A Review of Phase Change Materials

Guohui Feng, Tianyu Wang, Na He, and Gang Wang
Shenyang Jianzhu University, China

Abstract. Phase change materials (PCMs) use latent heat of phase change to store heat, which has the advantages of high energy storage density and low-temperature fluctuation. And it can be applied to many fields such as the building envelope and the Heating Ventilation and Air Conditioning (HVAC) system. The PCM is a kind of energy storage material with great potential, which positively impacts energy conservation and indoor environment improvement. In this paper, the relevant research on PCMs in recent years is reviewed, three common classification methods of PCMs are summarized, and the phase change temperature range is re-divided. The temperature of PCMs is less than 80°C for low-temperature PCMs, between 80°C and 200°C for medium-temperature PCMs, and above 200°C for high-temperature PCMs. Then, the characteristics and thermal properties of some commonly used PCMs are listed, including organic PCMs, inorganic PCMs, and some composite phase change materials (CPCMs). By summarizing the thermal properties of PCMs, it can provide a reference for the selection of PCMs. Finally, the article also introduces several kinds of preparation methods for CPCMs. The solutions to the problems of low thermal conductivity, supercooling, phase separation, and leakage of PCMs are discussed. And the future research topics of PCMs are prospected.

--- Corresponding author: Tianyu.Wang.wtv18841626036@163.com
1 Introduction

With the continuous improvement of people's requirements for the quality of life and the enhancement of environmental awareness, the concept of healthy and green life is gradually popularized. Excellent indoor air quality and appropriate indoor temperature and humidity are more and more attention by residents. And while maintaining the indoor environment at the same time energy conservation and emission reduction are also indispensable. This is not only a challenge to HVAC and other fields but also a boost to its development. In the process of realizing the above goals, many ideas and technologies have been proposed and applied. Among them, the research on PCMs has attracted the attention of many scholars. At present, there are three commonly used energy storage methods: sensible heat energy storage, latent heat energy storage, and chemical energy storage [1]. As a common energy storage material, PCMs mainly store heat through latent heat storage. And the latent heat storage has the advantages of high energy storage density and low-temperature fluctuation, and it is an efficient way of heat storage [2]. It is often used in the building envelope, the HVAC system, solar energy utilization, power peak cutting valley filling, and other fields [3-6]. There are many kinds of PCMs with different properties. Therefore, this paper summarizes the classification, characteristics, existing problems, and preparation methods of PCMs through the review of relevant research on PCMs and prospects the future research on PCMs.

2 Classification of PCMs

The common classification of PCMs is shown in Figure 1. The PCMs can be classified from three aspects: phase change form, material composition, and phase change temperature. However, different scholars divide the range of phase change temperature differently, as shown in Table 1. In this paper, various parameters of PCMs in relevant literature [6-11] in recent years are summarized. And the distribution diagram of phase change temperature and latent heat value of PCMs is drawn, as shown in Figure 2. According to this figure and referring to the division methods of other scholars, the phase change temperature is redivided. Figure 2(A) shows the distribution of paraffin, fatty acid, alcohol ester, inorganic hydrated salt, molten salt, metal, and alloy. As can be seen from the figure, the phase change temperature of molten salt, metal, and alloy is usually greater than 200°C, while that of paraffin and other materials is between -20°C and 120°C. In Figure 2(B), the phase change temperature distribution range of inorganic hydrated salt is the widest, while the phase change temperature of paraffin, fatty acid, and alcohol ester is mostly less than 80°C. Therefore, the phase change temperature range can be divided into the temperature of PCMs is less than 80°C for low temperature PCMs, between 80°C and 200°C for medium temperature PCMs, and above 200°C for high temperature PCMs.

![Fig.1. Classification of PCMs](image1)

<table>
<thead>
<tr>
<th>Time</th>
<th>Author</th>
<th>low temperature</th>
<th>medium temperature</th>
<th>high temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>2005</td>
<td>Hoshi et al</td>
<td>&lt;227°C</td>
<td>227-427°C</td>
<td>&gt;427°C</td>
</tr>
<tr>
<td>2018</td>
<td>Peng et al</td>
<td>&lt;20°C</td>
<td>20-250°C</td>
<td>&gt;250°C</td>
</tr>
<tr>
<td>2019</td>
<td>Zhang</td>
<td>&lt;100°C</td>
<td>100-250°C</td>
<td>&gt;250°C</td>
</tr>
<tr>
<td>2021</td>
<td>Huang et al</td>
<td>&lt;220°C</td>
<td>220-420°C</td>
<td>&gt;420°C</td>
</tr>
</tbody>
</table>

![Fig.2. Distribution diagram of PCMs](image2)

3 Commonly used PCMs

3.1 Commonly used organic PCMs

3.1.1 Paraffin

Paraffin is a low-temperature, solid-liquid, organic PCM. The chemical formula is C_{n}H_{2n+2}. With the increase of carbon atom number, the phase change temperature and latent heat also increase gradually [11]. Paraffin has the advantages of a wide phase change temperature range, high latent heat value, no supercooling or phase separation, low steam pressure, stable chemical properties, non-toxic, no pollution, safety, and low price. It is a commonly used PCM in the field of building energy conservation and solar energy utilization [10]. Due to its low thermal conductivity and leakage problems, further treatment is often required to improve its performance. It can be seen from Figure 2 that the phase change temperature of most kinds of paraffin is -15-70°C and the latent heat value is 50-280kJ/kg.
3.1.2 Fatty acids

Fatty acids are carboxylic acids with long hydrocarbon chains and terminal carboxylic groups, and their chemical formula is CH₃(CH₂)ₓCOOH. As the number of carbon atoms increases, the phase change temperature and latent heat also increase [12]. Fatty acids have the following advantages: high heat storage capacity, latent heat is usually higher than that of paraffin, low or no supercooling, non-toxic, good thermo-chemical stability, and huge resource reserves. However, it also has low thermal conductivity, easy leakage, a higher price than paraffin, a certain pungent smell, and other shortcomings. Figure 2 shows that the phase change temperature of fatty acids is 0-80°C, and the latent heat value is 140-250kJ/kg.

3.1.3 Alcohols

Alcohols are compounds containing hydroxyl groups bound to carbon on the side chains of hydrocarbons or benzene rings. Alcohol PCMs have the advantages of high latent heat value, suitable phase change temperature, low steam pressure, good thermo-chemical stability, non-toxic, non-corrosive, biodegradable, and so on. But its thermal conductivity is low, easy to sublimate, easy to dissolve in water, high price, and part of the alcohol supercooling degree is large [13]. Alcohols mainly include diols and polyols, among which the most used is polyethylene glycol (PEG). The phase change temperature and latent heat value of PEG increase with the increase of molecular weight. The phase change temperature of alcohols is mostly 19-55°C, and the latent heat value is 75-265kJ/kg.

3.2 Commonly used inorganic PCMs

3.2.1 Inorganic hydrated salt

Inorganic hydrated salt is a compound composed of inorganic salt and water, the chemical formula is generally AB·nH₂O, and the phase change process is a dehydration/hydration process [2]. Inorganic hydrated salt has the characteristics of high latent heat value, the small change of phase change volume, and many kinds. And it has almost twice the thermal conductivity of paraffin and is much cheaper. However, there are also some problems such as supercooling, phase separation, poor thermal stability, and short service life. Commonly used inorganic hydration salts include sulfate (Na₂SO₄·10H₂O, etc.), carbonate (Na₂CO₃·10H₂O, etc.), acetate (CH₃COONa·3H₂O, etc.), and chloride (CaCl₂·6H₂O, MgCl₂·6H₂O, etc.). The phase change temperature is 10-120°C and the latent heat value is 50-300kJ/kg.

3.2.2 Molten salt

Molten salt is a molten liquid of salt at a high temperature. Molten salt has a wide range of phase change temperatures, large heat capacity, low steam pressure, and no supercooling or phase separation, but it has some disadvantages, such as low thermal conductivity, a large change of phase change volume, easy leakage, and easy corrosion. It is often used in high-temperature waste heat recovery, aerospace, and other fields. The phase change temperature of molten salt is 300-900°C and the latent heat value is 180-1100kJ/kg.

3.2.3 Metals and their alloys

Metal alloys generally consist of low melting point metals and their alloys. It has the advantages of high latent heat, high thermal conductivity, low supercooling, small volume change, low steam pressure, good thermal stability, and so on [2]. The disadvantages are mainly low specific heat, poor oxidation resistance, poor compatibility, high-temperature corrosion, high supercooling of pure metal, unstable chemical properties of liquid metal, and may contain toxicity. Metals and their alloys are mainly used in industrial waste heat recovery and other fields of high-temperature energy storage. Commonly used metals and their alloys include aluminum alloy, magnesium alloy, copper alloy, zinc alloy, tin alloy, germanium alloy, nickel alloy, etc. Among them, aluminum base, magnesium base, and zinc base alloy are the most widely studied [11]. The phase change temperature of metals and their alloys is 190-800°C and the latent heat value is 60-400kJ/kg.

3.3 Commonly used composite PCMs

The composite phase change material (CPCM) is a new material that is made by combining PCM with another material through physical or chemical methods. This material usually has better thermal properties than the original PCM. The preparation of CPCMs is mainly through adding carrier materials (porous materials and polymers), shell materials (wall materials), and high thermal conductivity materials. This can solve the problems of supercooling, phase separation, leakage, and low thermal conductivity. The following will mainly introduce the graphite based CPCM and microcapsule CPCM.

3.3.1 Graphite based CPCMs

The commonly used composite graphite materials include expanded graphite(EG), graphite nanosheets (GNS), exfoliated graphite nanoplatelets(aGnP) and graphene (nano-graphene, graphene nanoplatelets(GNPs), graphene oxide(GO), graphene aerogel) and so on. D. Zhou et al. [14] added different mass fractions of EG into RT 27 paraffin and studied its heat transfer properties. The results show that the heat transfer properties of the CPCM increase with the mass fraction of EG. When the mass fraction is 9%, the heat transfer performance can be improved by 30%. Similarly, The GNPs can also enhance the heat transfer capacity of paraffin. When the mass fraction of GNPs reaches 10%, the thermal conductivity can be improved
by 400% [15]. Different types of graphite materials also have different effects on CPCMs. When the mass fraction is the same, graphene can improve the thermal conductivity better than exfoliated graphite sheet [16]. Li-wu Fan et al. [17] compared four kinds of carbon nanofills (short and long multi-walled carbon nanotubes, carbon nanofibers, and GNPs), and the experiment showed that when the mass fraction of GNPs was 5%, the thermal conductivity enhancement effect was the best, up to 164%. In addition, when the mass fraction of 20% graphene and MWCNT were added to the paraffin, the melting and solidification time of graphene/paraffin CPCM decreased more, and its thermal conductivity increased by 2800% [18].

By comparison, it can be seen that the strengthening effects of several materials are as follows: EG < GNS and xGNP < graphene. In addition, their preparation process is not the same. For example, the paraffin/EG CPCM is mostly prepared by the melt-blending process. The paraffin is melted in a high temperature water bath, then EG is added, stirred, and adsorbed for a certain time, and then the CPCM can be prepared. The paraffin/GNP CPCM can be prepared by a "two-step" process. Similarly, the paraffin is melted in a high temperature water bath, and GNPs are added and magnetic stirring for a certain period. Then the suspension is subjected to ultrasonic shock for some time. The preparation process is more complicated than that of EG, and dispersants are needed. The preparation of GO and graphene aerosols is more complex and requires reagents such as oxidants. The complexity of the preparation process of various PCPCMs is as follows: EG < GNS, xGNP < nano graphene < GO < graphene aerogel. Among the above materials, the EG is the simplest and most commonly used. However, its strengthening effect is slightly inferior to other materials. The preparation process of GNS and xGNP is slightly complicated, but in some cases, their strengthening effect is equal to or even better than that of graphene.

3.3.2 Microcapsules CPCMs

Microcapsule CPCMs are composed of core materials and wall materials. The core materials are mostly paraffin, fatty acids, and other PCMs, while the wall materials are usually organic or inorganic materials such as urea-formaldehyde resin (UF), gelatin, and polymethylmethacrylate (PMMA), as shown in Table 2. The preparation methods of microcapsule PCMs include in-situ polymerization, interfacial polymerization, complex coacervation, emulsion polymerization, phase separation, and spray-drying. And in-situ polymerization and interfacial polymerization are the most commonly used methods. Microcapsule PCMs can solve the leakage, supercooling, and phase separation problems in the phase change process to a certain extent, and have been applied in many fields such as energy storage and construction. However, there are also some problems such as poor stability, low packaging efficiency, and reduced latent heat value [19].

### Table 2. Commonly used core materials, wall materials, and preparation methods of microcapsule PCMs

<table>
<thead>
<tr>
<th>Core material</th>
<th>Wall material</th>
<th>The preparation methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>gelatin [20], gum arabic [20], UF [21], polyamine [22], carboxymethyl cellulose-urea-formaldehyde(CMC-UF) [23], melamine-formaldehyde(MF) [24], double alginate [25], styrene [26]</td>
<td>complex coacervation [20], spray-drying [20], in situ polymerization [21-24], repeated interfacial coacervation/crosslinking [25], miniemulsion polymerization [26]</td>
<td></td>
</tr>
<tr>
<td>paraffin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>stearic acid</td>
<td>SiO₂[27]</td>
<td>sol-gel method [27]</td>
</tr>
<tr>
<td>n-dodecanol</td>
<td>PMMA [28]</td>
<td>miniemulsion polymerization [28]</td>
</tr>
<tr>
<td>butyl stearate</td>
<td>polyurea [29]</td>
<td>interfacial polycondensation [29] suspension</td>
</tr>
</tbody>
</table>

4 Preparation of CPCMs

The preparation methods of CPCMs include porous adsorption, melt-blending, micro/nano capsule, and other chemical methods.

4.1 Porous adsorption method

The porous adsorption method takes the porous material as the carrier, by soaking the porous material in the liquid PCM (immersion method), so that the two materials are firmly combined to form the CPCM. When the PCM has a solid-liquid phase change, the CPCM is firmly adsorbed in the porous material channel under the action of microporous surface tension and capillary adsorption. This prevents liquid leakage and enables the shaping of the PCM. Although the PCM is a solid-liquid phase change, the CPCM is a solid-solid phase change macroscopically. The porous adsorption method has the advantages of simple process, low cost, improving the thermal conductivity of PCMs, and preventing liquid leakage, but the prepared CPCMs have poor heat resistance and mechanical stability, and a short service life [12]. Commonly used porous materials are carbon materials (EG, activated carbon, etc.), foam metal, and clay minerals (gypsum, kaolin, diatomite, etc.) [11].

4.2 Melt-blending method

The melt-blending method takes polymer as the carrier and blends the PCM and the carrier material in a certain proportion after heating and melting. In this way, the low melting point material is wrapped by the high melting point material, to prepare the CPCM. During the phase change process, the liquid is bound to flow through a three-dimensional network of polymer chains, thus forming the material. The PCM is a solid-liquid phase change, and the CPCM is a solid-solid phase change. The advantages of this method are simple, not easy to leak, safety, and stable performance.
The disadvantages include short service life and limited materials. It requires no chemical reaction between the PCM and the carrier material and good compatibility [12].

4.3 Micro/nano capsulation method

The micro/nano capsulation method is to use the organic polymer whose melting point is higher than the PCM as the wall material and encapsulates the PCM (core material) into micro/nano capsules. Microcapsule particle size is usually less than 1000μm, nano capsule particle size is less than 1000nm [11]. The common core materials are paraffin, fatty acid, inorganic hydrated salt, and other low temperature PCMs. The wall materials have good impact resistance and aging resistance, such as resin, polyester, and aromatic polyamide polymer materials. This method improves the thermal conductivity of PCMs, increases the heat transfer area, and solves the leakage problem. The CPCM has stable physicochemical properties and good thermal cycling. However, the preparation process is more complex, and the cost is relatively high.

5 Solutions to common problems

Although PCMs have high energy storage density, they generally have problems such as low thermal conductivity, supercooling, phase separation, and liquid leakage. The following are common solutions to these problems.

5.1 Heat transfer Problem

Since the thermal conductivity of PCMs is usually very low, the following methods are generally adopted to improve the heat transfer capacity [10,11]:

(1) Adding high thermal conductivity materials into the PCM by doping method to improve the overall thermal conductivity. Commonly used additives include carbon materials, metal, metal oxidation, and nanoparticles of inorganic materials.
(2) Preparation of CPCMs with carrier materials. The heat transfer performance of PCMs can be improved by using porous materials or polymers as carriers to prepare from stable PCMs or shape stabilized PCMs.
(3) Adopting microencapsulation. The PCMs are encapsulated in the capsules with extremely small particle sizes to increase heat transfer area and strengthen heat transfer.
(4) Optimizing the structure of the energy storage unit. The heat transfer performance can be improved by changing the geometry structure of the energy storage unit, installing fins, and changing packaging materials.

5.2 Supercooling problem

Supercooling refers to the phenomenon that the actual solidification temperature of PCMs is lower than the theoretical temperature during solidification. And the supercooling degree is the difference between actual and theoretical solidification temperature. There are several common methods to reduce the supercooling degree [31,32].

(1) Adding nucleating agent. Materials with similar crystal structure and lattice parameters are added to PCMs as nucleating agents. It can induce crystallization when the temperature drops to the theoretical crystallization temperature and reduce the supercooling degree. Table 3 shows the nucleating agents used in some studies.
(2) Applying external disturbance to the PCMs. The cavitation phenomenon, ultrasonic wave, electric current, and other methods are used to disturb the PCMs to reduce the supercooling degree and trigger nucleation.
(3) Adopting microencapsulation. The PCMs can be microencapsulated and changing the size of the microcapsule can reduce the supercooling degree.
(4) Using wall modification. The packaging wall materials are processed to optimize the properties of wall materials, such as the use of composite wall materials.

5.3 Phase separation problem

The phase separation often occurs in inorganic hydrated salt PCMs. During the melting process, the incompletely dissolved salt with low solubility is deposited at the bottom. When the temperature decreases, the PCMs will be stratified. The bottom layer of the PCMs is an undissolved solid layer, the middle layer is a crystalline hydrated salt layer, and the upper layer is a saturated solution layer. The undissolved solid layer at the bottom accumulates more and more as the PCMs heat up and cool repeatedly. This results in worsening heat storage performance. When the cycles reach a certain number, the PCM will lose its heat storage capacity [33]. The following are common solutions to the phase separation problem [32,33].

(1) Adding thickener. This is the most effective solution. By increasing the viscosity of the liquid solution, solid-liquid separation of PCMs can be greatly eliminated. Table 3 shows the thickeners used in some of the studies. The commonly used thickeners are super absorbent polymer (SAP) and carboxymethyl cellulose (CMC).
(2) Adopting microencapsulation. Microencapsulation of the PCMs can effectively solve the problem of phase separation.
(3) Agitation oscillation. The phase separation can also be weakened by stirring and oscillating the PCMs.
(4) Changing the properties of PCMs. The chemical modification method can be employed to prevent phase separation.

<table>
<thead>
<tr>
<th>PCMs</th>
<th>Nucleating agent</th>
<th>Thickener</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCl₂·6H₂O</td>
<td>SrCl₂·6H₂O [34], BaCO₃ [34], K₂CO₃ [34], K₂SO₄ [35], Na₃P₂O₇·10H₂O [36], AlN particles [37], Na₃P₂O₇·7H₂O [38,39],</td>
<td>SAP [35], CMC [36], starch [38], cellulose [38],</td>
</tr>
</tbody>
</table>
5.4 Leakage problem

The solid-liquid PCMs are usually accompanied by liquid leakage during the phase change process. The following methods are commonly used to solve the leakage problem.

1. Encapsulating PCMs. The PCMs can be wrapped by macro/micro encapsulation to prevent leakage.
2. Preparation of CPCM with the carrier material. The leakage problem can be solved by using the property that the carrier material can restrain the PCMs from flowing.

In summary, the above four problems can be effectively solved by microencapsulation of the PCMs, preparation of micro/nano capsules, and preparation of CPCMs with carrier materials. For organic PCMs, the main problems are heat transfer and liquid leakage. For inorganic materials, it is necessary to solve the problems of supercooling and phase separation.

6 Conclusions and future recommendations

This paper reviews the classification of PCMs and reclassifies them according to the phase change temperature. The thermal properties of some commonly used PCMs and the preparation methods of CPCMs are listed, which can provide a reference for the selection and preparation of PCMs. Finally, the existing problems and solutions in the application of PCMs are analyzed. Through the conclusion of the above aspects, it can be seen that:

1. Organic PCMs, inorganic PCMs, and CPCMs have their advantages and disadvantages. Compared with inorganic materials, organic materials have obvious advantages of no supercooling and phase separation, but inorganic materials have higher latent heat and thermal conductivity. The CPCMs have many advantages, but their cost is high, and further research is needed.
2. There are many methods to prepare CPCMs. Among them, the porous adsorption method, melt-blending method, and micro/nano capsule method are the most used. For different composite materials, appropriate preparation methods should be selected to reduce the production cost and achieve the mass production of CPCMs.

(3) The common problems in the application of PCMs are low thermal conductivity, supercooling, phase separation, and liquid leakage. Microencapsulation of PCMs and preparation of corresponding CPCMs are effective methods to solve these problems. However, the preparation technology of the two methods is complicated to be popularized. Therefore, when dealing with the common problems of PCMs, the solution should be selected pertinently, and its rationality and economy should be fully considered. Based on the analysis of the characteristics of PCMs, the following aspects can be studied in the future.

1. Enhancing the heat transfer performance of PCMs. Enhancing the heat transfer performance is always the focus of the PCMs research. Although the thermal conductivity of PCMs is effectively improved by many methods, other thermal properties of PCMs will be affected, such as the reduction of latent heat storage capacity. Therefore, it is still necessary to study the heat transfer performance of PCMs to maintain or even improve other thermal properties.
2. Improving the preparation method of CPCMs. Although the CPCMs have outstanding performance, it is often difficult to be widely used due to their complex manufacturing process and high cost. Therefore, it is particularly important to simplify the preparation method and save economic costs.
3. Preparation of new CPCMs. The research prospect of CPCMs is broad, and there are still many materials that have not been studied and combined with PCMs. In addition, the current CPCMs are mostly binary composites of two materials, and three or more kinds of multi-component composites are yet to be explored.

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References