



Recent Advances in Organic/Composite Phase Change Materials for Energy Storage

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Abstract

Phase change materials (PCMs) store and release energy in the phase change processes. In recent years, PCMs have gained increasing attention due to their excellent properties such as high latent heat storage capacity, appropriate solid-liquid phase change temperature, thermal reliability, and low cost. Herein, classification, characteristics, and evaluation criteria of organic/composite PCMs are systematically illustrated, and some typical preparation methods are introduced, such as in-situ polymerization, interfacial polymerization, spray drying method, porous materials adsorption method, sol-gel method, melt-impregnated and mixing method, electrospinning method, vacuum infiltration and ultrasonic method are introduced. In addition, this review presents some applications of PCMs in the utilization of solar energy, building materials, air conditioning, industrial waste heat recovery, and military camouflage and stealth. Finally, the development tendency of PCMs is discussed.

Keywords: Phase change materials (PCMs); Thermal energy storage; Preparation methods; Application.

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1. Introduction

Recent developments in social industrialization, energy, and environmental fields have gradually aroused a series of problems, and thereby restrict the social advancement. Accordingly, people have focused on using renewable energy. Phase change materials (PCMs) have revolutionized in this field, and have become the direction of efforts to resolve energy and environmental issues in the future. The phase transition process of PCMs is an approximately isothermal

process, with the energy being stored or released in this process.^[1-10] The PCMs are a group of materials that have an intrinsic capability of absorbing and releasing heat during phase transition cycles. These materials can be either organic, inorganic, or eutectic mixtures. PCMs primarily refer to the composite between two or more materials that can overcome the performance deficiencies of a single material, and often give some new excellent properties to the material. The use of PCMs in the field of heat storage has a series of advantages, such as high latent heat storage capacity, appropriate solid-liquid phase change temperature, thermal reliability, and low cost.^[11-24] Compared to the single system, it has high thermal storage density and low melting point. However, the thermal physical property data of composite PCMs is limited. In addition, some fatty acid eutectic PCMs have a strong smell, which limits its application. [Table 1](#) describes some composite PCM system. These PCM composite phase transition systems are well studied at present, they have moderate phase change temperature and high melting latent heat. If we can continue to explore the composition and proportion, better performances can be obtained to satisfy a broader application prospect. PCMs can be divided into solid-solid, solid-liquid, solid-gas, and liquid-gas types according to the phase change method. Due to the small volume changes of the solid-solid

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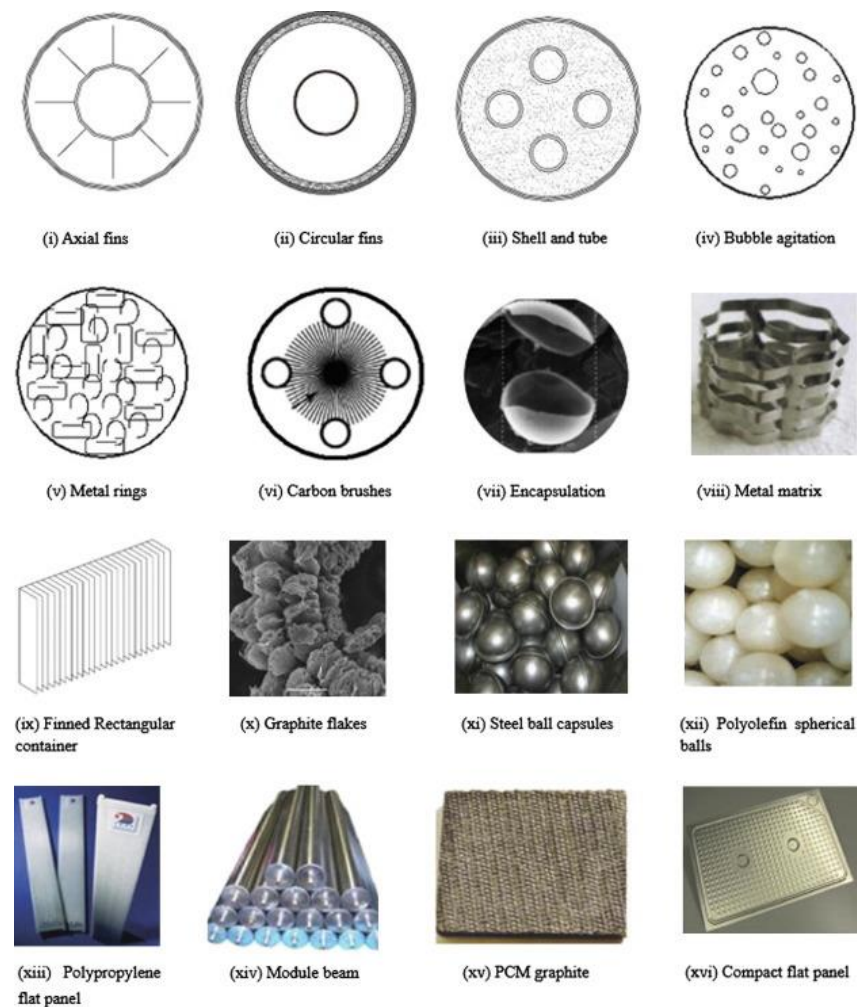


Fig. 1 Various types of PCMs encapsulations.^[27] Reproduced from Ref. 27, with permission from Elsevier.

PCMs, research and application have developed rapidly for this type. The solid-liquid PCMs have the advantage of high latent heat of phase change, while the liquid system must be maintained in a container during the phase change process, which leads to the high cost and limited application of this type of PCMs. Obviously, considering the huge volume change during the phase change process, both solid-gas and liquid-gas PCMs are not suitable for thermal energy storage and temperature control.^[26] Various types of PCM encapsulations are shown in Fig. 1.

The successful application of PCMs depends on the equipment development, which provides encapsulation for PCMs and container for heat transfer fluid (HTF). A typical PCM-based thermal energy storage (TES) device is composed of materials that are only functional when the materials are integrated into a system. It usually consists of two main components: (1) a suitable PCM for the required temperature range; and (2) a PCM package that provides the required heat transfer surface. Macroencapsulation of PCMs is a common method in TES. The components are assembled to facilitate a device, in which both liquid and gas phases can be used as HTFs. This type of TES component can also prevent phase separation and is easy to operate and be manufactured.^[28] The

geometry and structure of macroencapsulation vary from packed bed to shell, tube, and flat plate (Fig. 2).

In practical applications, PCMs should have some advantages such as higher latent heat of phase change, good thermal and chemical stability, less supercooling, high heat storage density, large storage capacity, no phase separation, environment friendliness, wide source, and low cost. Currently, many researchers have been devoted to the development of ideal energy storage materials with stable chemical properties, multiple cycles, environment friendliness, wide temperature range, and cost-efficiency. Thus, current scientific and technological progress and the expansion of research fields would drive the research on PCMs that could promote the industrialization of laboratory results and expand the scope of application of these materials.

In-situ polymerization, interfacial polymerization, spray drying, porous material adsorption and sol-gel method have been reported to prepare PCMs. The prepared PCMs have better properties and have good application prospects. The research methods mentioned are relatively mature and the materials prepared are reliable. PCMs have been widely used in industrial waste heat recovery, building energy saving, power peak shaving, solar energy utilization, military

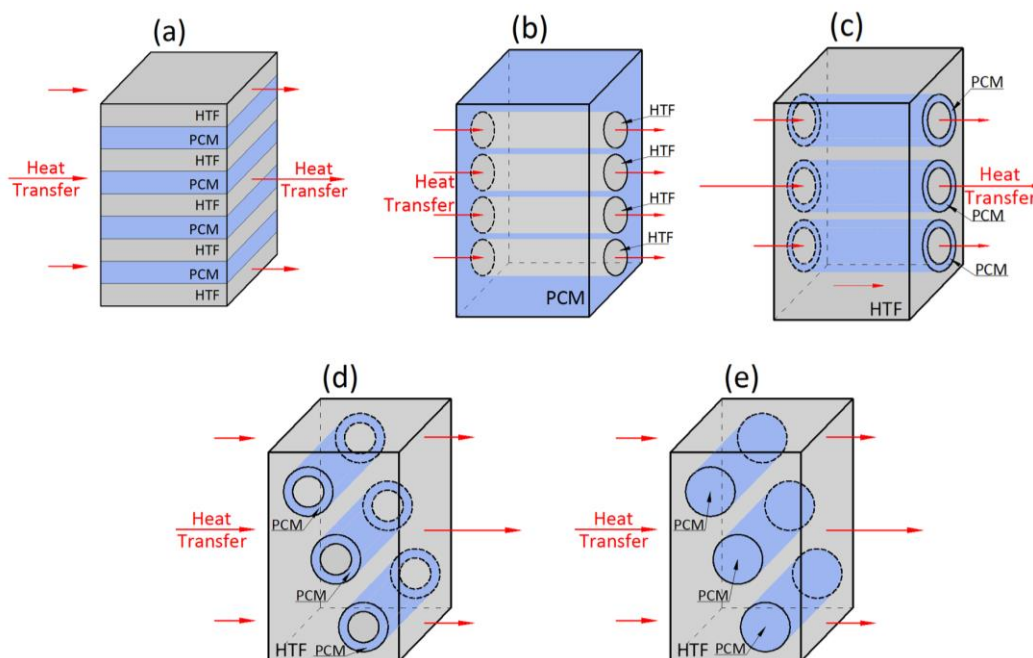


Fig. 2 Different types of TES devices: (a) Flat plate; (b) Shell and tube-internal flow; (c) Shell and tube-parallel flow; (d) Shell and tube-cross flow; and (e) Packed bed.

engineering, aerospace and other fields.^[29-31] In addition, because the temperature of PCMs is approximately constant in the process of phase change, it can also be used in temperature control systems. Compared with traditional thermal management methods, this thermal management technology can efficiently remove heat from the heat source without any energy input, while ensuring that its own temperature fluctuates only slightly.

Until now, most of the reviews on PCMs are focused on the properties and applications of materials, and many discussions have been made on the performance improvement of different composite methods. This review systematically summarizes the preparation, performance, and improvement of PCMs and in this review, some opinions are put forward for PCMs.

2. Preparation method and characteristics of the PCMs

2.1 In-situ polymerization

In the in-situ polymerization method, the soluble monomer and the catalyst are all located outside or inside the core of the PCM droplet. The reaction proceeds on the surface of the droplet to generate an insoluble polymer, which is deposited on the surface of the core. Before the reaction, the PCMs exist as a dispersed emulsion phase, and the outer shell materials are mostly monomers or mixtures of several monomers or low molecular weight prepolymers. Thus, the key step is the coating of the polymer on the outer surface of the core material.^[32] A number of researchers have adopted this mature method to prepare phase change energy storage materials.

In-situ polymerization involves a process whereby the chemical reaction takes place between two immiscible liquids

(water-soluble phase and oil-soluble phase) in a continuous phase such as emulsion/mini-emulsion, suspension, and interfacial polycondensations. Typically, the process consists of 4 steps: (1) oil/water (O/W) emulsion production, (2) preparation of prepolymer mixture liquid, (3) adding prepolymer mixture liquid into O/W emulsion to encapsulate core material particles, and (4) washing and drying microencapsulated phase change materials (MEPCM)/nanoparticle-enhanced phase change materials (NEPCM). Fig. 3 shows the encapsulation of n-octadecane with resorcinol-modified melamine-formaldehyde shell^[33] using the in-situ polymerization process.

Yu *et al.*^[34] used n-dodecanol as the core material and melamine-formaldehyde resin as the wall material in the used in-situ polymerization to synthesize smooth spherical phase change heat storage microcapsules with high heat storage density. When styrene-maleic anhydride (SMA) copolymer and polyoxyethylene octyl phenol ether-10 (OP-10) were used as emulsifiers (mass ratio 4:1), the mixing speed was 4500 rpm, and the mass fraction of n-dodecanol alcohol was 69% with the latent heat of phase change of 167 J/g. The encapsulation efficiency of n-dodecanol alcohol is about 97.5%, the phase transition temperature is 24°C, and the average particle size is about 30 μm. Zhang *et al.*^[35] utilized urea, melamine, and formaldehyde to prepare n-octadecane, n-nonadecane, and n-icosane microcapsules. Pan *et al.*^[36] synthesized novel PCM capsules from palmitic acid, n-pentanol, aluminum chloride hexahydrate, and ammonium bicarbonate. The melting point of this PCM microcapsule is 50°C, which is lower than that of palmitic acid. Su *et al.*^[37] synthesized a series of spherical microcapsules containing paraffin core material by the

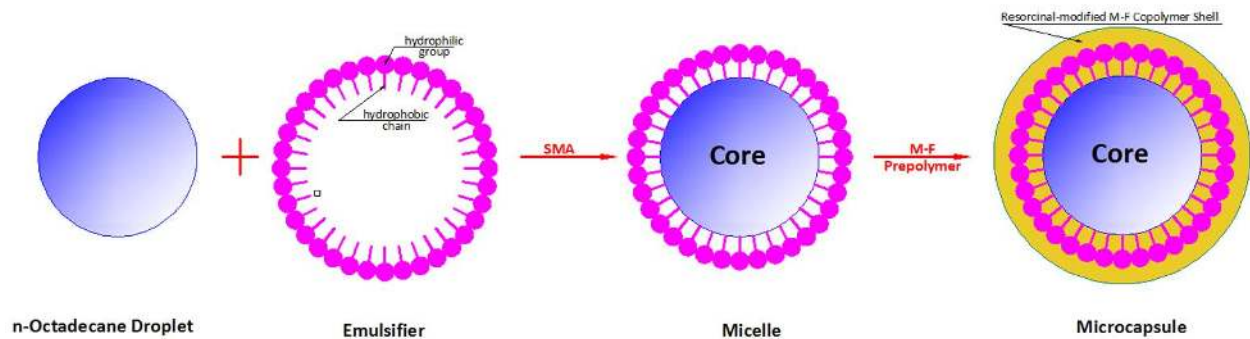


Fig. 3 Fabrication of the MEPCM by in-situ polymerization.

modifying melamine-formaldehyde resin with methanol. The surface of the microcapsule material is smooth. This modification method increases the cross-linking structure in the wall material, reduces the content of free formaldehyde, and improves the ability of deformation resistance and internal surface extrusion resistance of the wall material. Boh *et al.*^[38] used trimethylolmelamine-formaldehyde prepolymer and hexakis(methoxymethyl)-melamine-formaldehyde prepolymer as wall materials, and prepared paraffin microcapsules by in-situ polymerization and phase transition temperature of 25, 40, and 50°C.

2.2 Interfacial polymerization

Interfacial polymerization is the polycondensation of two monomers containing more than one functional group in two immiscible liquids. This method has the advantages of rapid reaction, mild reaction conditions, low purity requirements for the monomers, and less strict requirement of raw material ratio.^[32] Wei *et al.*^[39] used the interfacial polymerization method to produce a thermal storage thermoregulation phase change microcapsule for smart textiles. The microcapsules were mainly spherical, with a smooth surface and an average particle size of 10.6 μm . It was stable with acetone and absolute ethyl alcohol, and the mass fraction of paraffin in microcapsules was 84%, the latent heat of phase change was 118 J/g, and the phase change temperature was close to the comfortable temperature range of human body. Lan *et al.*^[40] prepared n-eicosane microcapsules by interfacial polymerization. The phase change temperature of the microcapsule material was about 36°C, the phase change enthalpy was 29.34–63.55 J/g, and the encapsulation rate of n-eicosane was about 75%. Malfiet *et al.*^[41] prepared paraffin microcapsules by interfacial polymerization, followed by electrodeposition of the copper on the surface of the microcapsules, and studied the potential application prospects of this material.

Fig. 4 shows the process used by Zhang *et al.*^[42] to synthesize microencapsulated n-octadecane with polyuria shells, which was produced with tolylene 2,4-diisocyanate (TDI) and three different amines, *i. e.*, ethylene diamine (EDA), diethylene triamine (DETA), and Jeffamine T403. The

oil solution was prepared by mixing TDI and n-octadecane and then water was added to the mixture at a stirring speed of 3000 rpm to produce O/W emulsion. Furthermore, an EDA solution consisting of 0.1 wt% SMA was added into the O/W emulsion at a stirring rate of 600 rpm to complete the interfacial polymerization process. The MEPCM produced with Jeffamine as the amine monomer exhibited an anti-osmosis property.

2.3 Spray drying

In the spray drying method, the wall material is dissolved into an aqueous solution; then, an oil-soluble core material is added to form an emulsion, which is then added to a spray drying device to obtain microcapsules.^[43] This method is simple, low cost, and the particle size of the obtained product is uniform, which are beneficial to large-scale industrial production. For example, Hawlader *et al.*^[44] used gelatin and gum arabic as the wall material and paraffin as the core material, and spray-dried to obtain paraffin microcapsules. The microcapsule material had an enthalpy value of 145–240 J/g and uniform particle size, which should be used in solar energy storage. Fei *et al.*^[45] used C_{18} as core material and TiO_2 as wall material, and the C_{18} microcapsule was prepared by spray drying. The microcapsules had a particle size of 0.1–5 μm , and a phase change enthalpy of 92–97 J/g.

2.4 Porous material adsorption

Porous materials have specific structures and strong polarization or capillary action. In order to prepare composite PCMs, a vacuum method is used to remove the fluid in the pores or layers of the materials and make them absorb a large number of PCMs. This method has the advantages of ease of application, low cost, no leakage, and easy for mass production. However, the thermal stability and life of these materials are not satisfactory. Since then, improved composite methods have been explored to resolve the issues of poor thermal stability and short life of the materials. Zhang *et al.*^[46] used paraffin as a PCM and expanded graphite as a support material, and prepared a paraffin/expanded graphite composite stereotyped phase change heat storage material with a paraffin wax content of 90%. The expanded graphite adsorbed the

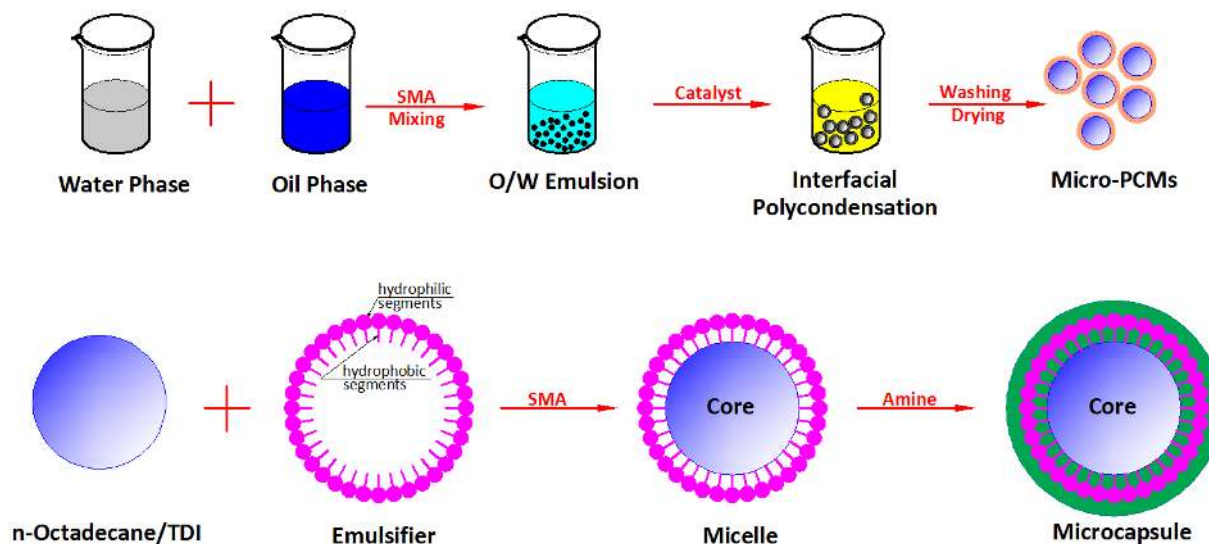


Fig. 4 Microcapsule manufactured by interfacial polycondensation.

paraffin but still maintained the original loose and porous worm-like morphology. The composite phase change heat storage material did not form new substances, and its phase change temperature was similar to paraffin. The phase change enthalpy is equivalent to the calculated phase change enthalpy based on the content of paraffin in the composite material. Zhou *et al.*^[47] used polyethylene glycol (PEG) as a PCM, intercalated with layered nano-montmorillonite, and selected polyethylene grafted maleic anhydride as a compatibilizer in a plasticizer to melt blend with low-density polyethylene (LDPE) resin. The phase change enthalpy range of the blend was 20.58–88.76 J/g, and the phase change temperature range was 47.5–63.6°C. Subsequently, Li *et al.*^[48] studied the paraffin/bentonite composite PCMs, and found that after organic modification, the layer spacing of bentonite was increased and paraffin was inserted into the interlayer of bentonite, which strengthened the heat transfer process of paraffin/bentonite composite PCMs and improved the heat transfer rate of the PCM. Wang *et al.*^[49] used porous SiO₂ and PEG to prepare an inorganic-organic solid-liquid PCM. The thermal conductivity of the material was increased by 21%, and the phase change enthalpy of PEG (80%)/SiO₂ (20%) material reached 137.7 J/g. Feng *et al.*^[50] used PEG, activated carbon, and SiO₂ molecular sieves to synthesize a series of PCMs. The PEG/polyacrylonitrile (AC) material with 80% PEG had the largest latent heat of phase change. It had the advantages of low melting point, low subcooling, and high heat storage efficiency. Chen *et al.*^[51] prepared a new type of lauric acid/montmorillonite PCM by melt embedding technology. The study found that the montmorillonite layer spacing increased from the original 2.8 to 6.4 nm, and the lauric acid in the composite remained solid during the solid-liquid phase change.

2.5 Sol-gel method

In the sol-gel method, the metal-organic or inorganic compound undergoes sol-gel treatment and the heat treatment causes the formation of oxides or other solid compounds. It is characterized by mild reaction conditions and uniform dispersion phases. Various polymer-based nanocomposites can be prepared with different properties by changing the reaction components.^[52] However, this method requires a prolonged aging duration, and the prepared material is prone to shrinkage, which might affect the morphology and performance of the material.

Table 1. The thermo-physical properties of composite PCMs.^[25]

PCM compound	Melting temperature (°C)	Heat of fusion (kJ/kg)
65.5% capric + 34.5% lauric acid	18–19.5	140.8
75.2% capric acid + 24.8% palmitic acid	22.1	153
26.5% myristic acid + 73.5% capric acid	22.4	152
34% C ₁₄ H ₂₈ O ₂ + 66% C ₁₀ H ₂₀ O ₂	24	147.7
66.6% CaCl ₂ ·6H ₂ O + 33.3% MgCl ₂ ·6H ₂ O	25	127
38% CaCl ₂ + 4.3 % NaCl + 0.4% KCl + 47.3 % H ₂ O	26.8	188
60% CH ₃ COONa·3H ₂ O + 40% CO(NH ₂) ₂	30	200.5

Zhang *et al.*^[53] prepared an organic-inorganic nanocomposite PCM by the sol-gel method, using tetraethyl orthosilicate and palmitic acid as the raw materials. This

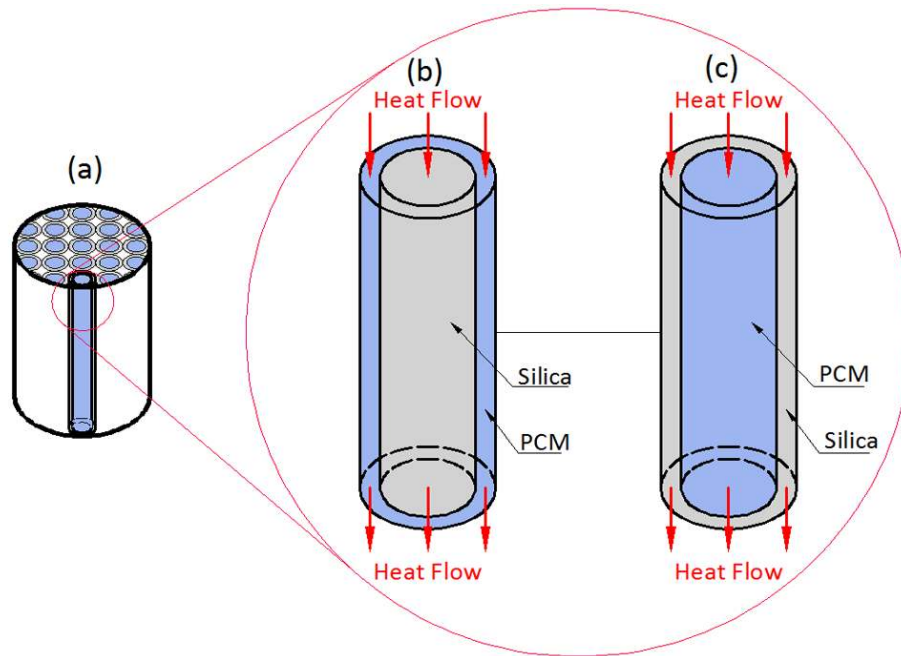


Fig. 5 Schematic representation of (a) melt-impregnated and mixing type PCMs package device; (b) and (c) shell and tube component, respectively.

composite exhibited sufficient thermal storage capacity and cyclic thermal stability and exhibited sufficient solar energy utilization. Zhang *et al.*^[54] prepared phase change microcapsules by the sol-gel method using C₁₈ as the core material and SiO₂ as the wall materials. This microcapsule material had a smooth surface, good thermal stability and compactness, and the thermal conductivity of the material was improved significantly.

2.6 Melt-impregnated and mixing method

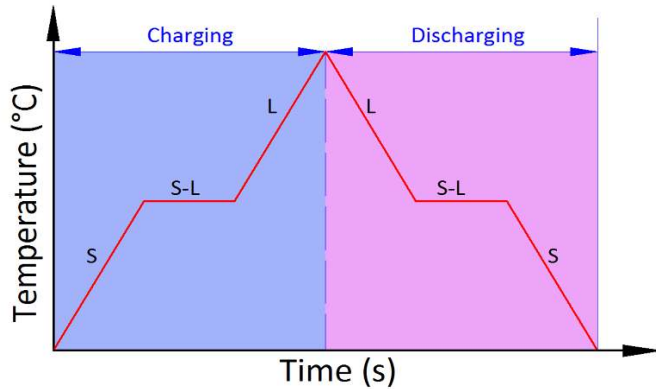


Fig. 6 Phase transition diagram for a latent heat storage material (S, solid phase; L, liquid phase; and S-L, solid-liquid).

The melt-impregnated mixing method is used to prepare the shaped composite phase change energy storage material. The common substrates are silica, expanded graphite, and diatomite. The high-porosity inorganic porous medium is used as the matrix, and the PCM is fixed by capillary force and surface adsorption. Thus, the shape setting phase change energy storage materials made by this method have good stability, and they are macron solid phase and micron liquid phase in the solid-liquid phase change. The shell and tube

types of silica based PCMs devices are widely utilized for commercial and industrial applications in medium and high temperature thermal energy storage fields,^[55] Fig. 5(a). In this type of configuration, silica is mainly contained in the space between the shell and the tubes with the PCM flowing through the tube, as shown in Fig. 5(b). In some cases, the silica could also be encapsulated within the tubes and the PCMs were designed to pass through the annular space, as shown in Fig. 5(c). The heat is transferred to or from the salts through the tube walls.

Wu *et al.*^[56] and Zhong *et al.*^[57] prepared porous composite phase change energy storage materials with high thermal conductivity, low supercooling, and optimal thermal stability by combining inorganic salt with expanded graphite. Ling *et al.*^[58] and Mochane *et al.*^[59] impregnated organic matter into expanded graphite, and the data analysis revealed that the prepared composite phase change energy storage material had high thermal stability and adequate thermal conductivity. With the increase in the mass of the expanded graphite, the thermal conductivity of the material was also increased. Yoldas *et al.*^[60] and Tang *et al.*^[61] prepared composite phase change energy storage materials with good thermal conductivity and high thermal stability using a binary fatty acid eutectic mixture, graphite nanosheet, and diatomite respectively. Chieruzzi *et al.*^[62] prepared three new shaped phase change energy storage materials, KNO₃/SiO₂, KNO₃/Al₂O₃, and KNO₃/SiO₂+Al₂O₃, and adding SiO₂ nanoparticles exerted a significant effect on the improvement of KNO₃ thermal storage performance. Scanning electronic microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) analysis showed that the composite phase change energy storage materials were evenly distributed in the interior of the SiO₂ nanoparticles. Moreover, the PCM

exudation occurs on the surface of Al_2O_3 and $\text{SiO}_2+\text{Al}_2\text{O}_3$ nanoparticles, which shows that porous SiO_2 nanoparticles cover the PCMs and avoids leakage during the phase change process.

Among the thermal energy storage technologies, latent heat storage is realized through enthalpy change of a PCM during phase transition and has attracted a great deal of attention in recent years. The heat storage and release mechanism of a PCM based latent heat storage^[63] can be illustrated in Fig. 6. During a charging process, when a PCM at solid state is heated, its temperature increases until it reaches the phase change point. Over this temperature range, heat is stored in the sensible form. Further heating of the material incurs solid to liquid phase transition and the heat is stored in the latent form while temperature is maintained constant during this period. Once the phase change is completed, the PCM is in liquid phase, further heating of the material increases its temperature and the heat is stored again in the sensible form. Further heating to the material leads to boiling, which is not normally used for thermal energy storage. The reverse of the processes described above releases the heat, which is also called discharge process.

2.7 Electrospinning method

The electrospinning method relies on the electric field force to prepare fibers. With the action of the electric field force, the polymer droplets are gradually stretched to the Taylor cone. When the electric field force is greater than the surface tension

of the polymer solution or melt, the jet is ejected from the surface of the Taylor cone, and collected on the receiving device to form a fiber felt. The shaped phase change composite material prepared by electrostatic spinning has the advantages of controllable structure and performance, adjustable size and direct usability. For example, Cai *et al.*^[64] prepared a composite phase change energy storage material of capric acid-lauric acid-palmitic acid (CA-LA-PA)/ SiO_2 by electrospinning method, and the eutectic mixing mass ratio of fatty acids was 61.9:31.0:7.1. The electrospinning SiO_2 nanofiber has high porosity and large specific surface area, and can absorb a large number of PCMs. The thermal storage property of the composite PCMs shows that it has a high thermal stability. Fig. 7 shows the microstructure and performance diagram. It shows that the SiO_2 nanofibers were well-separated in the mat with few microscopically identifiable locations of conglutination. The fibers had relatively smooth surfaces with cylindrical shape. Such porous structure increased its specific surface area, and was capable of absorbing a large amount of CA-LA-PA eutectic mixture. For the form-stable composite PCM, the CA-LA-PA eutectic mixture was absorbed in and supported by the porous structure of nanofibers, and the fiber diameters appeared to increase upon the absorption of CA-LA-PA eutectic mixture. In addition, the CA-LA-PA eutectic mixture might accumulate on or near the surfaces of nanofibrous mat, leading to unclear interfaces between nanofibers and CA-LA-PA eutectic mixture. It was concluded that the porous structure of

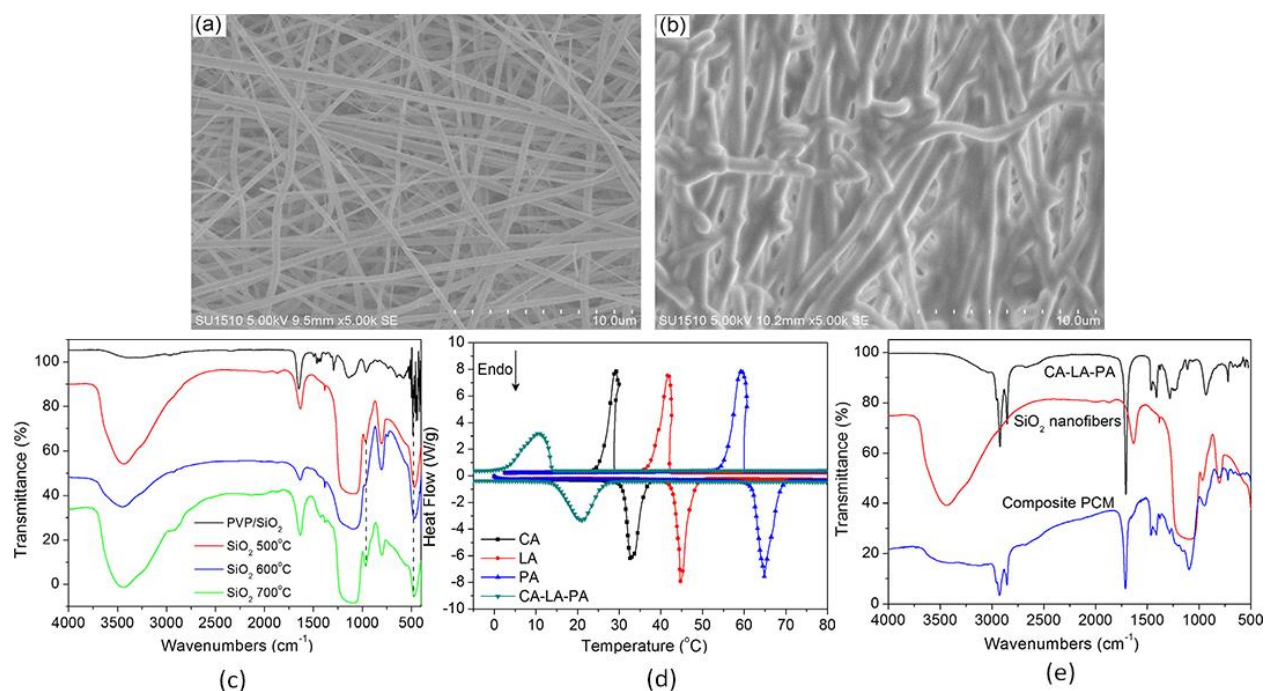


Fig. 7 (a) and (b) SEM images of electrospun SiO_2 nanofibers and form-stable composite PCMs; (c) FTIR spectra of as-electrospun PVP/ SiO_2 composite nanofibers and electrospun SiO_2 nanofibers at different annealing temperatures; (d) DSC curves of CA, LA, PA and CA-LA-PA eutectic mixture; (e) FTIR spectra of CA-LA-PA eutectic mixture, electrospun SiO_2 nanofibers and form-stable composite PCMs.^[64] Reproduced from Ref. 64, with permission from ELSEVIER.

nanofibers retained their overall shapes very well and effectively prevented the leakage of molten eutectic mixture due to the surface tension and capillary effect between CA-LA-PA and SiO₂.

2.8 Vacuum infiltration

Li *et al.*^[65] prepared nitrate mixture/SiC honeycomb ceramic (SCH) composite PCMs by vacuum infiltration. SEM showed that the nitrate mixture was dispersed and embedded into the porous structure of the SiC wall. The heat storage and release rate of the composite PCMs is increased with the elevated SCH mass fraction when SCH with different mass fractions are added into the composite PCMs. Compared to pure PCM, the melting temperature and solidification temperature of the composite PCM are altered slightly, while the heat storage and release time of the composite PCMs are also greatly reduced. Tian *et al.*^[66] prepared paraffin/EVA composite phase change energy storage materials with paraffin as the matrix, ethylene-vinyl acetate (EVA) as the support material, one-dimensional graphite, and one-dimensional carbon fiber as the conductive filler. After testing, the phase change temperature was detected as 45.63°C, and the phase change enthalpy was 167.4 J/g.

2.9 Ultrasonic method

Xiao *et al.*^[67] used the ultrasonic method to combine the molten salt of NaNO₃ and KNO₃ at a mass ratio of 6:4 with expanded graphite. The addition of expanded graphite improved the thermal conductivity of the composite PCM. Therefore, the composite PCMs of molten salt/expanded graphite are suitable for thermal conversion and thermal energy storage materials.

3. Main problems and research status of PCM

PCMs are environment-friendly energy storage materials and have extremely broad commercial application prospects in new fields such as temperature control and heat storage. But at the same time, problems such as low thermal conductivity and leakage of liquid PCMs hindered its widespread applications. In recent years, scientists have done a lot of research on the technical barriers that hinder the application of PCM, and promote the rapid development of phase change energy storage materials. The most commonly used low-temperature inorganic PCMs use coordination bond breaking to absorb and release energy. Similarly, they also have shortcomings such as supercooling, easy corrosion, and phase separation. High-temperature PCMs use solid-liquid phase change process to absorb and release energy. But due to their high phase change temperature, they are rarely used in practice. In addition, after endothermic transition occurs, PCMs are generally in liquid or molten state, their mechanical properties are usually poor.

3.1 Low thermal conductivity

The thermal conductivity of most PCMs is extremely low. For example, the thermal conductivity of the phase change paraffin is 0.1–0.3 W/(m·K), which is only 1/4 of liquid water

and 1/15 of solid ice. Therefore, in the process of application, it is normal that the material near the heat source is completely melted after absorbing heat, but the heat absorbed is significant. This form of heat would cause the temperature of this part to rise sharply. However, the material far away from the heat source part has not undergone a phase change. The uncoordinated state of different parts greatly reduces the effect of practical application of materials.

In order to improve the thermal conductivity of paraffin PCMs, the researchers mainly focus on two aspects: the use of high thermal conductivity framework and the incorporation of particles with high thermal conductivity, as shown in Fig. 8. The addition of high thermal conductivity material reduces the overall thermal resistance of the composite material, energy is quickly transferred along the high thermal conductivity material, and the thermal conductivity of the PCM is enhanced. With the increase of high thermal conductivity fillers, forming a network of conductive particles, the thermal resistance of the composites decreases, the heat transfers rapidly along the high thermal conductivity materials, and the thermal conductivity of PCMs increases. With the addition of high thermal conductivity framework or small volume fillers, the content of high thermal conductivity material can be reduced and the mechanical properties of PCMs can be improved without reducing the thermal conductivity.

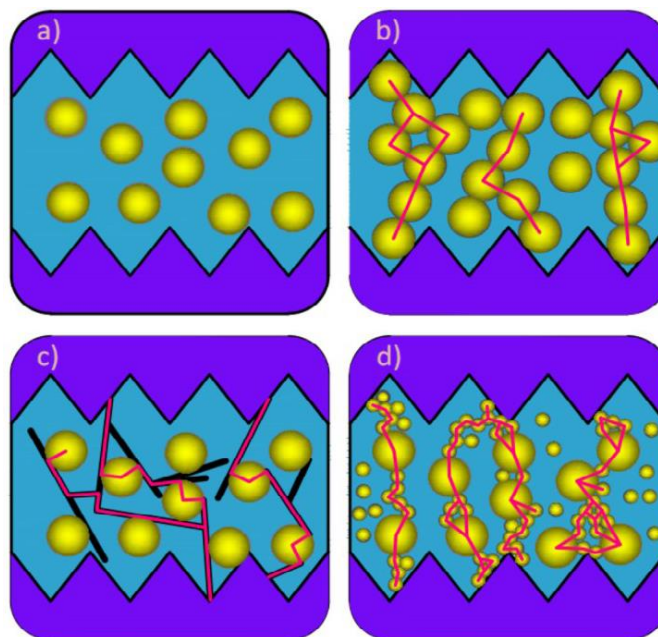


Fig. 8 Composite PCMs heat conduction principle. (a) PCMs structure diagram; (b) PCMs heat conduction path; (c) Heat conduction path of PCMs with high thermal conductivity framework; (d) Heat conduction path of PCMs with particles with high thermal conductivity.

The research of high thermal conductivity skeleton composite mainly focuses on graphite and metal foam skeleton. In the molten paraffin, the skeleton with high thermal conductivity was used to obtain the composite material by means of adsorption. In 2015, Wu *et al.*^[68] studied the

properties of paraffin/expanded graphite (EG) composites, they dispersed the paraffin between the layers of EG. The results showed that the maximum adsorption rate of EG for paraffin was 92%, and the phase change temperature of PCMs was basically unchanged compared to the paraffin, but the latent heat of phase change was decreased slightly with the increase of graphite volume fraction. At the same time, they figured out that with 20% EG, the thermal conductivity of PCMs was increased to 7.654 W/mK, and the latent heat of phase change was 141.74 J/g.

In recent years, the particles with high thermal conductivity in paraffin were used to improve the thermal conductivity of phase change paraffin, which had also achieved certain results. For example, Samimi *et al.*^[69] used 2 mm long, 0.46% carbon fiber composites to reduce the maximum temperature of the battery module by 45%. These two methods have improved the thermal conductivity of PCMs in recent years, but more research should be needed to make them a broader application prospect, in order to be applied to electronic packaging materials. The PCMs should be prepared to maintain higher thermal conductivity and phase change latent heat.

3.2 The leakage of PCMs

After absorbing heat, the solid-liquid PCMs will be melt into liquid phase, which greatly reduces the practicability and safety of the material. At present, shape setting PCMs method is mainly used to solve the problem of phase change leakage. Two main ways exist for shape setting PCMs. First, the molten adsorption method is used to inject the liquid PCMs into the porous framework such as EG and foam metal. Due to the capillary action, the framework absorbs the liquid material in the internal cavity, then reduces the leakage of PCMs. Second, a certain amount of styling agent is added to the PCMs to play a role in covering and locking the liquid PCMs. In 2016, Lv *et al.*^[70] used 30% LDPE to reduce the leakage rate of paraffin/graphite composite materials when working at 50°C from 8.58% to 1.01%.

3.3 Poor mechanical properties

In the process of using PCMs, the mechanical properties of the PCMs will be impacted. Therefore, when designing the PCMs, it is necessary to have certain requirements on the mechanical properties of the PCMs. However, the mechanical properties of some common PCM, especially paraffin composite PCMs, are poor, which cannot meet the needs of actual situations. For example, Lv *et al.*^[70] added LDPE with a mass fraction of 30% to the paraffin graphite PCM, and increased the bending strength, impact strength and hardness from 0.115 MPa, 3.89 kJ·m⁻², 6.58 HD to 1.82 MPa, 4.26 kJ·m⁻², 23.0 HD. Li *et al.*^[71] injected paraffin/graphite based PCM into the open-cell foam aluminum under a pressure of 6 MPa. While improving the thermal conductivity of the material, it also greatly improved the toughness and compressive strength of the material.

3.4 Delay of phase change

In the process of phase change, a certain degree of undercooling is needed to provide the power of phase change due to the thermal conditions of transformation, as shown in Fig. 9. When the temperature is at the theoretical phase change point (TPP), two phases are in a thermodynamic equilibrium state. When the ambient temperature reaches the actual phase change point (APP), there is an energy difference between these two phases and the phase change occurs. Most PCMs, especially inorganic PCMs, have a problem of supercooling during the phase change. At present, nucleating agents are often added to the materials to reduce nucleation dynamics requirements, promote nucleation, and achieve the goal of reducing supercooling. In addition, due to the reorganization of the lattice and the change of the distance between atoms, the volume of some PCMs changes after the phase change process. This kind of volume change caused by lattice reorganization and atomic spacing changes during the phase change will cause stress concentration and reduce the strength of PCMs, which is not conducive to the application of PCMs.

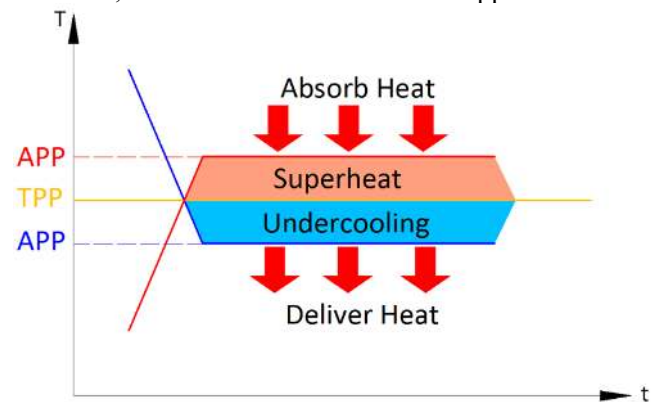


Fig. 9 Schematic diagram of delay of phase change.

3.5 Poor thermal stability

If there are two or more phases exist in the phase transition process, there will be the problem of phase change. Due to the existence of gravity difference, the low-density phase floats up and the high-density phase moves down, and then the ability to absorb and release energy is cyclically decreased, *i. e.*, the ability to store energy is decreased. When different atoms are combined in the form of bonds, the particle density is equal and can exist stably in the gravity field. In the process of phase change, the bond is broken and produces two phases with different densities, and the two phases separate under the action of gravity. After 200 exothermic cycles, the latent heat of phase transformation of the $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} - \text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was eutectic decreased by 50%.^[72] In addition, the same problem also exists in the high thermal conductivity nanoparticle composites. Due to the density difference between the thermal conductive particles and the matrix, the composite particles will float or sink.

4. Research on the application of PCMs

4.1 Research on the application of solar energy

Solar energy is clean energy with rich sources and is widely used in solar water heating systems and solar photovoltaic

power generation. However, due to the influence of night and weather conditions, the distribution of solar energy in time and space is unreasonable. Therefore, the development of solar energy storage materials is an effective way to resolve this contradiction.

Lv *et al.*^[73] found that PCMs can be added to the plaster wallboard to adjust the transfer of heat and cooling load to avoid the peak of power consumption by utilizing the ability of the materials to store or release heat. Compared to the ordinary rooms, the energy consumption of the air conditioning system can be greatly reduced by employing phase change wallboard, and the energy consumption of the air conditioning system thus can be reduced. Liu *et al.*^[74] showed that a new solid-solid phase change energy storage material polyurethane was synthesized by bulk polymerization, which has optimal thermal stability and great latent heat capacity, and can be applied to the field of solar energy storage. Yu *et al.*^[75] used different mass fractions of stearic acid as PCMs. The increase of the addition amount in expanded graphite leads to increased thermal conversion efficiency, which can be used in the field of low-temperature solar energy.

4.2 Building materials

PCMs can be added to traditional building materials. Phase change building materials (PCBMs) are functional composite materials, which can store energy in the form of latent heat and resolve the contradiction of uneven distribution of energy in time and space. However, PCMs have disadvantages, such as low thermal conductivity, leakage, short cycle life, and large volume change. These shortcomings that limit the application of PCMs in the field of building materials have been under intensive focus for resolution.

Taylor *et al.*^[76] applied hydrated salt PCMs to building walls, which can effectively maintain the temperature at 25–30°C. Shi *et al.*^[77] found that organic/inorganic composite PCM can be prepared using expanded graphite as adsorption medium and butyl stearate as PCM. This composite material is mixed into gypsum to prepare latent heat energy storage gypsum building materials, which maintain the stability of environment temperature, realize the transfer of energy at different time points, and are utilized as building energy-saving devices.

An unsteady-state heat transfer model was established in the rooms using PCMs or heat insulation materials both on the inside and outside of the roof, respectively. Installing heat insulation materials on the outside of the roof reduces the power consumption of the air conditioner up to 27.2%. Thus, the daily cost of air conditioning is reduced by 28.9%. Lee *et al.*^[78] found that when the PCMs were added to the wall panel with the optimal amount of 3 km/m², the temperature fluctuation was decreased. This novel wall panel can not only maintain a comfortable temperature in the room, but also reduce energy consumption by 20%.

4.3 Cool storage materials in air-conditioning

During the phase change process, the PCMs can absorb excess energy from the environment and reduce the environment temperature. However, this method does not need to consume excessive energy and can be used in a wide range of applications.

Li *et al.*^[79] identified a novel ternary composite phase change cold storage material that could be prepared by glycerin, sodium acetate, and water. Raw materials are cost-effective and readily available and can be widely used in large-scale cold storage and low-temperature logistics. Cheng *et al.*^[80] demonstrated that a thermal storage cooler could be constructed with PCMs containing paraffin, HDPE, and expanded graphite. The energy utilization efficiency of the household refrigerator with this kind of thermal storage condenser was increased by about 12%, without drastic increase in cost.

4.4 The use of industrial waste heat

Abundant energy-containing gas is emitted daily in chemical plants, which causes a huge waste of energy and reduces the utilization rate of energy. This is contrary to the grand goal of building a resource-saving and environment-friendly society. Thus, research focusing on improving the utilization of energy and reducing the impact on the environment is imperative. During the phase change process, the PCM can fully absorb the waste energy and utilize it, which will facilitate the recycling of the industrial waste heat. However, the research on the recovery and utilization of industrial waste heat with PCM is under-way, albeit technical issues are inevitable.

4.5 Military camouflage and stealth

Military camouflage and stealth are gaining importance in modern military war because the stealth performance directly affects the war. Owing to the large phase change enthalpy and excellent camouflage stealth performance, the PCMs have attracted great attention from military experts of various countries with respect to the development in military camouflage and stealth. For example, Huang *et al.*^[81] studied the process of encapsulating paraffin microcapsules with urea, formaldehyde, and melamine polymers. Then, paraffin and urea-formaldehyde resin were utilized to prepare microcapsule PCMs. The results showed that this microcapsule PCM could not only effectively simulate but also shield the infrared thermal characteristics of the targets.

5. Conclusions and outlook

Owing to the issues associated with the generation of energy and environmental problems, people have begun to pay attention to the recycling and efficient use of energy to reduce the pollution or damage to the environment in the process of industrialization. Phase change energy storage is an effective way to solve energy and environmental problems.^[81-94] However, there are still many problems that need to be resolved during the development of PCMs. For example, PCMs that use melamine resin and urea-formaldehyde resin as wall materials will release more or less free formaldehyde

during the usage, which endangers human health. At present, the thermal conductivity of PCMs is still not high enough, and the leakage occurs from time to time during the solid-liquid phase change. Due to the increase of the fillers, the mechanical properties of the PCMs are reduced compared to the substrate itself, which limits the development of PCMs. Due to the phase change delay and poor thermal stability, the phase transition temperature of the PCMs is usually uncertain and the undercooling degree is relatively large. Therefore, PCMs are the current cutting-edge materials. The general research directions of phase change energy storage materials in the future are as follows:

(1) In order to improve the mechanical properties of the materials and fulfill the requirements of practical application, other appropriate materials and PCMs should be chosen to prepare composite materials with excellent performance.

(2) Choose a variety of PCMs for compounding, develop PCMs with a wide phase-change temperature range, and meet the performance requirements of some specific fields, thereby broadening the application space of these materials.

(3) Develop PCMs that are pollution-free, long-life, and adequate stability to reduce or eliminate the harm to human health from the toxic gases liberated during the usage.

(4) Prepare PCMs with high thermal conductivity, low leakage and small volume change during phase change process, in order to expand the application range of PCMs.

(5) Improve the ability of heat storage, the utilization efficiency of energy and the phase change enthalpy of the PCMs, so that they can be used as environment-friendly materials.

(6) Choose a wider range of cheap raw materials to promote the industrial production of PCMs, in order to apply PCMs more in military industry.

PCMs are gaining increasing attention and becoming popular in the thermal energy storage field. Nowadays, a large number of studies about PCM microcapsules have been published to elaborate their benefits in thermal energy systems. Some aspects have been discussed in published studies: classification of PCMs, encapsulation shell materials, microencapsulation techniques, PCM microcapsules' characterizations, and thermal applications.^[95-110] This review aims to help the researchers from various fields better understand the PCM microcapsules and provides critical guidance for utilizing this technology for future thermal energy storage.

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Conflict of Interest

There is no conflict of interest.

Supporting Information

Not Applicable.

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