Review Article

Phase Change Material (PCM) Microcapsules for Thermal Energy Storage

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Phase change materials (PCMs) are gaining increasing attention and becoming popular in the thermal energy storage field. Microcapsules enhance thermal and mechanical performance of PCMs used in thermal energy storage by increasing the heat transfer area and preventing the leakage of melting materials. Nowadays, a large number of studies about PCM microcapsules have been published to elaborate their benefits in energy systems. In this paper, a comprehensive review has been carried out on PCM microcapsules for thermal energy storage. Five aspects have been discussed in this review: classification of PCMs, encapsulation shell materials, microencapsulation techniques, PCM microcapsules' characterizations, and thermal applications. This review aims to help the researchers from various fields better understand PCM microcapsules and provide critical guidance for utilizing this technology for future thermal energy storage.

1. Introduction

The fast technological and economic development for the progression of societies worldwide induces a quickly increasing energy demand. The most consumption of energy comes from fossil fuels, which are limited and drive severe environmental pollutions and climate changes [1]. Therefore, the effective utilization of energy becomes a major issue, which has compelled the trend to be shifted towards the utilization of sustainable and renewable energy resources [2]. Renewable energy sources, such as solar energy, are abundant, long-term available, accessible, and environmentally friendly, which make them alternative to fossil fuels. However, the intermittency of many renewable energy sources significantly reduces the energy conversion efficiency and becomes the major constraint of developing the relevant power generation technologies [3]. Thermal energy storage (TES) is a promising solution for this issue and therefore undergoes rapid development. The implementation of TES enhances the overall efficiency and the dispatchability of power generation

applications with renewable sources [4–6]. TES, which utilizes the change of the internal energy within the storage media, can be classified into thermochemical-, sensible-, or latent heat storage [7]. Compared to sensible heat, latent heat storage is a more efficient method and provides a much higher energy density with a smaller temperature difference between storing and releasing heat [8, 9].

Phase change materials (PCMs), also called latent heat storage materials, can store/release a large amount of energy through forming and breaking molecular bonds [10–12]. Traditional composite PCMs appear loose and diffuse to the surface gradually [13, 14]. In addition, PCMs have a limited thermal conductivity and suffer the leakage issue for melted storage materials [15]. To overcome these problems, microencapsulated PCMs have been developed [16–18]. PCM microencapsulation is a process of coating individual PCM droplet or particle with a continuous film to produce PCM microcapsules [19, 20]. PCM microcapsules contain two main parts: a PCM as the core and a polymer or an inorganic shell as the PCM container. Currently, a few

review articles on PCM microcapsules are available. Most of the review articles published previously on PCM microcapsules are related to their synthesis and applications. To the best of the authors' knowledge, previously reported literature has not adequately encompassed the characterization and applications of PCM microcapsules. This comprehensive review attempts to summarize the recent developments in PCM microcapsules and offers different aspects of PCM microcapsules for thermal energy storage applications. A brief introduction on PCMs (organic, inorganic, and eutectic) and encapsulation shell materials (organic, inorganic, and organic-inorganic hybrid materials) was presented. And the microencapsulation methods such as physical, chemical, and physical-chemical processes were introduced. The characterization of PCM microcapsules such as thermal conductivity, thermal stability, mechanical strength, and chemical properties was discussed and analyzed. Finally, the practical applications of PCM microcapsules for thermal energy storage and other industrial processes were reported.

2. Phase Change Materials (PCMs)

PCMs have a high heat of fusion in general and can store/release a large amount of energy during melting/solidifying processes [21, 22]. PCMs have been considered as storage media with a wide range of applications including cooling of food products, spacecraft thermal systems, textiles, building, solar systems, and waste heat recovery system [23, 24]. For example, PCMs can decrease the electricity consumption via reducing fluctuations in air temperature and shift cooling loads to the off-peak period in the building. PCMs can be classified into subcategories based on the solid-liquid, solid-solid, solid-gas, and liquid-gas phase transformation and vice versa [25]. For TES systems, solid-gas phase transformation and liquid-gas phase transformation are impractical because of large volume and high pressure of the system [26]. For example, the water-steam system is not commercially viable for large-scale TES. In the case of solid-solid PCMs, their heat of phase transition is much less than that of solid-liquid PCMs [27]. Thus, solid-liquid PCMs are ideal candidates for TES systems. The solid-liquid PCMs have favorable phase equilibrium, high density, minor volume changes, and low vapor pressure at the operation temperature during phase transition. In addition, solid-liquid PCMs also exhibit little or no subcooling during freezing, melting/freezing at same temperature and phase segregation, and sufficient crystallization rate. There are many factors influencing effectiveness and applications of solid-liquid PCMs: heat capacity, thermal conductivity, latent heat, phase transition temperature, and so on.

PCMs possess long-term chemical stability, are no fire hazard, are nontoxic and noncorrosive, do not undergo degradation after long-term thermal cycles, are nonexplosive compounds, and have compatibility with other materials and good chemical properties capable of completing reversible freezing/melting cycle [28]. They can be classified into three main groups as shown in Figure 1: organic PCMs, inorganic PCMs, and eutectic PCMs [29, 30]. Organic PCMs

are further described as paraffin and nonparaffin materials (fatty acids, alcohols, and glycols) [31, 32]. The paraffin, one of the by-products of petroleum refinery, consists of carbon and hydrogen atoms joined with the general formula C_nH_{2n+2} , where n is the number of carbon (C) atoms (if $1 \leq n \leq 4$, the material is gas; if $5 \leq n \leq 17$, the material is liquid; and if $n \geq 18$, the material is solid) [33]. Fatty acids are carboxylic acids with long hydrocarbon chain of carbon and hydrogen atoms with a general formula $CH_3(CH_2)_{2n}COOH$ ($10 \leq n \leq 30$) [34]. Organic PCMs are abundant and commercially available at reasonable cost. However, utilizing PCMs in traditional manner has several limitations, such as liquid leakage during melting state and low thermal conductivity [35, 36]. Inorganic PCMs contain salt hydrates, compounds, and metals. Salt hydrates can be considered as alloys of inorganic salts and water forming a typical crystalline solid with the general formula $M \cdot nH_2O$ (where M is the salt component and n is the molecular number). They suffer from several problems (such as tendency to supercooling, segregation, not melting congruently, high volume changes, corrosion, and phase separation over repeated phase change cycles), which limit their applications in TES facilities [37–39]. Inorganic compounds are generally regarded as being unsuitable for applications in TES because they own relatively small latent heat capacity and are harmful to the environment and human health [40, 41]. Metals, promising inorganic PCMs, diminish some of salt problems, but they are only suitable for high-temperature applications (4370 K) [42–44]. Eutectic PCMs can be defined as a minimum melting composition of two or more components, each of which freezes and melts congruently to form a mixture of the components' crystals in progress of crystallization [11, 28]. Eutectic PCMs can be adjusted by mixing inorganic-inorganic, organic-organic, or a combination of the two PCMs at a desired ratio for specific applications. They also possess high thermal conductivity and density without segregation and supercooling, while their specific heat capacity and latent heat are much lower than those of paraffin/salt hydrates [45, 46].

On the other hand, PCMs can also be categorized according to their phase transition temperatures: low-temperature PCMs (melting point $<220^\circ\text{C}$), intermediate-temperature PCMs ($220^\circ\text{C} \leq$ melting point $\leq 420^\circ\text{C}$), and high-temperature PCMs (melting point $>420^\circ\text{C}$) [47]. Generally, low-temperature PCMs are paraffin, fatty acids, polymeric materials, sugar alcohols, polyalcohol, and so on [48]. Melting points of most organic compounds are below 80°C ; thus, organic PCMs fall under the category of low-temperature PCMs. However, most of the inorganic-inorganic eutectic PCMs fall under the category of intermediate-temperature PCMs. High-temperature PCMs, including nitrates, metal carbonates, sulfates, fluorides, chlorides, and so on, can be widely applied for high-temperature TES requiring temperature $>500^\circ\text{C}$ [49].

3. Encapsulation Shell Materials

To effectively reduce the leakage of PCMs during the solid-liquid phase transition and avoid the reaction of the PCMs

FIGURE 1: Classification of phase change materials (PCMs).

with the surrounding environment, microencapsulation of the PCMs has been widely used in recent years. Microencapsulation technology can also provide high thermal cycling stability, relatively constant volume, and large heat transfer area for PCM-based thermal storage [50]. Shell materials play an important role in the morphology, mechanical properties, and thermal properties of the produced microcapsules [51] and can be classified according to the chemical nature into three categories of organic, inorganic, and organic-inorganic hybrid materials [22], as shown in Figure 2.

3.1. Organic Shells. Organic shell materials generally consist of the natural and synthetic polymeric materials, which possess good sealing properties, good structural flexibility, and excellent resistance to the volume change associated with repeated phase transformations of PCMs [52]. Commonly used organic shell materials include melamine formaldehyde (MF) resin [53–56], urea formaldehyde (UF) resin [57–59], and acrylic resin [60–65]. MF resin has the advantages of low cost, good chemical compatibility, and thermal stability [54]. Mohaddes et al. successfully used MF as the shell material to encapsulate *n*-eicosane and applied such microcapsules to textiles [66]. DSC results show that the melting and crystallization latent heats of the MF-based microcapsules are 166.6 J/g and 162.4 J/g, respectively. Fabrics doped with this type of microcapsules exhibit a lower value of thermal delay efficiency and higher thermoregulation capacity.

Among the group of acrylic resins, the copolymers of methacrylate possess nontoxicity, easy preparation, good thermal stability, and chemical resistance [52]. Alkan et al. reported that *n*-eicosane microencapsulated with polymethylmethacrylate (PMMA) shell had good thermal stability [67]. It is a three-step degradation process during thermogravimetric analysis (TGA) tests, and the phase change temperature remained mostly unchanged after 5000-cycle DSC tests. Ma et al. used poly(methylmethacrylate-*co*-divinylbenzene) (P(MMA-*co*-DVB)) copolymer as the shell material to successfully encapsulate the binary core materials, namely, butyl stearate and paraffin [68]. The prepared microcapsules exhibited compact surface and regular spherical shape with a relatively uniform size of 5–10 μm .

FIGURE 2: Shell materials of microencapsulation for PCMs.

Moreover, phase change temperature for such microcapsules can be adjusted by controlling the ratio of butyl stearate to paraffin. Wang et al. prepared capric acid@UF microcapsules by adding various contents of graphene oxide (GO) to investigate the effects of GO on the thermal properties of microcapsules [57]. It was found that the microcapsules with 0.6% GO had the highest enthalpy of 109.60 J/g and encapsulation ratio of 60.7%. Thermal conductivity was also greatly improved by adding more of GO. Additionally, the microcapsules with GO exhibited smoother surfaces than those without GO.

3.2. Inorganic Shells. Due to the flammability, low thermal conductivity, and poor mechanical properties of the polymeric shell materials [69], the application of microcapsules with organic shells has limitations in some situations. Instead, inorganic materials have been gradually employed as shell materials for microcapsule preparation in recent years. Compared with organic materials, inorganic shells generally have higher rigidity, higher mechanical strength, and better thermal conductivity [52]. Silica (SiO_2) [70–72], zinc oxide (ZnO) [73, 74], titanium dioxide (TiO_2) [75–77], and calcium carbonate (CaCO_3) [78–80] are generally utilized as inorganic shell materials.

The advantages of high thermal conductivity, fire resistance, and easy preparation lead silica to be one of the

most commonly used shell materials. Silica is often employed to microencapsulate organic paraffin waxes [78, 81], inorganic hydrated salts [71, 82–84], and fatty acids [85, 86]. Liang et al. used silica as the shell material and *n*-octadecane as the core material to prepare nanocapsules through interfacial hydrolysis and polycondensation of tetraethoxysilane (TEOS) in miniemulsion [87]. The thermal conductivity of such nanocapsules was measured to be above $0.4 \text{ W m}^{-1} \text{ K}^{-1}$. The melting enthalpy and encapsulation ratio reached 109.5 J/g and 51.5% , respectively. After 500 thermal cycles, the enthalpy of the nanocapsules remained almost unchanged and no leakage was observed.

The synthesis of the silica shell usually needs tetraethoxysilane (TEOS) as a silica precursor. However, the hydrolysis and polycondensation of TEOS could cause the silica shell to be not compact enough and have a relatively weak mechanical strength [88]. Compared with silica shells, CaCO_3 shells exhibit higher rigidity and better compactness. Yu et al. utilized CaCO_3 shells to encapsulate *n*-octadecane via a self-assembly method [88]. The obtained microcapsules showed spherical shape with a uniform diameter of around $5 \mu\text{m}$ and had good thermal conductivity, thermal stability, anti-osmosis properties, and serving durability.

Crystalline metal oxides, such as ZnO and TiO_2 , have multifunctional properties including catalytic, photochemical, and antibacterial characteristics. They are often used as shell materials to obtain PCM microcapsules with some interesting features. Li et al. employed ZnO as the shell material and *n*-eicosane as the core material to synthesize multifunctional microcapsules with latent heat storage and photocatalytic and antibacterial properties [73]. The thermal performance of the microcapsules depends on the ratio of *n*-eicosane to $\text{Zn}(\text{CH}_3\text{COO})_{22}\text{H}_2\text{O}$. In the study of Liu et al., TiO_2 shells were used to encapsulate *n*-eicosane via interfacial polycondensation followed by impregnation of ZnO [89]. The obtained microcapsules possessed both thermal storage and photocatalytic capabilities. The melting temperature and corresponding latent heat were 41.76°C and 188.27 J/g , respectively.

3.3. Organic-Inorganic Hybrid Shells. In order to overcome the disadvantages and combine the advantages of organic and inorganic materials, researchers have been turning to utilize organic-inorganic hybrid shells to microencapsulate PCMs. In organic-inorganic hybrid shells, inorganic materials can enhance mechanical rigidity, thermal stability, and thermal conductivity, whilst organic materials offer structural flexibility [52]. Shells formed from polymers, such as PMMA and PMF, and doped with SiO_2 or TiO_2 are widely used to encapsulate PCMs [90–93].

Wang et al. synthesized *n*-octadecane microcapsules with PMMA-silica hybrid shells through photocurable Pickering emulsion polymerization [94]. The produced microcapsules had good morphology and had particles ranging in the size from $5 \mu\text{m}$ to $15 \mu\text{m}$. When the weight ratio of MMA to *n*-octadecane is 1:1, the prepared microcapsules exhibited the highest encapsulation efficiency of 62.55% . Zhao et al. successfully prepared bifunctional

microcapsules by using *n*-octadecane as the core and PMMA doped with TiO_2 as the hybrid shell [95]. It was found that increasing TiO_2 could improve the thermal conductivity of microcapsules but led to lower enthalpy and encapsulation efficiency. The initial degradation temperature of the microcapsules with $6\% \text{ TiO}_2$ reached 228.4°C , which demonstrated that the microcapsules had good thermal stability. Multifunctional microcapsules consisting of *n*-octadecane cores and poly(melamine formaldehyde)/silicon carbide (PMF/SiC) hybrid shells were synthesized via in situ polymerization by Wang et al. [91]. The microcapsules displayed regular-spherical morphology. Contrasted to the microcapsules without SiC, heat transfer rate of the microcapsules with $7\% \text{ SiC}$ had a significant enhancement, and thermal conductivity improved by 60.34% .

4. Microencapsulation of PCMs

Microencapsulation is the utilization of a film-forming material to coat a solid or liquid and form $1\text{--}1000 \mu\text{m}$ particles, which are called microcapsules. Microencapsulation methods can be classified into three categories according to the synthesis mechanism: physical methods, chemical methods, and physical-chemical methods [15]. Detailed classification of these methods is listed in Figure 3.

4.1. Physical Methods. In physical methods, the formation of microcapsule shells only involves physical processes such as drying, dehydration, and adhesion. The commonly used physical methods for encapsulating PCMs are spray-drying and solvent evaporation. The process of spray-drying includes (1) preparing oil-water emulsion containing PCMs and shell materials, (2) spraying the prepared oil-water emulsion in a drying chamber by using an atomizer, (3) drying the sprayed droplets through drying gas stream at a suitable temperature, and (4) separating the solid particles by cyclone and filter [15]. Borreguero et al. synthesized microcapsules with a paraffin Rubitherm®RT27 core and polyethylene EVA shell with and without carbon nanofibers (CNFs) via spray drying [96]. With the addition of CNFs, both the mechanical strength and thermal conductivity of microcapsules were enhanced, and the heat storage capacity was maintained. DSC tests also showed that the microcapsules still possessed good thermal stability after the 3000-thermal charge/discharge cycles. Hawlader et al. utilized spray-drying method to microencapsulate paraffin with gelatin and gum arabic [19]. The obtained microcapsules possess spherical shape and uniform size. The heat storage and release capacity of the microcapsules prepared at the core-to-shell ratio of 2:1 reached 216.44 J/g and 221.217 J/g , respectively.

The basic steps of a solvent evaporation method are as follows: (1) preparing polymer solution by dissolving shell materials in a volatile solvent; (2) adding PCMs to solution to form O/W emulsion; (3) forming shells on the droplets by evaporating the solvent; (4) obtaining microcapsules through filtration and drying. Lin et al. used the solvent evaporation method to encapsulate myristic acid (MA) with

FIGURE 3: The classification of microencapsulation methods for PCMs.

ethyl cellulose (EC) [97]. The melting and solidifying temperatures were 53.32°C and 44.44°C, with melting and solidifying enthalpies of 122.61 J/g and 104.24 J/g, respectively. Wang et al. utilized solvent evaporation to synthesize microcapsules by using sodium phosphate dodecahydrate (DSP) as the core and poly(methyl methacrylate) (PMMA) as the shell [98]. The optimal parameters found through systematic analyses for preparing high-performance microcapsules are as follows: 80°C–90°C for the synthesis temperature, 240 min for the reaction time, and 900 rpm for the stirring rate, during microencapsulation process. The prepared microcapsules had an energy storage capacity of 142.9 J/g at the endothermic peak temperature of 51.5°C.

4.2. Chemical Methods. Chemical microencapsulation methods utilize polymerization or a condensation process of monomers, oligomers, or prepolymers as raw materials to form shells at an oil-water interface. The chemical methods mainly include in situ polymerization, interfacial polymerization, suspension polymerization, and emulsion polymerization. The differences between these four polymerization methods are shown in Figure 4.

In situ polymerization forms a shell on the surface of the droplet by polymerization of the prepolymers, which are formed by prepolymerization of the monomers (see Figure 4(a)). The general steps of the in situ polymerization process are as follows [99]: (1) preparing the O/W emulsion by adding PCMs to aqueous solution of surfactant; (2) forming a prepolymer solution; (3) adding the prepolymer solution to the O/W emulsion, followed by adjusting to the appropriate reaction conditions; and (4) synthesizing the microcapsule. Decanoic acid was successfully microencapsulated using poly(urea formaldehyde) (PUF), poly(melamine formaldehyde) (PMF), and poly(melamine urea formaldehyde) (PMUF) via in situ polymerization by Konuklu et al. [100]. The microcapsules coated by PUF

exhibited higher heat storage capacity but weaker mechanical strength and lower heat resistance, while the microcapsules with PMF shells had higher thermal stability but smaller thermal energy storage capacity. Compared to the PUF- and PMF-coated microcapsules, the PMUF-encapsulated microcapsules possessed perfect thermal stability in that no leakage was found at 95°C. Zhang et al. synthesized dual-functional microcapsules consisting of *n*-eicosane cores and ZrO₂ shells via in situ polycondensation [101]. These 1.5–2 μm spherical microcapsules showed the characteristics of thermal energy storage and photoluminescence. Additionally, the synthesized microcapsules possessed good thermal reliability, with the thermal property remaining almost unchanged after 100 thermal cycles. Su et al. microencapsulated dodecanol with methanol-modified melamine formaldehyde (MMF) prepolymer by in situ polymerization [102]. It was found that with increasing stirring rates, the average diameter of microcapsules sharply decreased, and the encapsulation efficiency increased. The highest encapsulation efficiency of microcapsules reached was 97.4%. In another study, Su et al. used MMF as the shell material to encapsulate paraffin via in situ polymerization [103].

In interfacial polymerization, as shown in Figure 4(b), two reactive monomers are dissolved separately in the oil phase and the aqueous phase, and polymerization then occurs at the oil-water interface under the action of an initiator. The general steps of interfacial polymerization are as follows: (1) forming an O/W emulsion containing PCMs and hydrophobic monomer; (2) adding the hydrophilic monomer to initiate polymerization under suitable conditions; (3) obtaining microcapsules through filtering, washing, and drying. This method is usually used in the preparation of organic shell materials such as polyurea and polyurethane [15]. The microencapsulation of butyl stearate (BS) and paraffin as binary core materials using polyurea/polyurethane as the shell material was successfully carried out via the interfacial polymerization method by Ma et al. [104]. The phase change temperature of microcapsules was adjusted by changing the ratio of the two core materials. The TGA results showed that the obtained microcapsules decomposed in three steps above 190°C, implying the microcapsules possessed good thermal stability. Lu et al. used polyurethane to form a cross-linked network shell to encapsulate the butyl stearate core via interfacial polymerization [105]. Siddhan et al. microencapsulated *n*-octadecane using toluene-2,4-diisocyanate (TDI) as a oil-soluble monomer and diethylene triamine (DETA) as a water-soluble monomer through interfacial polymerization [106]. The relevant results suggested that the core content and encapsulation efficiency of the microcapsules reached as high as 70% and 92%, respectively, when the ratio of core to monomer was 3.7 and the ratio of PCM to solvent was 6.

In the suspension polymerization process, dispersed droplets containing PCMs, monomers, and initiators are suspended in continuous aqueous phase by using surfactants and mechanical stirring. Free radicals of the oil-soluble initiator are then released into the emulsion system to initiate polymerization of the monomers under suitable

FIGURE 4: Schematic diagrams of various chemical microencapsulation methods: (a) in situ polymerization, (b) interfacial polymerization, (c) suspension polymerization, and (d) emulsion polymerization.

stirring rate and temperature [15], as shown in Figure 4(c). Wang et al. employed suspension polymerization to successfully microencapsulate *n*-octadecane using thermo-chromic pigment/PMMA shells with five different pigment/MMA ratios ranging from 0, 1.4, 4.3, 7.1, and 14.3 wt.% [107]. The microcapsules without pigment were found to achieve the highest melting and crystallization enthalpies of 149.16 J/g and 152.55 J/g, respectively. Sánchez-Silva et al. utilized different suspension stabilizers to microencapsulate Rubitherm®RT31 with polystyrene by suspension polymerization [108]. The DSC results showed that the microcapsules had the lowest (75.7 J/g) and highest (135.3 J/g) thermal storage capacity, when PVP and gum arabic were used as suspension stabilizers. Tang et al. used suspension polymerization to microencapsulate *n*-octadecane with *n*-octadecyl methacrylate (ODMA)-methacrylic acid (MAA) copolymer [109]. The prepared microcapsules exhibited spherical shape with an average diameter of around 1.60 μm . The microcapsules achieved the highest phase change enthalpy of 93 J/g when the ratio of monomers to *n*-octadecane was 2:1.

In emulsion polymerization, as shown in Figure 4(d), the dispersed phase consisting of PCMs and monomers is firstly suspended in continuous phase as discrete droplets with the aid of vigorous agitation and surfactants. Water-solution initiators are then added to trigger polymerization [110]. This method is often employed to polymerize organic materials such as PMMA and polystyrene to form microcapsule

shells. Şahan et al. utilized emulsion polymerization to encapsulate stearic acid (SA) cores using poly(methyl methacrylate) (PMMA) and four other PMMA-hybrid shell materials [111]. The microcapsules had a mean diameter of 110–360 μm and thickness of 17–60 μm . For all microcapsules, the heat storage capacity was below 80 J/g and the degradation temperature was above 290°C. Sari et al. successfully used PMMA shells to microencapsulate paraffin eutectic mixtures (PEM) containing four different contents via emulsion polymerization [112]. Spherical microcapsules with a particle size of 1.16–6.42 μm were obtained. The melting temperature for the microcapsules with the highest PEM content varied from 20°C to 36°C, and the heat storage capacity reached 169 J/g. Sari et al. also prepared polystyrene- (PS-) coated microcapsules containing capric, lauric, and myristic acids by using emulsion polymerization [113]. These microcapsules could melt and freeze in a wide temperature range of 22°C–48°C and 19°C–49°C, respectively. The corresponding latent heats for melting and freezing were located in the range of 87–98 J/g and 84–96 J/g, respectively. After 5000 thermal cycle tests, thermal properties of these microcapsules remained almost unchanged demonstrating that they had a good thermal reliability.

4.3. Physical-Chemical Methods. Physical-chemical method is the combination of physical and chemical processes. Physical processes, such as phase separation, heating, and

cooling, are combined with chemical processes, such as hydrolysis, cross-linking, and condensation, to achieve microencapsulation. The most representative and commonly used physical-chemical methods are coacervation and the sol-gel method.

The coacervation method can be further divided into single coacervation and complex coacervation. For preparation of microcapsules, single coacervation requires only one type of shell material, while complex coacervation requires two kinds of opposite-charged shell materials. Typically, the microcapsules prepared using complex coacervation have better morphology, more uniform size, and better stability. The main steps in complex coacervation processes are as follows [114]: (1) PCMs are dispersed in an aqueous polymer solution to form the emulsion; (2) a second aqueous polymer solution with opposite charges is added, leading the shell material to deposit on the surface of the droplet by electrostatic attraction; and (3) cross-linking, desolation, or thermal treatment is employed to obtain stable microcapsules.

Hawladar et al. adopted complex coacervation to encapsulate paraffin cores with gelatin and acacia [19]. The authors reported that the melting and solidifying enthalpies of the microcapsules could reach as high as 239.78 J/g and 234.05 J/g, respectively, when the homogenizing time was 10 min, the amount of used cross-linking agent was 6–8 ml, and the ratio of core to shell was 2 : 1. Similarly, three types of core materials, i.e., *n*-hexadecane, *n*-octadecane, and *n*-nonadecane, were microencapsulated with natural and biodegradable polymers, in the form of a gum Arabic-gelatin mixture through complex coacervation by Onder et al. [115]. The microcapsules containing *n*-hexadecane and *n*-octadecane were prepared at the dispersed content of 80% in the emulsion and showed good enthalpies of 144.7 J/g and 165.8 J/g, respectively. For microcapsules with *n*-nonadecane obtained at the dispersed content of 60% in the emulsion, the enthalpy value was only 57.5 J/g.

The sol-gel method is an economical and mild process to synthesize PCM microcapsules. The general steps in microcapsule preparation are as follows: (1) the reactive materials involving PCMs, precursor, solvent, and emulsifier, are uniformly dispersed in a continuous phase to form a colloidal solution by hydrolysis reaction; (2) through condensation polymerization of monomers, a gel system with a three-dimensional network structure is formed; and (3) the microcapsules are formed after drying, sintering, and curing processes [114]. Sol-gel methods are usually used to synthesize inorganic shells, such as SiO₂ and TiO₂ shells. Latibari et al. successfully fabricated nanocapsules containing palmitic acid (PA) as the core and SiO₂ as the shell via the sol-gel method by adjusting the pH value of the solution [116]. The results indicated that the capsules obtained at the pH value of 11, 11.5, and 12 had an average particle size of 183.7 nm, 466.4 nm, and 722.5 nm, respectively, and the corresponding melting latent heats were 168.16 kJ/kg, 172.16 kJ/kg, and 180.91 kJ/kg, respectively. Cao et al. microencapsulated paraffin with TiO₂ shells through sol-gel process and reported that the sample with a microencapsulation ratio of 85.5% had melting and solidifying latent

heats of 161.1 kJ/kg (at the melting temperature of 58.8°C) and 144.6 kJ/kg (at the solidifying temperature of 56.5°C), respectively [117].

5. Characterization of PCM Microcapsules

The physical, thermal, chemical, and mechanical properties of PCM microcapsules are significantly affected by the raw materials and synthesis processes during microencapsulation. Since these properties are of great importance to applications of PCM microcapsules, there is an increasing demand for accurate quantification and characterization of the physical, thermal, chemical, and mechanical properties.

5.1. Physical Characterization. Traditionally, the size distribution of microcapsules is analyzed by two methods: particle size analyzer (PSA) and observation statistics. For PSA, microcapsules are first dispersed in a suitable medium, and a laser particle size analyzer is then employed to detect the microcapsules' size distribution. Abadi et al. used a dynamic light scattering analysis apparatus from Malvern Instruments Co. UK to obtain microcapsules size distribution [122]. The analysis results showed that the size distribution curve of all the microcapsule samples presented a single peak and approximated a normal distribution curve. The average size was found to increase from 145 nm to 200 nm with the increasing amount of core materials (*n*-hexadecane). For observation statistics, scanning electron microscopy (SEM) and optical microscopy (OM) were first used to take images of a number of microcapsules randomly and the size distribution was then statistically determined by measuring the diameter of each microcapsule. Sun et al. combined SEM micrographs with Image-Pro analysis software to analyze the particle size distribution of microcapsules [118]. By measuring more than 200 microcapsules, the particle size was found to range from 10 μm to 74 μm with a mean diameter of 42.77 μm. Wang et al. measured and analyzed the diameters of 300 microcapsules from the SEM and OM images to obtain an average diameter of 121.66 μm [119].

In the microencapsulation process of PCMs, not all PCMs are encapsulated by shells. Productive ratio, which is defined as the ratio of the mass of microcapsules to the total mass of core and shell materials, is usually used to evaluate the conversion rate of raw materials. This parameter is dominated by many factors including core-shell ratio, emulsifier concentration, and agitation rate. Xu et al. prepared paraffin@PMMA microcapsules using a redox initiator [61]. When the concentration of paraffin was less than 70%, the productive ratio of microcapsules was higher than 95%. Roy et al. found that the productive ratio was irrelevant to the content of the crosslink agent glutaraldehyde (GTA) [120]. However, increasing the biopolymer ratio of chitosan (CH) to type-B gelatin (GB) from 1.3 to 1.5 or lowering the core/shell ratio from 3.75 to 2.50 could lead to a higher productive ratio.

Encapsulation efficiency, which is defined as the ratio of the mass of core to the mass of shell (or microcapsule),

reflects the core contents in microcapsules. However, it is difficult to directly measure the mass of the core and shell for a single microcapsule. Therefore, the encapsulation efficiency is usually evaluated by calculating the ratio of the latent heat of PCM microcapsules to that of pure PCMs using Ref. [99, 101, 121], as shown in equations (1) and (2):

$$\text{encapsulation efficiency} = \frac{\Delta H_{\text{microcapsules}}}{\Delta H_{\text{PCMs}}} \times 100\%, \quad (1)$$

or

$$\text{encapsulation efficiency} = \frac{\Delta H_{\text{m,microcapsules}} + \Delta H_{\text{c,microcapsules}}}{\Delta H_{\text{m,PCMs}} + \Delta H_{\text{c,PCMs}}} \times 100\%. \quad (2)$$

where $\Delta H_{\text{microcapsules}}$ is the latent heat of microcapsules containing PCMs and ΔH_{PCMs} is the latent heat of pure PCMs. $\Delta H_{\text{m,microcapsules}}$ and $\Delta H_{\text{c,microcapsules}}$ are the latent heat of melting and the crystallization for microcapsules, respectively; $\Delta H_{\text{m,PCMs}}$ and $\Delta H_{\text{c,PCMs}}$ are the latent heats of melting and crystallization for pure PCMs, respectively. Equations (1) and (2) have a slight difference when supercooling phenomena occur. According to equation (1), Zhang et al. acquired a highest encapsulated paraffin content of 89.5% [121]. Zhang et al. prepared microcapsules containing *n*-eicosane core and ZrO_2 shell [101]. It was found that the encapsulation ratio could be improved from 52.43% to 61.98% by changing the mass ratio of core to shell from 1 : 1 to 2 : 3.

Optical microscopy (OM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) are the most commonly-used techniques to characterize the morphology of microcapsules. Since microencapsulation of PCMs is sensitive to the raw materials, additives, and synthesis conditions, the obtained microcapsules can have various smoothness, sizes, and shapes. Figure 5(a) shows the SEM image of microcapsules having smooth and compact surfaces. However, as shown in Figure 5(b), the OM is economic and easy to be operated but has relatively low magnification compared with the other two techniques. Compared with OM, SEM has higher resolution to accurately measure the thickness of microcapsule shells (see Figure 5(c)). OM can provide the true color images of microcapsules compared with SEM and TEM. The OM images of microcapsules observed under natural light shown in Figure 5(d) indicated that the *n*-octadecane@PMMA microcapsules were transparent.

5.2. Thermal Characterization. In addition to high stability, PCM microcapsules gain increasing popularity due to their high thermal storage capacity. Differential scanning calorimetry (DSC) is used to analyze the thermal properties of pure PCMs and microcapsules. A DSC thermogram is composed of endothermic and exothermic curves, which contain the critical information for the thermal properties, such as the onset and peak temperature of the melting and

crystallization process or enthalpy on DSC cooling and heating runs. Since shell materials have lower latent heat storage capacity, the overall heat capacity for PCM microcapsules is significantly lower than pure PCMs. The implementation of thermal insulation over the shell, geometric confinement, or absence of nucleation agents gives rise to the encounter of supercooling, a shift of onset phase change temperature. Supercooling will lead a longer thermal discharge time and casts significant effects on the overall thermal performance of PCM microcapsules [122]. To suppress this phenomenon, Wu et al. added 1-tetradecanol and paraffin into the oil phase of *n*-octadecane@polyurea microcapsules as nucleation agents [123]. However, the supercooling degree further increased as 1-tetradecanol increased from 8.3 wt.% to 12.5 wt.%, and paraffin encapsulated into core materials was helpful for promoting the formation of triclinic crystal *l* in *n*-octadecane. This study indicated that paraffin had a positive impact on the crystallization of *n*-octadecane. Chen et al. successfully suppressed supercooling of *n*-octadecane/melamine formaldehyde microcapsules by adding alkylated graphene into core materials [124]. This is because the added alkylated graphene, which advanced the crystallization of the core material to a certain degree, enhanced heterogeneous nucleation and thermal transfer.

PCM microcapsules are usually exposed to extreme circumstances especially high temperatures, which can cause severe thermal degradations. Thermal stability is used to describe the resistance to thermal decomposition of PCMs microcapsules. Thermogravimetric analysis (TGA) is used to test thermal stability by increasing the temperature at a very stable step with a small interval and measuring the weight loss of the sample simultaneously. The TGA curve shows the varying of weight ratio with temperature changing. Jiang et al. investigated the thermal properties of PCM microcapsules based on paraffin wax core and P(MMA-*co*-MA) shell with nanoalumina (nano- Al_2O_3) [125]. Core material paraffin degraded at the onset temperature of 159.88°C and remained about 20.63 wt.% mass at 200°C. Almost no char was maintained at 230°C. P(MMA-*co*-MA) shells also presented a one-step degradation with a rapid weight loss rate at 342.3°C and decomposed completely at around 450°C. When PCMs were encapsulated in shells, they showed a three-step degradation. The first stage was related to the evaporation of the leakage core materials out of the broken shell starting at around 150°C. The second stage was attributed to PCMs from the inside of microcapsules completely evaporating at around 230°C. Finally, at around 350°C, the P(MMA-*co*-MA) shell underwent pyrolysis and the products decomposed thoroughly. The increase in the onset temperature of the second stage indicated the protective effect of shells, which enhanced the thermal stability of core materials.

Thermal reliability is qualitatively analyzed by subjecting PCM microcapsules to an extremely large number of repeated cycles of phase change, and after multiple cycles of melting and crystallization, change of thermal storage capacity (by DSC), thermal stability (by TGA), chemical characterization (by FTIR (Fourier-transform infrared

FIGURE 5: Images of microcapsules: (a) surfaces smooth and compact with defects, (b) rough and porous, (c) shell thickness, and (d) regular spherical structure.

spectroscopy)), and so on was detected. Zhang et al. conducted a 100-loop scan of phase-change circulations [101]. All the curves in the DSC thermograms had a surprising high coincidence with the first loop. The melting peaks, the crystallization peaks, and the onset points maintained stably after 100 loops, and the peak temperatures only showed minor deflection within 0.5°C. Liu et al. investigated microcapsules' reliability with dodecanol core and melamine formaldehyde (MF) resin shell [126]. They obtained the DSC curves of MEPCM/GO CNT after 25, 50, 75, and 100 phase change cycles, which presented little difference from the first. Similar conclusions were obtained by other works [67, 127]. Comparison between the two spectra found that the frequency values of characteristic peaks did not change, which indicated that the chemical structure of microcapsules was not affected by thermal cycling.

Under the steady-state condition, the thermal conductivity of a material is defined as the heat flow through a unit cross-sectional area under a unit temperature gradient. Higher thermal conductivity can provide faster heat transfer rate, which is of great importance to many applications. The efficiency of energy storage and release can be improved by increasing thermal conductivity. Due to the small size of microcapsules, it is difficult to directly measure the thermal conductivity of single microcapsules. The theory was proposed to calculate the conductivity of single microcapsules by [128]

$$\frac{1}{k_p d_p} = \frac{1}{k_c d_c} + \frac{d_p - d_c}{k_w d_p d_c}, \quad (3)$$

where $(d_c/d_p)^3 = \rho_s/\rho_p + \gamma\rho_c$, k_p , k_c , and k_w represent the thermal conductivities of the single microcapsule, core material, and shell material respectively, d_p is the diameter of the microcapsule particle, while d_c is the diameter of the core. However, the performance of multiple microcapsules' thermal conductivity is more critical in actual applications. Thus, the thermal conductivity is often analyzed in bulk microcapsules. It can be approximately performed by putting microcapsules between two plates, with heat flowing through the sample. Establishing an axial temperature gradient, the temperature difference is measured based on the heat output from the heat flow transducer at thermal equilibrium. The equation becomes [129]

$$\theta = A \frac{\chi}{h} (T_1 - T_2), \quad (4)$$

where θ is the heat, χ is thermal conductivity, A is the surface area, h is the thickness of the sample, and T_1 and T_2 are the temperatures of two surfaces. To improve the thermal conductivity of microcapsules, researchers usually add extra materials with high thermal conductivity, such as graphite, carbon nanotubes, and nanometals, directly to the core or shell of the microcapsules. Li et al. improved the compatibility of carbon nanotubes with core materials by grafting stearyl

alcohol (SA) onto carbon nanotubes and then coating PCMs with melamine resin [130]. It was found that the addition of carbon nanotubes improved the performance of microcapsules, and the thermal conductivity of microcapsules of carbon nanotubes increased by 79.2%. Wang et al. employed the same strategy to obtain the thermal conductivity of paraffin/calcium carbonate microcapsules with different high-thermal-conductivity fillers [131]. With different concentrations of flake graphite (FG), expanded graphite (EG), and graphite nanosheets (GNS), the results revealed a significant improvement of thermal conductivity. When phase change composites contained 20 wt.% GNS, they could form a stable and dense thermal conductivity network with a thermal conductivity of $25.81 \text{ Wm}^{-1}\text{K}^{-1}$, which is 70 times that of pure paraffin wax. Jiang et al. [83] prepared microcapsules with paraffin as a phase change material and polymethyl methacrylate as a wall material and then embedded nano- Al_2O_3 on the wall material [125]. Microcapsules with 16% monomer mass fraction of nano- Al_2O_3 had the best performance, and the enthalpy and thermal conductivity were 93.41 Jg^{-1} and $0.31 \text{ Wm}^{-1}\text{K}^{-1}$, respectively. Sarier et al. separately coated *n*-octadecane and *n*-hexadecane core materials with urea formaldehyde resin and then added reduced nanosilver particles to the wall material to prepare PCMs microcapsules [132]. The microcapsules modified by the nanosilver particles had higher thermal conductivity than the pure urea formaldehyde resin wall material microcapsules. The microcapsules modified by different methods exhibit better thermal conductivity and improved the thermal regulation performance.

5.3. Chemical Characterization. The chemical structure and composition of PCMs, shell, partial additives, and microcapsules are analyzed by Fourier transform infrared (FTIR) spectroscopy. The infrared spectrum belongs to the absorption spectrum, which is obtained by the absorption of infrared light with a specific wavelength when the compound molecules vibrate. Zhang et al. studied microcapsules containing an *n*-eicosane core and ZrO_2 shell [101]. These microcapsule samples were prepared with different core-shell ratios and some of them were prepared with the addition of NaF. It showed a series of similar characteristic absorption bands. Three intensive absorption peaks were observed at the wavelength of 2959 cm^{-1} , 2919 cm^{-1} , and 2853 cm^{-1} , respectively, due to the alkyl C-H stretching vibrations of methyl and methylene groups. Moreover, there were two absorption bands at 1472 cm^{-1} and 1379 cm^{-1} , which are caused by the C-H stretching vibration of methylene bridges. The infrared spectra also exhibited an absorption peak at 722 cm^{-1} in accordance with the in-plane rocking vibration of methylene groups. There was a broad absorption peak centered at 3437 cm^{-1} , which could be assigned to the stretching vibration of the O-H bond of adsorptive water. Moreover, it can provide the existence of some specific elements or bands. For example, through FTIR spectra, Zhang et al. found the characteristic absorption at 474 cm^{-1} due to the ZrO stretching vibration [91], confirming they successfully prepared the microcapsules with zirconia shells [133].

X-ray diffraction (XRD) is another technique to efficiently identify the specific materials in samples. If the shell material is inorganic, XRD is more suitable to recognize its composition [15]. Each crystal material has its specific structure, which can be used not only to recognize the chemical composition but also to distinguish the state of the existence. Xu et al. obtained XRD patterns that helped to determine the crystalline structures of microcapsule shells [134]. Moreover, the diffraction peaks in the XRD patterns presented the $\text{MnO}_2/\text{SiO}_2$ hierarchical shell, which were consistent with those reported for MnO_2 compound patterns, which confirmed that the microcapsules they synthesized were in interfacial polycondensation and a nanoflake-like MnO_2 layer was fabricated onto the surface of SiO_2 shell through template-directed self-assembly. In addition, this study also identified an amorphous nature of the SiO_2 shell.

5.4. Mechanical Characterization. The characterization of the mechanical properties of microcapsules can be divided into detection of a single microcapsule and detection of multiple microcapsules at the same time. The mechanical properties of a single microcapsule are mainly characterized by atomic force microscopy (AFM), micro/nano indentation detection, and microcompression. All these methods have nearly the same detection theory: by applying a small load on a single microcapsule that can be monitored and controlled in real time, researchers acquire the load deformation curve or failure characteristics of the microcapsule. Then, the mechanical properties of the tested samples can be analyzed. The elastic modulus and other mechanical parameters of the single microcapsule can be determined by this method, and one can recognize the strength characteristics of different microcapsules by comparing the rupture loads of separate microcapsules. AFM is an analytical technique which can be used to study the surface structure of solid materials including insulators. In an AFM test, one end of the microcantilever that is sensitive to weak force is fixed, while the other end has a tiny tip in light contact with the surface of the sample. Because of the extremely weak repulsive force between the tip and the sample surface atom, the microcantilever with the tip of the needle will undulate in a direction perpendicular to the surface of the sample. Based on this theory, the microcapsules can be loaded-tested by a microcantilever. Giro-Paloma et al. analyzed the force needed to break phase change slurry microcapsules and evaluated the effective Young's modulus by AFM [135]. Micronal®DS 5007X and PCS28, a laboratory-made sample, were used to characterize. The results showed that the mean effective Young's modulus of Micronal®DS 5007 X and PCS28 was 200 MPa and 43 MPa at 23°C , respectively. The needed forces to break the microcapsules were $11 \mu\text{N}$ and $2.5 \mu\text{N}$.

AFM analysis of the mechanical properties of microcapsules is relatively simple, but there are shortcomings. Firstly, there can be a significant error in calculating the applied load using the displacement of the microcantilever. When the tip of the cantilever beam is not in contact with the

surface of the sample, the cantilever beam may be bent due to the attraction between the atoms. It is difficult to recognize the contact zero point. In addition, when a load is applied, the measured value may be deviated due to the deformation of the cantilever beam, as shown in Figure 6(a). Secondly, during operation, it is necessary to ensure that the tip is pressed directly above the microcapsules and that no offset occurs. Otherwise, the cantilever beam will be subjected to additional bending moments, and the expected capsule failure mode will not be obtained. Thirdly, since the microcapsules are deformed during the pressing process, the measured displacement is not equal to the tip indentation depth.

The micro/nanoindentation method applies a load to the microcapsules by using different shapes of indenters to obtain a load displacement curve and analyze mechanical properties of the microcapsules. Compared to AFM analysis, the nanoindentation method is superior in that its load can be detected directly by the inductor on the pressin device as shown in Figure 6(b). However, similar problems exist in nanoindentation: it is hard to ensure that the indenter is pressed from the top of the microcapsules, and the microcapsules will deform during the pressing process, which affects the accuracy of the measurement results. Yang et al. prepared microcapsules with nano CaCO_3 /organic composite shells by in situ polymerization [136]. Young's modulus values of the microcapsules were in a range of 2.75–3.46 GPa using micro-nanoindentation. Lee et al. found that the modulus and hardness of hardener-loaded microcapsules both increased with size, with Young's modulus and hardness of the microcapsules measured 3 to 5 times by nanoindentation [137]. Microcompression, also known as a micromanipulation system, uses a cylindrical flat head (larger than the microcapsule size) to uniaxially compress a single microcapsule placed on a glass slide as shown in Figure 6(c). By detecting the shape variation occurring when the indenter is in contact with the microcapsule, the force change of the microcapsule during the compression test can be measured until the microcapsule broke. The microcapsule compression load-displacement curve is obtained, which is used to analyze the mechanical properties of individual microcapsules. The advantage of the microcompression method is that the mechanical properties of the microcapsules under large deformation can be determined, and not only the elastic deformation and plastic deformation of the microcapsules but also the damage load and deformation of the microcapsules can be accurately determined. However, the accuracy of the microcompression test results greatly depends mainly on the resolution of the test instrument. The instrument can only perform compression tests on a single microcapsule at a time and cannot achieve continuous compression tests. It is also necessary to use relevant theoretical models to determine the mechanical parameters such as the elastic modulus of the microcapsule wall material.

Sun et al. used micromanipulation to test the mechanical properties of microcapsules made of two different wall materials [96], including MF resin and UF resin [138]. MF and UF microcapsules showed that the yield point of

deformation was $19 \pm 1\%$ and $17 \pm 1\%$, and deformation at bursting was $68 \pm 1\%$ and $35 \pm 1\%$, respectively. The force needed to break the microcapsule and deformation at bursting for both microcapsules increased proportionally with their diameter. Zhang tested bursting force of single dry microcapsules in two samples, different in size and wall thickness by this micromanipulation [139]. The bursting force of the microcapsules in one sample ranged from 50 to 220 μN and the diameter from 1.3 to 7.0 μm , while the bursting force in the other was from 20 to 175 μN and the diameter from 0.7 to 3.7 μm .

There are mainly two ways to test the mechanical properties of multiple microcapsules. The first method is to place multiple microcapsules between two plates as shown in Figure 6(d). By applying pressure to the plate to break the microcapsules, the load displacement curve is detected in this process. The mechanical properties of the microcapsule are then obtained. We can also observe the deformation and failure of the microcapsule in different stages by loading the microcapsules in multiple steps. The second way is to measure the mechanical properties of microcapsules by the shear test. The microcapsules are dissolved in a solvent and broken by means of oscillation and centrifugation, etc. Then, the quality of the microcapsule after the destructive test is obtained. By comparing with the original microcapsule, the broken ratio is obtained, which is used to measure the overall mechanical properties of the microcapsule. In comparison to the detection of a single microcapsule, the detection of multiple microcapsules can only obtain qualitative results, and accurate mechanical parameters cannot be obtained. The detection results have relatively large errors. In contrast, the advantage of multiple microcapsule detection is that it is simple to operate and low in cost. By depositing multiple microcapsules between two plates, Su et al. observed the surface morphological structure change after compressing [140]. When the mass ratio of the core and shell material was 3 : 1, the yield stress of microcapsules was about 1.1×10^5 Pa. When the compression was increased beyond this value, the microcapsules showed plastic behaviors. Moreover, it was found that the mechanical intensity of double-shell microcapsules was better than that of single shelled ones. Li et al. mixed microcapsules with alcohol and centrifuged [130]. The precipitate was then washed by distilled water and dried. The mechanical strength of microcapsules was characterized by using the breakage rate which is calculated using the following equation:

$$\text{breakage rate (\%)} = \frac{\text{initial mass} - \text{mass after centrifugation}}{\text{initial mass}} \times 100\%, \quad (5)$$

the breakage rates of microcapsules at 6000 rpm for 20 min and 8000 rpm for 10 min were 1.15% and 1.56%, respectively. However, the breakage rate of microcapsules having carbon nanotubes grafted with stearyl alcohol (CNTs-SA) at the same speed for the same time was 0%. The breakage rate at 8000 rpm for 20 min was 3.98% for microcapsules and 2.15%

FIGURE 6: Schematic diagram of microcapsule mechanical properties testing: (a) atomic force microscopic analysis, (b) micro-nano-indentation detection, (c) micromanipulation system, and (d) multiple microcapsules between two plates.

for microcapsules/CNTs-SA, which indicated that the mechanical property of microcapsules/CNTs-SA was better than that of microcapsules without modification. This was mainly attributed to the modified CNTs which showed stronger mechanical properties when compared with polymers.

6. Applications of PCM Microcapsules

PCM microcapsules expand the application fields of the PCMs, due to their unique properties such as (1) chemical and thermal stabilization, (2) higher amount of energetic changes, and (3) suitable solid-to-liquid phase transition. PCM microcapsules provide a reliable way for mixing liquid and solid PCMs with polymer and other structural materials, which reduce toxicity and protect core material from environmental influence. Figure 7 shows potential applications of PCM microcapsules, and we will give more details in this section.

6.1. Textile. The application of PCM microcapsules in the textile industries is an old topic but draws continually growing attention by the researchers. For example, PCM microcapsules are used for protection from extreme cold weather outdoor wear such as snowsuits, trousers, ear warmers, boots, and gloves [15, 141], to provide extra protection from extreme cold weather. PCM microcapsules can be coated on the surface of fabric or embedded within the fiber, to enhance their thermal storage capacities (by 2.5–4.5 times compared to the reference fabric/fiber for particular temperature intervals) [115, 141]. Sarier

FIGURE 7: Potential applications of PCMs microcapsules in textile, slurry, building, foams, solar/electrical-to-energy, and biomedicine.

et al. indicated that the PCM microcapsules with silver nanoparticles had high thermal stability, high thermal storage capacities, good durability, and improved thermal conductivity. Therefore, this technology is promising for textile industry applications such as automotive and agriculture textiles, sportswear/protective clothing, and

medical textiles [132]. Nejman et al. found that the modified fabric obtained by the printing method had the largest enthalpy value and the lowest gas permeability, while the padding method had the smallest enthalpy value and the highest air permeability [142]. Scacchetti et al. investigated the thermal and antimicrobial properties of cotton with silver zeolites functionalized via a chitosan-zeolite composite and microcapsules of PCMs [143]. They recommended to use chitosan zeolite for the production of textiles for superior antibacterial and thermoregulating properties. PCM microcapsules as additives improve the thermal comfort and flame-retardant property of the textiles, the results showed that PCM microcapsules were distributed onto textile substrates homogeneously and was durable with repeated washings [144, 145]. In addition, thermoregulating properties of the fabrics with PCM microcapsules were supported through thermal history measurement results.

6.2. Slurry. Another interesting application of PCM microcapsules is in the slurry industry. PCM microcapsules slurry with high latent heat has been widely used in the fields of cooling and heating because of its high heat rate as an enhanced heat transfer fluid (HTF) and thermal storage medium (TSM). PCM microcapsules slurry has all the benefits of PCM suspension, without coalescing problem due to the shells preventing the contact between PCM droplets [146]. There are many research and review papers on characterization of thermal/rheological properties for PCM microcapsules [147–150]. They used heat transfer coefficient, Nusselt number, and wall temperature, to directly and indirectly reflect the heat transfer properties of PCM microcapsules slurry. Song et al. investigated laminar heat transfer of PCM microcapsules slurry and demonstrated that the heat transfer coefficient increased with increasing Reynolds number and volume concentration of microcapsules [151]. Roberts et al. compared the heat transfer performance of metal-coated PCM microcapsules slurry with nonmetal-coated PCM microcapsules slurry with same PCM content [152]. They observed a further 10% increase in heat transfer coefficient and PCM microcapsules inducing pressure drop in slurry. Zhang and Niu studied the thermal storage properties of PCM microcapsules slurry storage device and stratified water storage tank [153]. They showed that PCM microcapsules slurry had higher thermal storage capacity. Xu et al. proposed the PCM microcapsules with Cu-Cu₂O/CNTs (carbon nanotubes) as the shell and their dispersed slurry for direct absorption solar collectors [154]. They pointed out that the high heat storage capability and excellent photothermal conversion performance of PCMs@Cu-Cu₂O/CNTs microcapsule slurry made it as one of the most potential heat transfer fluids for direct absorption solar collector.

6.3. Building. In building applications, PCM microcapsules can be embedded into concrete mixes, wall boards, cement mortar, gypsum plaster, sandwich panels, and slabs to meet the energy demand of the building for cooling, heating, air

conditioning, ventilation, domestic hot water systems, and lighting [155]. In fact, the concrete is the major construction material in building, and the embedment of PCM microcapsules into concrete enhances the thermal and acoustic insulation of walls. Cabeza et al. investigated a new concrete with PCM microcapsules for superior thermal properties [156]. They showed that the concrete wall containing PCM microcapsules had smoother fluctuations of temperature and thermal inertia, indicating this technology can provide promising energy saving for buildings. In addition, adding PCM microcapsules to concrete was found to significantly increase the overall mechanical resistance and stiffness [157, 158]. In addition, the existence of PCM microcapsules had no effect on drying shrinkage of cementitious composites, and the thermal deformation coefficient of PCM microcapsules was similar to the shell materials [122]. Su et al. studied nano-silicon dioxide hydrosol as the surfactant for preparation of PCM microcapsules for thermal energy storage in buildings [159]. They pointed out that nano-silicon dioxide hydrosol could be used as a surfactant and for improving the shell integrity/core material content of PCM microcapsules, which had an additional benefit for thermal conductivity enhancement. Essid et al. studied compressive strength and hygric properties of concretes by incorporating PCM microcapsules [160]. They indicated that it was sufficiently safe to use the mixture of concrete and PCM microcapsules as structural material, though its compressive strength is lower and porosity is higher than the pure concrete. PCM microcapsules can also be embedded into wall boards, cement mortar, gypsum plaster, sandwich panels, and slabs in buildings to reduce the power demand in both residential and commercial building sectors [161–166].

6.4. Foams. Applying PCM microcapsules in foams can improve thermal performances, especially in the thermal-insulating ability. Borreguero et al. investigated rigid polyurethane foams containing PCM microcapsules and indicated that thermal energy storage capacity of rigid polyurethane foams was improved [167]. Bonadies et al. presented hot storage and dimensional stability of poly(vinyl alcohol)- (PVA-) based foams containing PCM microcapsules [168]. They pointed out that microcapsules influenced the amount of water uptake and the formation of crystalline domain, which affected the number of intra- and intermolecular hydrogen bonds since several -OH groups of PVA interact with microcapsule shells. Li et al. proposed a new strategy for enhanced latent heat energy storage with PCM microcapsules saturated in metal foam [169]. Compared with the surface temperature of pristine PCM modules, with the thermal conductivity enhancement of metal foam, the surface temperature for the PCM microcapsule/foam and PCM/foam composite modules was reduced from about 90°C to 55°C and 45°C, respectively. Both leakage and low thermal conductivity issues were solved with PCM microcapsule/foam composites. Moreover, enhanced thermal management with PCM microcapsule infiltrated in cellular metal foam was considered [170]. The low thermal conductivity of PCM and contact thermal resistance

between PCMs microcapsules resulted in remarkable surface temperature increase and huge temperature difference at the vicinity of heated surface for pure PCM microcapsules.

6.5. Others. Moreover, PCM microcapsules still have other potential applications such as solar-to-thermal energy storage, electrical-to-thermal energy storage, and biomedicine [114]. Zhang et al. studied solar-driven PCM microcapsules with efficient Ti_4O_7 nanoconverter for latent heat storage [171]. They indicated that solar absorption capacity of the novel PCM microcapsules was calculated up to 88.28%, and the photothermal storage efficiency of the $\text{PCMs@SiO}_2/\text{Ti}_4\text{O}_7$ microcapsules was up to 85.36% compared with 24.14% for pure PCMs. Zheng et al. proposed a joule heating system to reduce the convective heat transferring from electrothermal system of the surrounding by inserting the highly conductive and stable PCMs microcapsules [172]. They showed that the working temperature could be improved by 30% with loading of 5% PCMs microcapsules even at lower voltage and ambient temperature. Zhang et al. developed the multifunctional PCMs microcapsules for sterilization [173]. They discovered high antibacterial activity especially against *E. coli*, *S. aureus*, and *Bacillus subtilis*, and the antibacterial effectiveness of 2-hour contacting PCM microcapsules was inhibited up to 64.6%, 99.1%, and 95.9%, respectively.

7. Conclusions and Outlook

Microencapsulation technology is employed to fabricate PCM microcapsules, as new types of polymer/composite materials for thermal energy storage. PCMs were classified into three categories, i.e., organic, inorganic, and eutectic materials. And shell materials were also classified into three categories, i.e., organic, inorganic, and organic-inorganic hybrid materials. Available microencapsulation techniques for PCMs were reviewed and classified into three categories, such as physical, chemical, and physical-chemical processes. The selection of the best suited microcapsule technique mainly depends on the specifications of PCM microcapsules, including materials of the core/shell, microcapsule size, thickness of the shell, mechanical behaviors, and thermal properties. Additionally, this comprehensive review paper examined the technologies being used to characterize PCM microcapsules. For example, DSC is employed to analyze thermal properties, FTIR is used to characterize the chemical structure and composition, and AFM is utilized to measure the mechanical properties, respectively. The thermal, physical, chemical, and mechanical properties of PCM microcapsules are heavily dependent on the raw materials and synthesis processes during microencapsulation. Finally, the applications of PCM microcapsules in textile, slurry, building, and foams were presented and explained in detail. PCM microcapsules still have other potential applications such as solar-to-thermal energy storage, electrical-to-thermal energy storage, and biomedicine. The results are quite promising for their future utilization in practice. Although PCM microcapsules may seem attractive thermal energy

storage materials, there is still much to be explored and improved in fabrication, characterization, and commercial utilization. For example, the encapsulation efficiency is unsatisfactory, the contents of materials should be enhanced, particle sizes should be reduced, and the crosslinking time is too long. Regarding characterization methods, a standard mechanical characterization method for PCM microcapsules is needed due to most of the PCM microcapsules not tested for leakage. Last but not least, a major obstacle to the industrial application of PCM microcapsules is supercooling that should be solved in future.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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