multi-functional
fields, like cosmetics, thermal solar energy storage, functional textiles, and even medical & therapeutic applications [45]-[50].

1) Physical Characterization of PCMs Encapsulation
Following the fundamental concept of PCMs encapsulation, there are several indicators and calculations below assessing and penetrating the physical properties of PCMs encapsulation.

- Encapsulation efficiency, as a measurement of the encapsulation synthesis process, is the ratio of the mass of coated capsules to the total mass of capsules, calculated below [47], [51].
  \[
  \eta (\%) = \frac{\text{weight of undissolved PCMs}}{\text{total weight of dry sample PCMs}} \times 100\%
  \]
  \[
  \eta (\%) = \frac{\sum m_{\text{microparticles}} - m_{\text{xylitol}}}{m_{\text{monomers}}} \times 100\%
  \]

- Encapsulation ratio is the ratio of core PCM to shell material, formulated below [52].
  \[
  \eta (\%) = \frac{H_{\text{micro-PCM}}}{H_{\text{PCM}}} \times 100\%
  \]

- Leakiness is the tradeoff between the shell wall protecting the core material and the encapsulation ratio corroborated by the centrifugal shear force test [52].

2) Classification of PCMs Encapsulation
The last segment of this section is going to introduce the classification of PCMs encapsulation with the exhaustive description of some examples constructed in the table below.

- Macro-encapsulated PCMs (above 1 mm) are the most well-noted approach of encapsulation for TES systems with spherical, tubular, cylindrical or rectangular container shapes [53]-[55].
- Micro-encapsulated PCMs (0 – 1000 µm) has more efficient heat transfer rates than macro-encapsulated PCMs due to more delicately manufacturing requirements [47], [56].
- Nano-encapsulated PCMs (0 – 1000 nm), as the most innovated method of encapsulation, has been realized by the advanced nano-scale techniques [48], [57], [58]. As proof, the nano-encapsulation possesses a more stable structure in comparison with macro-and micro-encapsulation [54].
Table 2.1.2 Specifications of Encapsulated PCMs

<table>
<thead>
<tr>
<th>PCM</th>
<th>Shell Material</th>
<th>Microcapsules Size (μm)</th>
<th>Encapsulation Approach</th>
<th>Applied Area / Potential</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffin</td>
<td>Polymer</td>
<td>17-20</td>
<td>Coacervation¹</td>
<td>Building material</td>
<td>[59]</td>
</tr>
<tr>
<td>Paraffin wax</td>
<td>Polymer</td>
<td>5</td>
<td>Coacervation¹</td>
<td>Building conditioning</td>
<td>[47]</td>
</tr>
<tr>
<td>Coco fatty acid</td>
<td>Melamine-formaldehyde</td>
<td>1-1000</td>
<td>Coacervation¹</td>
<td>-</td>
<td>[45]</td>
</tr>
<tr>
<td>n-Octacosane</td>
<td>PMMA</td>
<td>0.15-0.33</td>
<td>Emulsion polymerization²</td>
<td>Immense energy storage potential</td>
<td>[60]</td>
</tr>
<tr>
<td>Docosane</td>
<td>PMMA</td>
<td>0.14-0.47</td>
<td>Emulsion polymerization²</td>
<td>-</td>
<td>[61]</td>
</tr>
<tr>
<td>Paraffin mixture</td>
<td>Epoxy resin</td>
<td>-</td>
<td>Polyaddition³</td>
<td>-</td>
<td>[62]</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>Melamine-formaldehyde resin</td>
<td>5-20</td>
<td>Polycondensation⁴</td>
<td>-</td>
<td>[49]</td>
</tr>
<tr>
<td>Octadecane</td>
<td>Melamine-formaldehyde resin</td>
<td>5-20</td>
<td>Polycondensation⁴</td>
<td>Low cost</td>
<td>[49]</td>
</tr>
<tr>
<td>Lauryl alcohol</td>
<td>Melamine-formaldehyde resin</td>
<td>5-10</td>
<td>Polycondensation⁴</td>
<td>-</td>
<td>[63]</td>
</tr>
<tr>
<td>Butyl stearate</td>
<td>Polyurea</td>
<td>20-35</td>
<td>Polycondensation⁴</td>
<td>-</td>
<td>[46]</td>
</tr>
<tr>
<td>n-Dodecanol</td>
<td>Melamine-formaldehyde resin</td>
<td>30.6</td>
<td>Polycondensation⁴</td>
<td>-</td>
<td>[50]</td>
</tr>
<tr>
<td>n-Tetrade- cane</td>
<td>Urea-formaldehyde resin</td>
<td>100nm</td>
<td>Polycondensation⁴</td>
<td>-</td>
<td>[48]</td>
</tr>
<tr>
<td>n-Octade- cane</td>
<td>Polyurea</td>
<td>3-25</td>
<td>Polycondensation⁴ (Interfacial)</td>
<td>High encapsulation efficiency</td>
<td>[64]</td>
</tr>
</tbody>
</table>

¹Coacervation is a mutually neutralized encapsulated process of, at least, two oppositely charged colloids in a liquid solution to divide coacervated particles from original polarized status [65].

²Emulsion polymerization is a simple process with a system where the surfactants stabilize the monomers that are going to be dispersed in an aqueous phase [54], [66], [67].
Polyaddition is a chemical reaction in which the successive addition of monomers with the presence of radical intermediates \[68\].

Polycondensation is a chain reaction in which the production results from monomers with the elimination of small molecular by-products \[69\].

### (2) PCMs Shape-Stabilization

It is inevitable taking cost and budget of encapsulation into consideration once the production is involved with the market promotion. With this limitation, the researching orientation and scientists’ attention have veered away from encapsulation and then concentrated on the shape-stabilization PCMs technology. At the same time, shape-stabilization PCMs provide a feasible alternative to address the situation where the composites of the encapsulated PCMs, as also noted as the PCM and shell material, exhibit distinct molten temperatures \[70\]-\[72\]. Table 2.2 below limns a logical configuration of PCMs shape-stabilization with different matrices classified by their attribution.

**Table 2.2 Shape-stabilization of PCMs Attribution**

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Explorations</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylic</td>
<td>The attestation of the maximum percentage of PEG blended with acrylic polymers without no leakage above the molten points of PEG [73].</td>
<td>Trackable producing procedure with a highly economical advantage.</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>A Functional Comparison between soft and hard Fischer-Tropsch paraffin waxes with low-density polyethylene (LDPE) [74].</td>
<td>Widely used.</td>
</tr>
<tr>
<td>Polyurethanes</td>
<td>The protection from leaking by PCMs with the influx of polyurethane foams [75].</td>
<td>Remarkable chemical insulation from ambience and superior energy absorbency.</td>
</tr>
<tr>
<td>Polyvinyl chloride</td>
<td>The admixture of PVC/PA and PVA/PA [76].</td>
<td>Stiffen acceptance of practical systems.</td>
</tr>
</tbody>
</table>

All the above-mentioned matrices and relative experiments, not limited to, have spoken for themselves regarding their research value as an alternative method of PCMs improvement to be on the industrial scale.

### 3. Application of Phase Change Materials

As a pivotal fragment of the renewable energy industry, PCMs application into all walks of life symbolizes that one of the most accountable natural-refillable energy sources has proverbially made a significant difference in people’s daily life.

**1) Thermal Storage Building Systems of PCMs**

The PCMs have been adopted as building materials to avoid fluctuating inner temperature of the entire edifice without the compromise with elasticity, flexibility, portability, durability and toughness of buildings for many years since before 1980.
According to realistic scenarios that a piece of building material may encounter throughout the year-long vicissitude, the design requirement of a piece of PCMs building material is to simulate the biological significance of skins toward human beings maintaining inner body temperature within an ideal range regardless how fiercely change of ambient temperature goes through across a year. Naturally, to meet this particular criterion, temperature controlling systems intelligently operating with cooling and heating applications unfold in both passive and active methods\cite{77}, \cite{78}. For instance, there are a series of tentative explorations of paraffins with the differential compound percentage upon different design requirements\cite{56},\cite{79}. Besides that, a group of verisimilar experiments about the impregnation of PCM into its corresponding porous container has been conducted by some researchers in detail for the past several years. The outcomes of these experiments have been summarized in the table below comprehensively.

<table>
<thead>
<tr>
<th>PCM</th>
<th>Porous Container</th>
<th>Outcome</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffin wax</td>
<td>Plasterboard</td>
<td>Immersion process achieved by two chemical treatments</td>
<td>\cite{80}–\cite{89}</td>
</tr>
<tr>
<td>Fatty acids and paraffin wax</td>
<td>Gypsum wallboards</td>
<td>Dynamic thermal examination of gypsum wallboards</td>
<td>\cite{90}–\cite{92}</td>
</tr>
<tr>
<td>Na$_2$S$_2$O$_3$∙5H$_2$O</td>
<td>Concrete</td>
<td>Investigation of composite PCM (salt-hydrate) concrete system</td>
<td>\cite{88},\cite{93},\cite{94}</td>
</tr>
</tbody>
</table>

Nevertheless, there are few qualified reports about the interaction between the impregnated layer of PCMs and their porous containers from case to case\cite{95}. This interaction could either deteriorate or aggrandize the thermal performance of impregnation systems, such as the thermal endurability, the thermal stability, the thermal isolation as well as the prolonged phase transition of PCMs. Apart from this, other barriers in the way of commercializing PCMs as building materials are super-cooling, phase segregation and cost\cite{96}.

\section*{(2) Solar Energy Storage Systems of PCMs}

As an application of PCMs into the solar energy industry, it is beyond doubt that the accountability and efficiency of solar energy systems have been substantively enhanced to a wildly popular level with an economical fabricating procedure\cite{97},\cite{98}.

\subsection*{1) PCMs Solar Water Heating Systems}

Solar energy has to be transferred to thermal energy by the introduction of thermal energy storage technologies and the presence of a variety of PCMs\cite{99},\cite{100}. Where the PCM layer is placed at the bottom of the heater, taking a primary type of water heater as an example, is the energy transferring area to accumulate heat\cite{101}. Furthermore, in order to observe how efficient it is supposed to be by applying PCMs into systems, PCM-, water- and rock-based systems were taken to be compared\cite{102}.
As proof, the efficiency of the PCM-based system has been raised considerably \[103\]. Whereas, there is still much procedure needed to be made to find the most optimum PCMs applied to solar water heating systems \[104\].

2) Solar Cooking Systems
Solar cookers with a storage medium are prevalent in developing countries underlain by their reliability. The utility of solar cookers have been improved by the introduction of PCMs, to a great extent, even available during the evening/limited-sunshine period \[105\]. Case in point: some researchers innovated cooking systems with a PCM storage unit \[106\]. Moreover, the capacity of these cooking systems has been augmented considerably by novel PCMs \[107\], \[108\]. After several rounds of experiments and tests, the recommended phase change temperature of PCM should locate at the range of 105 and 110 °C \[108\].

3) Solar Drying Systems
The diminution of products’ moisture at an operating temperature between 40 and 60 °C is to store agricultural products, such as grain, at an ideal condition varied for specified products. The viability of selecting paraffin wax as PCMs of solar dryer systems has been verified by some researchers \[109\]. Meanwhile, excessive solar heat would be absorbed by the LHS system and released in the condition of inadequate sunlight coverage \[110\]. As more exquisite components installing into the drying systems, such as solar accumulator, drying chamber and centrifugal fans, the thermal performance has been elevated to another level \[111\]. Nonetheless, how to improve the thermal conductivity of PCM is still going to be a research focus to bring solar drying systems to the next generation.

(3) Textiles Systems of PCMs
PCMs incorporate in textiles to counteract the converse-influence of temperature fluctuations by absorbing heat and releasing pre-stored heat \[112\]. As proof, the manufacture of microcapsules utilized in textiles systems would result in a consolidation of thermo-physiological comfort \[113\]. More explicitly, the table below enumerates the sophisticated approaches of incorporation subsuming coatings, lamination, as well as fiber technology \[114\].

<table>
<thead>
<tr>
<th>Incorporation Procedures</th>
<th>Description</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coatings</td>
<td>Elastic fabric with wetted and dispersed microspheres phase change materials are coated with one another.</td>
<td>[115]</td>
</tr>
<tr>
<td>Lamination</td>
<td>The lamination is realized by the synthesis of the thin polymer film of PCM and the inner side of the fabric system.</td>
<td>[13], [116]</td>
</tr>
<tr>
<td>Fiber Technology</td>
<td>PCMs are infused into liquid (melt) polymer solution [117]; or base material is spun into the porous fiber by traditional manners.</td>
<td>[13], [118]</td>
</tr>
</tbody>
</table>
The textile materials embedded with PCMs or micro-encapsulated PCMs have been permeating variegating industrial applications by adapting their integration state. The gist below particularizes how PCMs make a significant difference in the following areas [119].

1) Aerospace
   The PCMs were designed to help astronauts withstand extremely cold temperatures during their working hours in outer space. Synchronously, the spacesuits should put astronauts in a comfortable condition.

2) Cloth
   A piece of qualified sport cloth should leverage a thermal balance between the heat dissipated to the ambiance and the heat generated by athletes intelligently. To illustrate, PCMs with the heat collected from the ardent physical activity would not be unleashed until the cold environment refrigerates body temperature down to a specific degree. Besides this, practicing this concept in bedding accessories would prevent ambient temperature disturbing the body temperature from heating and cooling. In a word, all garments theoretically relative with exothermic or endothermic body heat could incorporate in PCMs textiles such as shoes, hats and socks.

3) Medical Assistance
   A constant temperature treatment could mitigate the wounding exacerbation effectively. Hence, PCMs textiles have an immense market potential on account of their temperature-stabilized ability.

4. Conclusion
   This paper has comprehensively presented the mainstream of PCMs application systems with two prevailing PCMs enhancement treatments upswing PCMs to be commercially available. However, there have been still some other alternative PCMs application systems out of this paper’s review scope. More explicitly, the power generator storage related to cooling and heating procedure is a vital application [120]. Apart from this, the off-peak electricity storage, as another PCMs application, is to gap the electrical demand discrepancy between the peak and off-peak period [121] [122]. Because of the similar principle that has been used in each system, these PCMs-involved systems have been represented by the mainstream of PCMs application systems in a large proportion, which they are not necessarily to introduce exclusively and exhaustively.
Works Cited

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