

# Manufacturing Methods of Phase Change Materials

## Microcapsules

Subjects: Engineering, Chemical

Contributor: Refat Al-Shannaq, Mohammed M. Farid, Charles A. Ikutegebe

Thermal energy storage (TES) has been identified by many researchers as one of the cost-effective solutions for not only storing excess or/wasted energy, but also improving systems' reliability and thermal efficiency. Among TES, phase change materials (PCMs) are gaining more attention due to their ability to store a reasonably large quantity of heat within small temperature differences. Encapsulation is the cornerstone in expanding the applicability of the PCMs. Microencapsulation is a proven, viable method for containment and retention of PCMs in tiny shells. Currently, there are numerous methods available for synthesis of mPCMs, each of which has its own advantages and limitations.

Keywords: microencapsulation ; phase change materials ; PCM

---

## 1. Introduction

Microencapsulation has already been proven as a successful technology in commercial applications, such as in the pharmaceutical and agrochemical industries <sup>[1]</sup>, and recently in the textile industry <sup>[2]</sup> and in thermal energy storage applications <sup>[3]</sup>. Microencapsulation of PCMs is not only advantageous to mitigate the drawbacks of PCMs but also improves their thermophysical properties. For example, the heat transfer rate for PCM charging/discharging is significantly enhanced when PCM is microencapsulated <sup>[4]</sup>. In general, microencapsulation may be categorized into four groups, namely, physical–mechanical, physical–chemical, chemical–mechanical, and chemical processes.

## 2. Chemical Methods

Chemical methods utilize polymerization or a condensation process of monomers, oligomers, or prepolymers as raw materials to form shells at an oil–water interface. Commonly, chemical methods include (a) in situ polymerization, (b) interfacial polymerization, (c) suspension polymerization, and (d) emulsion/miniemulsion polymerization. In the in situ polymerization, the prepolymer, which is usually melamine-formaldehyde (MF) or urea-formaldehyde (UF), is cross-linked at oil–water droplet interfaces to form a continuous shell around the PCM droplets; however, in the interfacial polymerization method, the shell forms due to the reaction between a water-soluble monomer and an organic-soluble monomer at the oil–water interface. In contrast, the polymer particles form within a PCM droplet in the presence of an organic-soluble initiator and then precipitate out at the oil–water interface in the case of suspension polymerization. The emulsion polymerization method involves combining the monomer with a surfactant in an oil phase, while the initiator is dissolved in the water phase. Because the initiator is only present in the aqueous phase, the polymerization reaction begins outside of the droplets and micelles and subsequently progresses to the micelles. More details of chemical methods used for microencapsulation of PCMs with the most relevant published work will be discussed in the following subsections.

### 2.1. In Situ Polymerization

The most common example of this method is the condensation polymerization of urea or melamine with formaldehyde to form cross-linked UF or MF capsule shells. In this method, droplets are first formed by dispersing the core material (PCMs) into an aqueous phase containing a small fraction of emulsifier, followed by the addition of proper monomers or prepolymers of urea with formaldehyde or melamine with formaldehyde. After the pH of the system is lowered, the polycondensation reaction starts, yielding cross-linked urea–formaldehyde or melamine–formaldehyde resins. When the resin reaches a high molecular weight, it becomes insoluble in the aqueous phase, precipitates out, and deposits at the oil–water interface of the droplets. Subsequently, the resin hardens to form microcapsule shells.

Several research have been published over the last decade on the microencapsulation of PCMs using in situ polymerization <sup>[5][6][7][8][9][10]</sup>. Konuklu et al. (2014) <sup>[11]</sup> synthesized mPCMs containing caprylic acid PCM with different wall

materials, including UF, MF, and urea–melamine–formaldehyde (UMF) resins. SEM tests revealed that the mPCMs having melamine in their outer walls dominated the spherical structure. However, lower latent heat storage capacity was obtained when PMF or PUMF was used for outer wall material instead of PUF. The caprylic acid/PUF mPCMs enthalpy is 93.9 J/g, corresponding to 59 wt.% of PCM mass content. Han et al. (2020) <sup>[12]</sup> prepared mPCMs with paraffin as the core material and MUF polymer as the shell material under different processing conditions. The optimal operating conditions were found when the core-to-shell ratio was 1.5, concentration of SMA was 20 mg/mL, and reaction temperature, reaction time, and final pH values were 80 °C, 2 h, and 5.5, respectively. Under these conditions, the mPCMs' melting enthalpy was found to be equal to 134.3 J/g, corresponding to an encapsulation efficiency of about 77.1%. Srinivasaraonai et al. (2020) <sup>[13]</sup> synthesized mPCMs with fatty acids eutectic mixture (75% SA + 25% CA) as the core and MF as the shell using in situ polymerization. The obtained results reveal that at the optimized pH (3.2) and agitator speed (1500 rpm), the microcapsules possess smooth surface morphology and are spherical in shape with particle sizes of approximately 10 µm. Furthermore, the encapsulation efficiency and latent heat of fusion of mPCMs were 85.3% and 103.9 kJ/kg, respectively. Kumar et al. (2021) <sup>[14]</sup> prepared mPCMs through a facile in situ polymerization process using 1-dodecanol as the core PCM and the MF as the shell material. The results revealed that the capsules have surface roughness with no chemical interaction between the core and the shell materials. The TGA results showed that the mPCMs start losing weight at 132.8 °C, which was higher than that of the pure PCM. Furthermore, the mPCMs exhibited moderate storage capacity of 79.5 kJ/kg but with excellent thermal reliability (reliability index of 94.4%).

Furthermore, Zhang et al. (2022) <sup>[15]</sup> fabricated 4 µm capsules with MF resin shell via cellulose nanocrystal (CNC)-stabilized Pickering emulsion in situ polymerization. The phase change enthalpy of commercial paraffin wax and n-octadecane microcapsules are as high as 164.8 and 185.1 J/g, corresponding to PCM core material content of 87.0 and 84.3%, respectively. The results also showed that the mPCMs exhibit good thermal reliability during the phase change process, since they displayed almost the same phase change enthalpy after 200 heating/cooling thermal cycles, and the retention rate of  $\Delta H$  reaches up to 99.7%. Moreover, the mPCMs are self-extinguishing due to the flame-retardant properties of the MF shell. Mustapha et al. (2022) <sup>[16]</sup> reported a range of emulsifiers and their role in the formulation of volatile core microcapsules via the one-step in situ polymerization process. The results showed that the emulsifiers functional group type plays an important role for final mPCMs' product quality, where emulsifiers having carboxyl groups speed up the reaction rate to the extent that the UF particles become too large to maintain controlled and steady deposition onto the O/W interface, leading to porous microcapsules. In contrast, the emulsifiers with hydroxyl groups created small UF particles leading to poor encapsulation. Intermediate reactions were displayed with amine/amide groups or a combination of groups. Notable emulsifiers with successful results include gelatine (GEL), methylcellulose (MC), xanthan gum (XG), chitosan (CHI), polyacrylamide (PAM), and poly(ethylenimine) (PEI).

UF or MF resins are some of the commonly reported shell materials utilized for the fabrication of microcapsules through the in situ polymerization technique. However, due to their toxic nature, the production of formaldehyde-based microcapsules needs to adopt a significant preparation route coupled with stringent safety precaution measures. In addition, some of the residues of these formaldehyde resins in shells can cause environmental and health problems. Therefore, many researchers have been considering manufacturing mPCMs with low remnant formaldehyde content <sup>[17]</sup> <sup>[18]</sup>. Sumiga et al. (2011) <sup>[19]</sup> fabricated MF mPCMs with ammonia as a scavenger for residual formaldehyde reduction. Furthermore, Su et al. (2011) <sup>[20][21][22]</sup> used a novel methanol-modified MF prepolymer as a shell material for fabrication of low remnant formaldehyde-content PCM microcapsules. Results show that this can reduce the free formaldehyde in shell material by increasing the cross-linking structure, enhance the resistance deformation of MF shell, and achieve a reasonable encapsulation efficiency of 85.4% with a PCM content of 71 wt.%.

## 2.2. Interfacial Polymerization

This method is characterized by wall formation via rapid polymerization of monomers at the surface of the droplets of dispersed core material. Droplets are first formed by emulsifying an organic phase consisting of core materials and oil-soluble reactive monomers, which are usually isocyanate or acid chloride, in an aqueous phase. By adding a water-soluble reactive monomer, rapid reaction happened between the two monomers at the interface of the droplets to form a polymer shell. Several research have been published over the last few years on microencapsulation of PCMs using in interfacial polymerization technique <sup>[23][24][25]</sup>. Cai et al. (2020) <sup>[26]</sup> synthesized eco-friendly mPCMs via the interfacial polymerization of toluene-2, 4-diisocyanate (TDI), and diethylenetriamine (DETA). A facile solvent-free synthesis route was developed owing to the good compatibility of TDI and dodecanol dodecanoate, in which the cosolvent (cyclohexane) can be removed during the polymerization process. The as-prepared mPCMs were in the size scope from 10 to 40 µm and had a latent heat of fusion in the range of 103–140 J/g, which depends on the PCM to wall mass ratio. Nikpourian et al. (2020) <sup>[27]</sup> nanoencapsulated paraffin wax with polyurethane (PU) via the interfacial polymerization. Prior to encapsulation, the spherical and solid nanoemulsion of paraffin wax with control size distribution were prepared using the

novel semisolvent–nonsolvent method in the presence of sodium dodecyl sulfate (SDS). Then, the obtained nanoparticles were encapsulated with a polyurethane shell, based on TDI. The field emission scanning electron microscopy (FESEM) confirms the formation of spherical paraffin wax nanoparticles with a particle size distribution of 25–185 nm. The melting enthalpy of prepared nanocapsules is 153.9 J/g, corresponding to 80.2 wt.% of core content. Furthermore, the nanocapsules exhibit good thermal reliability and stability after 100 heating/cooling cycles. Lone et al. (2013) [28] reported an easy and effective approach for fabricating highly monodisperse PCM polyurea microcapsules using a tubular microfluidic technique. Yoo et al. (2017) [29] successfully fabricated a microencapsulated PCM (methyl laurate) with poly(urethane) (PU) composite shells containing the hydrophobized cellulose nanocrystals (hCNCs) using an in situ emulsion interfacial polymerization process. Gao et al. (2021) [30] prepared chitosan-based polyurethane (c-PU) mPCMs using the interfacial polymerization reaction of hexamethylene diisocyanate and chitosan accompanied by the attraction-assisted charge. The mPCMs with a c-PU green shell exhibited reasonable heat storage capacity of 106.3 J/g with an equivalent PCM content of 71.4% and with excellent thermal stability and cyclic durability. The c-PU mPCMs with reversible photochromic properties show promising application in the fields of anticounterfeiting technology and flexible, wearable, UV-protective clothing.

### 2.3. Suspension Polymerization

This method is a heterogenous radical polymerization process that is used for the production of many common commercial resins, such as polyvinyl chloride (PVC) [31], polystyrene [32], and poly(methyl methacrylate) (PMMA) [33]. Over time, suspension polymerization has been used comprehensively for the synthesis of functional microspheres [34] and for the fabrication of PCM microcapsules [35][36][37][38]. The oil phase, which consists of PCMs, water-insoluble monomers, and free radical oil-soluble initiators, is dispersed in the aqueous phase as droplets by high shear homogenization along with the use of small amounts of suspending agents. When the temperature reaches the decomposition temperature of the free radical initiator, the reaction starts to take place inside the droplets, and the generated polymer precipitates out of the PCM monomer mixture to form polymer particles. These particles continue to grow in number and size as polymerization continues and are deposited at the oil/water interface by the action of hydrophobicity to form the capsule shell.

In the suspension polymerization method, there are two sources of energy used to produce free radicals that initiate polymerization. (i) Thermal decomposition: the initiator is heated until a bond is homolytically cleaved, producing two radicals. This method is used most often with organic peroxides or azo compounds. (ii) Photolysis: in this case, several steps occur. They are: (a) a UV light of a certain spectra emission attacks and overlap the photo-initiator absorption spectra; (b) upon absorption, the photo-initiator molecule is promoted from the ground to either a single or triple excited electronic state; and (c) the excited molecule undertakes a cleavage (or reaction) with another molecule to produce initiating free radicals.

#### Thermal Microencapsulation

The choice of the ideal shell material for engulfing PCMs is central for manufacturing high performing mPCMs. Several polymers and copolymers have been extensively used to encapsulate PCM [35][36]. Chaiyasat et al. (2011) [39] and Supatimusro et al. (2012) [40] employed poly(divinylbenzene) as a shell material to encapsulate octadecane PCM using the suspension polymerization approach. Sánchez-Silva et al. (2011) [41] used polystyrene to encapsulate Rubitherm® RT31. Qiu et al. (2013) [42] prepared mPCMs using acrylic-based polymer shells. Qiu et al. (2013) [43] microencapsulated n-alkane with a p(n-butyl methacrylate-co-methacrylic acid) shell. Al-Shannaq et al. (2015 and 2016) [35][39] successfully synthesized cross-linked methyl methacrylate mPCMs via the suspension polymerization technique. Sánchez-Silva et al. (2010) [44] microencapsulated PCMs with shell materials made from styrene-methyl methacrylate copolymer. Similarly, with the suspension polymerization approach, microcapsules comprising of n-hexadecane as the core and PMMA and poly(butyl acrylate-co-methyl methacrylate) (poly(BA-co-MMA)) as the shells were prepared [45]. Furthermore, previous works have demonstrated that acrylic resins, such as PMMA, are promising shell materials to be used for microencapsulation of PCMs because they possess high mechanical strength, good chemical stability, are nontoxic, and are ease to use [46]. Al-Shannaq et al. (2015) [39] investigated the microencapsulation of paraffin (core) using PMMA (shell) by means of suspension polymerization. They found that by the utilization of mixed surfactants, long-term emulsion stability and microcapsules of regular spheres with smooth surfaces could be achieved. Sari et al. (2009) [47] encapsulated octacosane into a PMMA shell and reported that the microcapsules displayed good chemical stability and energy storage potential. They demonstrated that the Octacosane/PMMA capsules had an average latent heat of about 87.45 J/g during phase transition, with excellent thermal reliability even after 5000 thermal cycles. Thermal microencapsulation is an energy-intensive process since it is performed at a high temperature (70 to 90 °C) and needs a long reaction time exceeding 4 h. Additionally, it is unfavorable for microencapsulation of low-melting-temperature PCMs.

UV microencapsulation is an alternative to the thermal process since the reaction can occur at room temperature and within a shorter time.

## UV Microencapsulation

Nevertheless, in comparison to traditional thermally induced processes, the use of UV photo initialization polymerization is becoming attractive due to its suitability for low-temperature microencapsulation of PCMs. Thermally induced polymerization is usually performed at higher temperatures, which could damage heat-sensitive PCMs. Beyond this, they require a considerable reaction time, especially when considered for large-scale production. In that sense, suspension polymerization with the UV irradiation-initiated approach offers a better alternative to thermal treatment by reducing the polymerization time and energy consumption [37]. The technique also helps to retain the thermophysical properties of temperature-sensitive PCMs. PMMA/paraffin microcapsules were fabricated by the continuous stirring of the oil/water emulsion placed in a low-columned quartz container for 30 min at a speed of 600 rpm and irradiated by a medium-pressure mercury UV lamp (1000 W). The results show that the latent heat of mPCMs is 165.01 kJ/kg, which is equivalent to 61.2 wt.% of core materials inside the microcapsules [48]. Similarly, a UV photoinitiated dispersion polymerization approach was used to microencapsulate a high melting paraffin wax (peak melting point of 56.3 °C) and MMA. The oil/water emulsion was irradiated by a medium-pressure mercury UV lamp having a power of 2500 W for 30 min. According to their findings, the optimal performing mPCMs retained up to 66 wt.% PCM in the shells, with an average latent heat of 109.6 J/g. Increasing the PCM content beyond this point led to poor encapsulation efficiency [49]. Wang et al. (2014) [50] studied the effect of UV light-initiated emulsion polymerization on the nanoencapsulation of stearic–eicosanoic acid with MMA. A medium-pressure mercury UV lamp of 2500 W rating was positioned at a height of 20 cm over the top of the low-column quartz container. The produced capsules have an average latent heat of about 127 J/g and melting temperature of 56.9 °C. According to the research, both cationic and nonionic emulsifiers are suitable for obtaining high-quality nanocapsules. Zhang et al. (2017) [51] investigated the development of PMMA/stearic acid microcapsules through UV-initiated emulsion polymerization using iron (III) chloride as the photosensitive reagent. A medium-pressure mercury UV lamp having 2500 W was used. Other studies in this area have encapsulated PCMs of a higher melting temperature with an encapsulation efficiency not exceeding 70% [52]. Investigators from The University of Auckland (New Zealand) established a rapid, scalable, and energy-efficient way for the low-temperature microencapsulation of PCMs using both thin film UV reactor [53] and coiled-tube UV reactor [37]. A peristaltic pump was used to recirculate the emulsion at different volumetric flow rates from the holding tank to the coiled tube reactor. The influence of two mercury lamps (medium pressure) having power ratings of 450 W and 250 W on the process parameters were studied. Each lamp was placed at the center of the reaction cell to photo-induce the polymerization reaction of MMA. When using a suitable organic soluble photoinitiator such as Irgacure 918, the optimum encapsulation yield, conversion, encapsulation efficiency, and PCM content were achieved after only 10 min of polymerization. According to their findings, a higher emulsion flowrate (of 31.2 L/h) offers better PCM encapsulation in terms of both PCM content and encapsulation efficiency. Consequently, increasing the PCM-to-monomer mass ratio up to 2:1 led to a corresponding increase in the latent heat of microencapsulated PCMs, with irregular spherical shapes of microcapsules. In summary, the study showed that photo-induced polymerization with UV radiation represents a better alternative to thermal treatment by reducing polymerization time and energy consumption.

The low temperature PCM microcapsules may be mixed with a suitable fluid and applied as an efficient heat transfer slurry in air handling units or used to form parts of walls and ceiling components of refrigeration trucks or cold chambers for the preservation of perishable food. Being able to satisfy the cost and quality of perishable food products through the deployment of these type of mPCMs gives economic value not just to the producers of perishable foods but also to retailers and final consumers. According to the research, these types of low-temperature PCM microencapsulations may be difficult to achieve via thermally induced polymerization. This was because the temperature-sensitive PCM may become denatured when the operating condition during the microencapsulation process exceeds 40 °C. An effect of this is the resulting changes in the thermophysical properties of the PCM. The mass-loss analysis of the developed mPCMs stabilized within the first eight days of continuous heating in a temperature-controlled oven set at 40 °C after losing only 0.6% of its initial weight. The capsules had an average latent heat of 131.1 kJ/kg and a peak melting temperature of about 8 °C. Notable low-melting PCMs suitable for cold storage application include methyl laurate, tetradecane, tetrahydrofuran, pentadecane, Microtek PCM 6, Sasol Parafol 14–97, PureTemp PT-series (PT4, PT6, PT7, PT8, and PT15), and Rubitherm® RT-series (RT4, RT6, RT12, and RT15).

The use of UV radiation also benefits primarily from the possibility of being performed at low temperatures and can therefore be used to encapsulate heat-sensitive PCMs. It is noteworthy to mention that the encapsulation efficiency and monomer conversion reported are commercially unsatisfactory. Therefore, further research should focus on approaches to

enhance process efficiency through selecting more appropriate photoinitiators and using an energy efficient UV lamp, e.g., an LED lamp.

## 2.4. Emulsion Polymerization

The most common polymers used for microencapsulation of PCMs via emulsion polymerization are PMMA [54][55], polystyrene [56], poly(styrene-co-ethylacrylate) [57], n-nonadecane-vinyl copolymer [58], and poly(methyl methacrylate-co-methacrylic acid) [59]. Sari et al. (2010) [54] synthesized a novel n-heptadecane/polymethylmethacrylate mPCM by means of the emulsion polymerization method. The diameters of mPCMs were found in the narrow range (0.14–0.40  $\mu\text{m}$ ) under a stirring speed of 2000 rpm. The DSC analysis shows that the temperatures of melting and latent heats of melting of the PMMA/heptadecane microcapsules were 18.2 °C and 84.2 J/g, respectively. The microencapsulation ratio of the heptadecane in the PMMA microcapsules was found as 38 wt.%. Further, Sari et al. (2014) [60] prepared polystyrene-coated microcapsules containing capric, lauric, and myristic acids by using emulsion polymerization. The mPCMs melting temperature range of 22–48 °C and a latent heat in range of 87–98 J/g were reported. The mPCMs had a good thermal durability with a PCM retention rate of 95.6% after 5000 cycles.

The production of miniemulsions results when monomers are dispersed in water by means of strong mechanical stirring using a mixed emulsifier system, with a classical emulsifier and a water-insoluble cosurfactant, such as a long-chain fatty alcohol or alkane (e.g., cetyl alcohol or hexadecane). The resulting capsules possess about the same size as the starting monomer droplets. Additionally, the nanoscale particle size capsules have a distribution broader than those obtained by emulsion polymerization. Karaipekli et al. (2019) [61] prepared nanoencapsulated PCMs, where n-octadecane was used as PCM and poly(styrene-co-methacrylic acid) as shell materials by means of the miniemulsion polymerization method. The phase change temperatures of the nanoencapsulated PCMs were in the range of 32.16–32.42 °C and the latent heats were measured as 89.12 J/g and 87.42 J/g for melting and freezing, respectively. The encapsulation ratio of n-nonadecane was determined as 54 wt.%. Şahan et al. (2019) [62] synthesized capsules using SA as the PCM, which was encapsulated in PMMA and four PMMA-hybrid shell materials. The nanoencapsulation was accomplished by miniemulsion polymerization. The mean diameter and the thickness of the spherical shells varied over relatively narrow ranges of 110–360 nm and 17–60 nm, respectively. The variance was indicative of the functional groups of the shell material.

In conclusion, synthesizing mPCMs using chemical methods is void of complications and can be accomplished using the simple polymerization technique. For example, condensation polymerization reactions (in situ and interfacial polymerization) can produce uniform morphological coating with high encapsulation efficiency. However, high skill is needed for preparation due to the nature of the materials' toxicity. Moreover, the formation of polymer shell with a lower molecular weight will result in a weak shell strength and high wall permeability. In contrast, free radical polymerization reactions (suspension and emulsion polymerization) lead to the formation of higher molecular weight shells and thus higher mechanical strength but lower encapsulation efficiency.

## 3. Microencapsulation of PCMs with Other Methods and Shell Types

### 3.1. Coacervation-Phase Separation

The coacervation-phase separation is a microencapsulation technique that involves a physicochemical approach for the preparation of mPCM. It comprises two oppositely charged polyelectrolytes (polycation and polyanion) in an aqueous solution. The polycation is typically gelatine, while the polyanion is Arabic gum. Tiny droplets of the oil phase (PCMs) are dispersed in the aqueous phase containing polycation as an emulsion. The polyanion solution is then added proportionately to the formed emulsion with moderate agitation. Upon lowering the pH system using acid, phase separation is induced, and a polymer-rich phase (coacervate) is formed and deposits on the oil-interface droplets to form a gelatinous shell on cooling. The shell can then be cross-linked using glutaraldehyde, which hardens and prevents the gelatine from melting during PCM phase transitions.

Several works in the literature have surfaced over the last two decades on PCM microencapsulation using coacervation-phase separation [63][64][65]. Wu et al. (2017) [66] prepared a novel mPCM by complex coacervation. The ingredients used include modified gelatin containing vinyl groups and gum Arabic. The approach uses a spironolactone derivative color former-phenolic hydroxyl compound color developer and 1-hexadecanol, respectively, being the cosolvent and PCM. The impact of several key parameters such as the substitution degree of vinyl groups on modified gelatin, the type and amount of divinyl cross-linkers, and the core/shell ratio on properties of the mPCMs were investigated. Stable microcapsules (of uniform particle diameters in the range of 7–10  $\mu\text{m}$ ) with latent heat of about 72 kJ/kg and encapsulation efficiency >85% were produced. The as produced mPCMs possess good thermal reliability after 100 thermal cycles. An obvious change in

color was observed after multiple thermal cycles were performed. The dispersion was white at 60 °C, indicating fully charged PCM, whereas the white color turned gray at 15 °C, signaling completely discharged PCM. There was no color change after 100 thermal cycles.

### 3.2. Spray Drying

Spray drying is a suitable microencapsulation technique for containing heat-sensitive materials and has been widely used in the food [67] and pharmaceutical industries [68], as well as for PCMs [69]. Spray drying is a promising technique when utilized on an industrial scale as it offers lower production costs, limited loss of raw materials and process waste, and ease of control and potential scale up to a large, continuous process [70]. Methaapanon et al. (2020) [71] prepared mPCMs with silica shell matrices using the spray drying method. The silica solid shell was formed through polycondensation during the spray drying of the PCM/sol–gel emulsion. Hawlader et al. (2003) [64] prepared microcapsules using the spray drying technique. In their study, gelatin-acacia was used as the polymer shell and paraffin wax as PCM. The microcapsules possess high core loading up to 80% with an average particle size of 0.15 µm. Depending on the core-to-coating ratio, the encapsulation efficiency was in the range of 60–92%. Similar techniques involving the use of low-density polyethylene (LDPE) and ethyl vinyl acetate (EVA) copolymer to form shells were reported [69].

The synthesis of mPCMs using the spray drying process consists of the following:

- (1) Homogeneous liquid solution (feed stream) preparation—consists of phase change material and dissolved polymer, which is achieved through the use of a proper solvent;
- (2) Atomization of the as-prepared solution by means of a carrier gas stream (such as compressed nitrogen);
- (3) Solvent evaporation, where the particles were dried by hot nitrogen stream (dried nitrogen) in the drying chamber, and then the final product was recovered in the collector.

In general, the mPCMs produced using the spray dryer technique face the problem of PCM leaking out of the shell due to the formation of pores.

As noted earlier, the use of polymeric shells in the microencapsulation of PCMs are common, owing to their ease of processing, excellent sealing characteristics, structure flexibility, and chemical and thermal stability. Nevertheless, their use is limited because of the polymer susceptibility to flame and poor thermal conductivity issues [72]. Therefore, investigating alternative shell materials that possess good flame retardancy, high thermal conductivity, and rigidity, such as inorganic shells, is required. In the following subsections, the common methods used to encapsulate PCMs with inorganic shell are discussed.

### 3.3. Sol–Gel Method

This method is classified under the physical–chemical category, and the common shell materials used are silica [73] and titanium oxide [74]. It attracts more attention from researchers due to its mild processing conditions.

- (1) The formation of PCM O/W emulsion through the mixing of PCM with a surface-active solution containing surfactant (emulsifier);
- (2) The aqueous acidic phase (sol solution) prepared by dissolving the precursor compound, e.g., tetraethyl orthosilicate (TEOS) or sodium silicate precursor in water;
- (3) Microcapsules formation via condensation polymerization by dropwise addition of the sol solution into the PCM O/W emulsion.

TEOS and Tetra-n-butyl titanate (TNBT) are the mostly used precursors for producing mPCMs with SiO<sub>2</sub> and TiO<sub>2</sub> shells, respectively [75][76][77][78][79]. Ji et al. (2021) [80] prepared composite GO/TiO<sub>2</sub> paraffin microcapsules by interfacial condensation polymerization in a sol–gel system. The composite appeared to have a spherical core-shell structural morphology, and the GO nanosheets self-assemble on the surface of the microcapsules by sharing electrons and hydrogen bonds. The latent heat of microcapsules was more than 160.75 J/g, and the thermal conductivity enhanced from 0.195 to 0.297 W/(m·K). Jin et al. (2017) [81] investigated the effect of acidic pH on the encapsulation efficiency of n-eicosane with different inorganic silica precursors, including TEOS and sodium silicate. According to the research, mPCMs synthesized at pH of 2.20–2.30 resulted in the formulation of nanoencapsulated n-eicosane and displayed spherical shapes of excellent phase change properties and high encapsulation efficiency. Overall, the n-eicosane/sodium

silicate nanocapsules presented good properties and thermal stability when prepared at pH 2.90–3.00. However, pH lower than 2.9 resulted in very poor encapsulation efficiency and low enthalpies. Later on, Yuan et al. (2019) [73] studied the influence of alkaline pH on the formation of lauric acid/SiO<sub>2</sub> nanocapsules via the sol–gel process. The results showed that the pH range of 9.4–10.2 is suitable for the synthesis of nanocapsules with high latent heat (160.0 J/g) and small particle size (357 nm).

The encapsulation of PCM with shells such as TEOS and TNBT are relatively expensive and unattractive, especially when considered for use at the lab scale. To this end, He et al. (2014) [82] examined the manufacture of PCM microcapsules via the sol–gel method utilizing a sodium silicate precursor, which is cost effective. At a controlled pH of 2.95–3.05, spherical PCM microcapsules were prepared. Nevertheless, the mPCMs showed a core/shell mass ratio and microcapsule efficiency, respectively, of 41.8 wt.% and 41.5%. A few years later, Pourmohamadian et al. (2017) [83] microencapsulated PA with inorganic SiO<sub>2</sub> shell via the sol–gel method in alkaline medium via sodium silicate precursor. The optimum pH was found to be pH 11, where the sample had a perfect spherical shape with a smooth surface. Further, DSC measurements showed that the as-prepared mPCMs have similar phase change behaviors as those of pure PA PCM, which melts at 67.2 °C, freezes at 56.5 °C, and possesses an average latent heat of 107.2 kJ/kg. Zhang et al. (2021) [84] successfully prepared mPCMs through in situ dehydration and condensation reaction. The microcapsules consist of silica shell derived from sodium silicate and paraffin wax (PW) forming the core. The mPCMs with core to shell mass ratio of 4:1 showed interesting results in terms of energy storage capacity. Following that, the DSC, TGA, and thermal reliability tests demonstrated that the prepared mPCMs possessed depressed supercooling, good thermal stability, and long-term thermal stability against the heating/cooling cycling. The low cost and availability of sodium silicate and PW makes the encapsulation technology proposed have great potential for practical application in the field of thermal management, including packaging, clothing, and architecture.

### 3.4. Self-Assembly Method

Thermal performance, stability, and reliability are critical parameters that are carefully considered in the production of PCM microcapsules. Studies have shown that although PCM microcapsules synthesized with SiO<sub>2</sub> shell may display improved thermal performance, their shells are not robust enough to withstand harsh conditions; hence, the microcapsules are easily damaged. Furthermore, the TEOS precursor is not cheap when considered for upscaled production of PCM microcapsules. Consequently, finding an inexpensive and easy to process alternative inorganic shell is of great interest to many researchers. There is no doubt that calcium carbonate (CaCO<sub>3</sub>) has the properties of low cost, higher thermal conductivity, high rigidity, and good thermal and chemical stabilities compared to synthetic polymer [72]. Yu et al. (2014) [85] microencapsulated n-octadecane PCM using CaCO<sub>3</sub> as the shell material through a self-assembly technique. At first, the PCM O/W emulsion is formed by mixing PCM with a surfactant, and in this case, a blend of Span 80 and Tween 80 surfactants was utilized. Following that, the CaCl<sub>2</sub> aqueous solution was added dropwise into the emulsion system, where the Ca<sup>2+</sup> was assembled on the surface of the PCM micelles through the complexation taking place between Ca<sup>2+</sup> and hydroxyl groups of surfactants. Finally, an aqueous solution of Na<sub>2</sub>CO<sub>3</sub> was introduced to the emulsion and the precipitation reaction between Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> was observed to be responsible for the formation of the calcium carbonate shells. PCM microcapsules with core/shell structure were attained with an excellent spherical morphology. The thermal conductivity, durability, and stability of the PCM microcapsules were improved in comparison to those of the SiO<sub>2</sub> shell. Additionally, the CaCO<sub>3</sub> shell enhances the n-octadecane crystallinity due to the induced  $\alpha$ -form crystallization by heterogeneous nucleation.

Several research have been published on the use of CaCO<sub>3</sub> as a shell material for microencapsulation of PCMs via the self-assembly method [86][87][88]. Sari et al. (2021) [89] synthesized mPCMs with calcium carbonate as a shell and heptadecane (HD) as a core via the self-assembly method. The DSC results revealed that the produced HD/CaCO<sub>3</sub> microcapsules had a melting temperature of around 16 °C, and the latent heat capacity ranged from 85.6 to 147.3 J/g. The cycled microcapsules showed excellent chemical stability and remarkable TES dependability with the 1000-cycling treatment. The microcapsules had outstanding thermal durability, as demonstrated by their thermal degradation over the phase change temperature of HD. Jiang et al. (2018) [90] synthesized modified PCM microcapsules with CaCO<sub>3</sub> and graphene oxide (GO) shells for improved thermal energy storage and PCM exudation problems. Excellent spherical core-to-shell structures with an encapsulation ratio of 73.2%, thermal conductivity of 0.86 W/(m·K), and good mechanical properties were obtained when 1.0 wt.% of GO was added to the system. The addition of GO led to crack formation on the CaCO<sub>3</sub> shell. Nevertheless, it is believed that the GO possesses a good barrier property that precludes PCM from leaking. Wang et al. (2021) [91] synthesized mPCM with control morphology using a CaCO<sub>3</sub> shell. The microcapsules' apparent morphologies could be altered from spherical to spindle shapes by increasing reaction temperature and surfactant concentrations.

Other shell materials were used to encapsulate PCMs via a self-assembly method. Gao et al. (2017) <sup>[92]</sup> used cuprous oxide ( $\text{Cu}_2\text{O}$ ) to encapsulate n-eicosane by using an emulsion-templating self-assembly method along with in situ precipitation.

The microstructures and morphologies of the as-prepared mPCMs were impacted by the surfactant, alkali concentrations, and copper source. When synthesized at the optimum conditions (CCTAB = 0.15 mol/L, CNaOH = 5.00 mol/L, and 1:1 mass ratio of PCM to  $\text{Cu}_2\text{O}$  shell), the microcapsules displayed an octahedral morphology and typical core-shell structure. The as-prepared mPCMs possess high encapsulation efficiency and storage capacity, rapid thermal response, as well as an excellent thermal stability and thermal reliability. There was also an increase in the mPCMs' thermal conductivity, coupled with a low degree of supercooling due to the encapsulation of n-eicosane with a highly thermally conductive inorganic wall. The mPCMs showed solar thermal energy-storage capability through solar photothermal conversion and displayed a high solar photocatalytic activity toward organic dyes under sunlight radiation. Furthermore, in the presence of the  $\text{Cu}_2\text{O}$  shell, the microcapsules showed a gas-sensitive property to some harmful organic gases.

Furthermore, Cia et al. (2022) <sup>[93]</sup> successfully fabricated paraffin mPCMs ( $\text{Pn@PWO}$ ) with lead tungstate ( $\text{PbWO}_4$ ) shell by in situ precipitation and self-assembly methods. The amount of trisodium citrate dihydrate (TSCD) plays significant role in determining the capsules' surface morphology, including a spindle or spherical shape, through control growth of  $\text{PbWO}_4$  shell. The as-prepared mPCMs possess a high latent heat-storage capacity over 100 J/g, and exhibit high thermal conductivity over 0.596 W/(m·K), and positive leakage-prevention performance. The mass attenuation coefficients of microcapsules at 86.5 keV and 105.3 keV reach 1.98 and 2.08, respectively, showing excellent gamma shielding performance. This type of mPCMs has a potentially wide application, including textiles and nuclear engineering buildings which require simultaneous gamma radiation shielding and thermal regulation.

### 3.5. Microfluidic Method

Some unique PCM microencapsulation methods are rarely reported in the literature, such as the microfluidic PCM microencapsulation technique <sup>[94][95]</sup>. Lone et al. (2013) <sup>[28]</sup> presented, for the first time, a microfluidic approach toward the fabrication of highly monodisperse polyurea microcapsules containing n-octadecane as the core. According to the study, the mPCMs had a diameter size in the range of 35–500  $\mu\text{m}$ . The synthesis consisted of the following two steps:

- (1) Emulsification of n-octadecane, isophorone diisocyanate (IPDI), and dibutyltin dilaurate (DBTDL) in an aqueous mixture of tetraethylenepentamine (TEPA), poly (vinyl alcohol), and sodium dodecyl sulfate (SDS);
- (2) In situ polycondensation between TEPA and IPDI along and outside the tube length.

Consequently, through the microfluidic approach with coflowing channels, Fu et al. (2014) <sup>[96]</sup> were able to prepare elastic silicone/n-hexadecyl bromide microcapsules. According to the research, the procedure involved the formation of a double oil1-in-oil2-in-water ( $\text{O1/O2/W}$ ) droplet with a core-shell geometry. The as-prepared mPCMs had a spherical shape with a low PCM content of 49 wt.%. However, the PCM content may increase by adjusting the rate of the three fluids used in the microfluidic system.

Furthermore, Rahman et al. (2012) <sup>[97]</sup> produced monodisperse mPCMs using membrane emulsification followed by suspension polymerization. Monodisperse O/W emulsion was prepared with Shirasu Porous Glass hydrophilic membranes. The selected membrane pore sizes are 10, 10.2, and 20  $\mu\text{m}$ , and the polymerization of MMA was carried out in a batch reactor at a temperature range of 70–90 °C. The results showed that the different membranes (10, 10.2, and 20  $\mu\text{m}$ ) produced mPCMs with excellent average diameters of  $22.4 \pm 1.5$ ,  $25.4 \pm 0.8$ , and  $37.5 \pm 1.69$   $\mu\text{m}$ , and average latent heats of  $113.9 \pm 12$ ,  $116.7 \pm 1.4$ , and  $109.9 \pm 8.7$  J/g, respectively. However, the mPCMs produced using this method exhibited low mechanical strength in comparison with commercially available mPCMs. Likewise, Akamatsu et al. (2019) <sup>[98]</sup> encapsulated paraffin's PCM with silicone-based shells, using a glass capillary device. A few years later, Watanabe et al. (2022) <sup>[99]</sup> adopted the same approach to formulate microcapsules where a monodisperse biocompatible cellulose acetate (CA) constituted the shell materials and HD was used as the core material.

### 3.6. Solvent Evaporation/Phase Separation

The microencapsulation method involving solvent evaporation and phase separation is commonly used for microencapsulating bioactive materials used in the pharmaceutical industry. The approach is consistent with the encapsulation of hydrophobic materials which involves an o/w emulsion system. However, encapsulation of hydrophilic materials such as water-soluble drugs can also be accomplished by double water-in-oil-in-water (w/o/w) emulsions. A benefit of the double emulsion process is the possibility of encapsulation of hydrophilic cores. In this method, the polymer



is dis-solved in a core material (PCM) with the help of proper solvent, and then the mixture is added to the water solution which contains surfactant under stirring; thus, oil droplets are obtained. The evaporation of the solvent triggered the internal phase separation in the polymer/PCM/solvent droplets. The phase separation of the polymer-rich part is caused by the interfacial tension interaction between core, polymer, and aqueous phases. Hence, the polarity and interfacial tension of the polymer within the PCM droplets are crucial for forming the core/shell structure mPCMs with complete polymer shell coverage.

Xing et al. (2021) [100] prepared a fatty acid eutectic ((CA-PA) mPCMs using polyvinyl chloride (PVC) as a shell material. The microcapsules were prepared by the solvent evaporation method and tetrahydrofuran (THF) was used as a solvent. The as-prepared mPCMs with a core-to-shell mass ratio of 2:1 had a latent heat of 92.1 J/g, corresponding to a PCM content of 57.7 wt.%. Additionally, the mPCMs showed an excellent thermal reliability following 500 thermal cycles. Microcapsules containing sodium phosphate dodecahydrate (inorganic PCM) were prepared using the solvent evaporation precipitation method [101]. Modified PMMA microcapsules containing disodium hydrogen phosphate heptahydrate ( $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ ) were prepared by means of the suspension copolymerization solvent volatile method [102]. This method is not commonly used for the fabrication of mPCMs due to the nature of the porous shell formed and low PCM mass content.

### 3.7. Microencapsulation of Inorganic PCM

The majority of studies involving the microencapsulation of PCMs have focused mainly on encapsulating organic-based PCM, with only a few currently focusing on the encapsulation of inorganic PCMs at the microscale. The reason for this is traced to the hydrophobic nature of organic PCMs [103]. Ideally, the two solvents constituting the core and shell parts of the microcapsules should not be miscible. This makes it possible to form the desired o/w emulsion prior to the polymerization process. Being able to microencapsulate PCM improves the handling, enhances compatibility of the PCM with the surrounding as the shell serves as a barrier, and enhances the heat transfer of the PCM resulting from a larger surface area compared to its volume. It is noteworthy to mention that inorganic PCMs are classified as salt hydrates, salts, and metals. A key advantage to that their usage as a thermal energy storage material is because they possess higher phase change enthalpy. The downside to their usage is that most inorganic PCMs exhibit features such as corrosion, subcooling, phase segregation, thermal instability, and phase segregation. Notwithstanding, some recent studies have reported the microencapsulation of inorganic PCMs through the solvent extraction–evaporation approach. In one study, sodium phosphate dodecahydrate (core) was microencapsulated with a shell material which was made of various organic solvents, cellulose acetate butyrate, and methylene diisocyanate as a cross-linker. The study achieved the microencapsulation process through solvent evaporation–precipitation technique. According to the research, the final mPCMs' surface morphology was largely influenced by the nature of the solvent used (Salaun et al. [101]). The suspension copolymerization/solvent volatile technique was adopted in a study by Huang et al. [102] for the microencapsulation of inorganic disodium hydrogen phosphate heptahydrate using modified PMMA as the polymeric shell material with different organic solvents. The microencapsulated  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ , having a mean diameter of about 6.8  $\mu\text{m}$ , was verified as the core of the mPCM resulting from the dehydration of the  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  precursor. When the microcapsules were subjected to heating within a temperature range of 30–84 °C, a mass loss of <10% was recorded, which is considered too high. The DSC results also revealed that the PMMA/  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$  had a melting temperature of approximately 51 °C and latent heat of 150 J/g. With the loss of about 10%, the inorganic PCM salt is highly thermally unstable, especially when tested for the long term. Hassabo et al. [104] investigated the microencapsulation of various metal PCM salts such as calcium nitrate tetrahydrate,  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , disodium hydrogen phosphate dodecahydrate, ferric nitrate nonahydrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), and magnesium (II) nitrate hexahydrate in tetraethoxysilane (silica) shells via polycondensation. The technique adopted was based on dis-solving silica in toluene and mixing the resultant dispersion in the hydrated salt, and through ultrasonic emulsification, a Pickering emulsion was formed and about 20% of poly(ethoxysiloxane) in toluene was added in a dropwise manner. According to the research, only mPCMs made with  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  and  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  as core materials displayed good phase change properties when incorporated in the polypropylene film polymer matrix. However, a thermal cycling test which would provide an indication of the thermal stability of the fabricated composite was not conducted in the study.

To further elucidate the microencapsulation of inorganic PCM, a particle fluidization process for the microencapsulation of two inorganic PCMs was considered for the microencapsulation of magnesium chloride hexahydrate ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ) and bischofite polymer as the core and acrylic as the shell material [105]. The solvent used was chloroform and the preferred atomization flowrate was 2 kg/h at an atomization time of 2 min. In this process, crystal particles are suspended in an air flow system inside a fluidization column.

The thermal analysis result showed that both the  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ /acrylic and Bischofite/acrylic microcapsules had an average latent heat and melting temperatures of 106.8 J/g and 61 °C, and 99.8 J/g and 80.3 °C, respectively. The encapsulation efficiency reported was within the range of 87.02% and 92.22%, which is considered very high.

---

## References

1. Paulo, F.; Santos, L. Design of experiments for microencapsulation applications: A review. *Mater. Sci. Eng. C* 2017, 77, 1327–1340.
2. Valdes, A.; Ramos, M.; Beltran, A.; Garrigos, M.C. Recent Trends in Microencapsulation for Smart and Active Innovative Textile Products. *Curr. Org. Chem.* 2018, 22, 1237–1248.
3. Al Shannaq, R.; Farid, M.M. 10—Microencapsulation of phase change materials (PCMs) for thermal energy storage systems. In *Advances in Thermal Energy Storage Systems*; Cabeza, L.F., Ed.; Woodhead Publishing: Sawston, UK, 2015; pp. 247–284.
4. Yan, W.-M.; Ho, C.J.; Tseng, Y.-T.; Qin, C.; Rashidi, S. Numerical study on convective heat transfer of nanofluid in a minichannel heat sink with micro-encapsulated PCM-cooled ceiling. *Int. J. Heat Mass Transf.* 2020, 153, 119589.
5. Zhang, X.-X.; Tao, X.-M.; Yick, K.-L.; Wang, X.-C. Structure and thermal stability of microencapsulated phase-change materials. *Colloid Polym. Sci.* 2004, 282, 330–336.
6. Choi, J.-K.; Lee, J.G.; Kim, J.H.; Yang, H.-S. Preparation of microcapsules containing phase change materials as heat transfer media by in-situ polymerization. *J. Ind. Eng. Chem.* 2001, 7, 358–362.
7. Konuklu, Y.; Erzin, F. Preparation of pentadecane/poly(melamine-urea-formaldehyde) microcapsules for thermal energy storage applications. *Int. J. Energy Res.* 2019, 43, 6322–6326.
8. Zhang, H.; Wang, X. Fabrication and performances of microencapsulated phase change materials based on n-octadecane core and resorcinol-modified melamine–formaldehyde shell. *Colloids Surf. A Physicochem. Eng. Asp.* 2009, 332, 129–138.
9. Sánchez-Silva, L.; Lopez, V.; Cuenca, N.; Valverde, J.L. Poly(urea-formaldehyde) microcapsules containing commercial paraffin: In situ polymerization study. *Colloid Polym. Sci.* 2018, 296, 1449–1457.
10. Zhang, H.; Li, W.; Huang, R.; Wang, N.; Wang, J.; Zhang, X. Microstructure regulation of microencapsulated bio-based n-dodecanol as phase change materials via in situ polymerization. *New J. Chem.* 2017, 41, 14696–14707.
11. Konuklu, Y.; Unal, M.; Paksoy, H.O. Microencapsulation of caprylic acid with different wall materials as phase change material for thermal energy storage. *Sol. Energy Mater. Sol. Cells* 2014, 120, 536–542.
12. Han, S.; Chen, Y.; Lyu, S.; Chen, Z.; Wang, S.; Fu, F. Effects of processing conditions on the properties of paraffin/melamine-urea-formaldehyde microcapsules prepared by in situ polymerization. *Colloids Surf. A Physicochem. Eng. Asp.* 2020, 585, 124046.
13. Srinivasaraonai, B.; Singh, L.P.; Tyagi, I.; Rawat, A.; Sinha, S. Microencapsulation of a eutectic PCM using in situ polymerization technique for thermal energy storage. *Int. J. Energy Res.* 2020, 44, 3854–3864.
14. Kumar, G.N.; Al-Aifan, B.; Parameshwaran, R.; Ram, V.V. Facile synthesis of microencapsulated 1-dodecanol/melamine-formaldehyde phase change material using in-situ polymerization for thermal energy storage. *Colloids Surf. A Physicochem. Eng. Asp.* 2021, 610, 125698.
15. Zhang, Z.; Zhang, Z.; Chang, T.; Wang, J.; Wang, X.; Zhou, G. Phase change material microcapsules with melamine resin shell via cellulose nanocrystal stabilized Pickering emulsion in-situ polymerization. *Chem. Eng. J.* 2022, 428, 131164.
16. Mustapha, A.N.; Zhang, Y.; Zhang, Z.; Ding, Y.; Li, Y. A systematic study on the reaction mechanisms for the microencapsulation of a volatile phase change material (PCM) via one-step in situ polymerisation. *Chem. Eng. Sci.* 2022, 252, 117497.
17. Lawson, C.M.; Virgallito, D.R.; Lawson, J. Methods for Making Low Remnant Free Formaldehyde Microcapsules and Microcapsules Made by Same. EP3337604B1, 24 March 2021.
18. Li, W.; Zhang, X.-X.; Wang, X.-C.; Niu, J.-J. Preparation and characterization of microencapsulated phase change material with low remnant formaldehyde content. *Mater. Chem. Phys.* 2007, 106, 437–442.
19. Šumiga, B.; Knez, E.; Vrtačnik, M.; Savec, V.F.; Starešinić, M.; Boh, B. Production of Melamine-Formaldehyde PCM Microcapsules with Ammonia Scavenger used for Residual Formaldehyde Reduction. *Acta Chim. Slov.* 2011, 58, 14–25.

20. Su, J.-F.; Wang, S.-B.; Zhang, Y.-Y.; Huang, Z. Physicochemical properties and mechanical characters of methanol-modified melamine-formaldehyde (MMF) shell microPCMs containing paraffin. *Colloid Polym. Sci.* 2011, 289, 111–119.
21. Su, J.-F.; Wang, S.-B.; Zhou, J.-W.; Huang, Z.; Zhao, Y.-H.; Yuan, X.-Y.; Zhang, Y.-Y.; Kou, J.-B. Fabrication and interfacial morphologies of methanol–melamine–formaldehyde (MMF) shell microPCMs/epoxy composites. *Colloid Polym. Sci.* 2011, 289, 169–177.
22. Su, J.-F.; Wang, X.-Y.; Wang, S.-B.; Zhao, Y.-H.; Zhu, K.-Y.; Yuan, X.-Y. Interface stability behaviors of methanol-melamine-formaldehyde shell microPCMs/epoxy matrix composites. *Polym. Compos.* 2011, 32, 810–820.
23. Zhang, H.; Wang, X. Synthesis and properties of microencapsulated n-octadecane with polyurea shells containing different soft segments for heat energy storage and thermal regulation. *Sol. Energy Mater. Sol. Cells* 2009, 93, 1366–1376.
24. Lu, S.; Shen, T.; Xing, J.; Song, Q.; Shao, J.; Zhang, J.; Xin, C. Preparation and characterization of cross-linked polyurethane shell microencapsulated phase change materials by interfacial polymerization. *Mater. Lett.* 2018, 211, 36–39.
25. Ho, C.J.; Chang, P.-C.; Yan, W.-M.; Amani, M. Microencapsulated n-eicosane PCM suspensions: Thermophysical properties measurement and modeling. *Int. J. Heat Mass Transf.* 2018, 125, 792–800.
26. Cai, C.; Ouyang, X.; Zhou, L.; Liu, G.; Wang, Y.; Zhu, G.; Yao, J.; Militky, J.; Venkataraman, M.; Zhang, G. Co-solvent free interfacial polycondensation and properties of polyurea PCM microcapsules with dodecanol dodecanoate as core material. *Sol. Energy* 2020, 199, 721–730.
27. Nikpourian, H.; Bahramian, A.R.; Abdollahi, M. On the thermal performance of a novel PCM nanocapsule: The effect of core/shell. *Renew. Energy* 2020, 151, 322–331.
28. Lone, S.; Lee, H.M.; Kim, G.M.; Koh, W.-G.; Cheong, I.W. Facile and highly efficient microencapsulation of a phase change material using tubular microfluidics. *Colloids Surf. A Physicochem. Eng. Asp.* 2013, 422, 61–67.
29. Yoo, Y.; Martinez, C.; Youngblood, J.P. Synthesis and Characterization of Microencapsulated Phase Change Materials with Poly(urea–urethane) Shells Containing Cellulose Nanocrystals. *ACS Appl. Mater. Interfaces* 2017, 9, 31763–31776.
30. Gao, Y.; Geng, X.; Wang, X.; Han, N.; Zhang, X.; Li, W. Synthesis and characterization of microencapsulated phase change materials with chitosan-based polyurethane shell. *Carbohydr. Polym.* 2021, 273, 118629.
31. Dumistracel, I.; Ponchel, G.; Danila, G.; Duchene, D.; Carpov, A. Poly(vinylbenzyl chloride) microsphere synthesis and their chemical modifications. *J. Microencapsul.* 2000, 17, 45–55.
32. Abd El-Mageed, A.I.A.; Dyab, A.K.F.; Mohamed, L.A.; Taha, F.; Essawy, H.A. Suspension polymerization for fabrication of magnetic polystyrene microspheres stabilized with Hitenol BC-20. *Polym. Bull.* 2022, 79, 3379–3393.
33. Bux, J.; Manga, M.S.; Hunter, T.N.; Biggs, S. Manufacture of poly(methyl methacrylate) microspheres using membrane emulsification. *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.* 2016, 374, 20150134.
34. Cai, S.; Weng, Z.; Zheng, Y.; Zhao, B.; Gao, Z.; Gao, C. High porosity microspheres with functional groups synthesized by thiol–yne click suspension polymerization<sup>11</sup>Electronic supplementary information (ESI) available. *Polym. Chem.* 2016, 7, 7400–7407.
35. Al-Shannaq, R.; Farid, M.; Al-Muhtaseb, S.; Kurdi, J. Emulsion stability and cross-linking of PMMA microcapsules containing phase change materials. *Sol. Energy Mater. Sol. Cells* 2015, 132, 311–318.
36. Giro-Paloma, J.; Al-Shannaq, R.; Fernández, A.I.; Farid, M.M. Preparation and Characterization of Microencapsulated Phase Change Materials for Use in Building Applications. *Materials* 2015, 9, 11.
37. Ansari, J.A.; Al-Shannaq, R.; Kurdi, J.; Al-Muhtaseb, S.A.; Ikutegbe, C.A.; Farid, M.M. A Rapid Method for Low Temperature Microencapsulation of Phase Change Materials (PCMs) Using a Coiled Tube Ultraviolet Reactor. *Energies* 2021, 14, 7867.
38. Al-Shannaq, R.; Kurdi, J.; Al-Muhtaseb, S.; Dickinson, M.; Farid, M. Supercooling elimination of phase change materials (PCMs) microcapsules. *Energy* 2015, 87, 654–662.
39. Chaiyasat, P.; Chaiyasat, A.; Boontung, W.; Promdsorn, S.; Thipsit, S. Preparation and Characterization of Poly(divinylbenzene) Microcapsules Containing Octadecane. *Mater. Sci. Appl.* 2011, 2, 1007–1013.
40. Supatimusro, D.; Promdsorn, S.; Thipsit, S.; Boontung, W.; Chaiyasat, P.; Chaiyasat, A. Poly(divinylbenzene) Microencapsulated Octadecane for Use as a Heat Storage Material: Influences of Microcapsule Size and Monomer/Octadecane Ratio. *Polym.-Plast. Technol. Eng.* 2012, 51, 1167–1172.
41. Sánchez-Silva, L.; Rodríguez, J.F.; Sánchez, P. Influence of different suspension stabilizers on the preparation of Rubitherm RT31 microcapsules. *Colloids Surf. A Physicochem. Eng. Asp.* 2011, 390, 62–66.

42. Qiu, X.; Song, G.; Chu, X.; Li, X.; Tang, G. Preparation, thermal properties and thermal reliabilities of microencapsulated n-octadecane with acrylic-based polymer shells for thermal energy storage. *Thermochim. Acta* 2013, 551, 136–144.
43. Qiu, X.; Song, G.; Chu, X.; Li, X.; Tang, G. Microencapsulated n-alkane with p(n-butyl methacrylate-co-methacrylic acid) shell as phase change materials for thermal energy storage. *Sol. Energy* 2013, 91, 212–220.
44. Sánchez-Silva, L.; Rodríguez, J.F.; Romero, A.; Borreguero, A.M.; Carmona, M.; Sánchez, P. Microencapsulation of PCMs with a styrene-methyl methacrylate copolymer shell by suspension-like polymerisation. *Chem. Eng. J.* 2010, 157, 216–222.
45. Lashgari, S.; Arabi, H.; Mahdavian, A.R.; Ambroggi, V. Thermal and morphological studies on novel PCM microcapsules containing n-hexadecane as the core in a flexible shell. *Appl. Energy* 2017, 190, 612–622.
46. Ahangaran, F.; Navarchian, A.H.; Picchioni, F. Material encapsulation in poly (methyl methacrylate) shell: A review. *J. Appl. Polym. Sci.* 2019, 136, 48039.
47. Sarı, A.; Alkan, C.; Karaipekli, A.; Uzun, O. Microencapsulated n-octacosane as phase change material for thermal energy storage. *Sol. Energy* 2009, 83, 1757–1763.
48. Ma, S.; Song, G.; Li, W.; Fan, P.; Tang, G. UV irradiation-initiated MMA polymerization to prepare microcapsules containing phase change paraffin. *Sol. Energy Mater. Sol. Cells* 2010, 94, 1643–1647.
49. Wang, Y.; Shi, H.; Xia, T.D.; Zhang, T.; Feng, H.X. Fabrication and performances of microencapsulated paraffin composites with polymethylmethacrylate shell based on ultraviolet irradiation-initiated. *Mater. Chem. Phys.* 2012, 135, 181–187.
50. Wang, Y.; Zhang, Y.; Xia, T.; Zhao, W.; Yang, W. Effects of fabricated technology on particle size distribution and thermal properties of stearic–eicosanoic acid/polymethylmethacrylate nanocapsules. *Sol. Energy Mater. Sol. Cells* 2014, 120, 481–490.
51. Zhang, T.; Chen, M.; Zhang, Y.; Wang, Y. Microencapsulation of stearic acid with polymethylmethacrylate using iron (III) chloride as photo-initiator for thermal energy storage. *Chin. J. Chem. Eng.* 2017, 25, 1524–1532.
52. Wang, H.; Zhao, L.; Chen, L.; Song, G.; Tang, G. Facile and low energy consumption synthesis of microencapsulated phase change materials with hybrid shell for thermal energy storage. *J. Phys. Chem. Solids* 2017, 111, 207–213.
53. Farid, M.; Al-Shannaq, R.; Al-Muhtaseb, S.; Kurdi, J. Method for Low Temperature Microencapsulation of Phase Change Materials. U.S. Patent 10,913,882, 9 February 2021.
54. Sarı, A.; Alkan, C.; Karaipekli, A. Preparation, characterization and thermal properties of PMMA/n-heptadecane microcapsules as novel solid–liquid microPCM for thermal energy storage. *Appl. Energy* 2010, 87, 1529–1534.
55. Sarı, A.; Alkan, C.; Biçer, A.; Altuntaş, A.; Bilgin, C. Micro/nanoencapsulated n-nonadecane with poly(methyl methacrylate) shell for thermal energy storage. *Energy Convers. Manag.* 2014, 86, 614–621.
56. Zhang, B.; Zhang, Z.; Kapar, S.; Ataeian, P.; da Silva Bernardes, J.; Berry, R.; Zhao, W.; Zhou, G.; Tam, K.C. Microencapsulation of Phase Change Materials with Polystyrene/Cellulose Nanocrystal Hybrid Shell via Pickering Emulsion Polymerization. *ACS Sustain. Chem. Eng.* 2019, 7, 17756–17767.
57. Konuklu, Y.; Paksoy, H.O.; Unal, M. Nanoencapsulation of n-alkanes with poly(styrene-co-ethylacrylate) shells for thermal energy storage. *Appl. Energy* 2015, 150, 335–340.
58. Khadiran, T.; Hussein, M.; Zainal, Z.; Rusli, R. Nano-Encapsulated n-Nonadecane Using Vinyl Copolymer Shell for Thermal Energy Storage Medium. *Macromol. Res.* 2015, 23, 658–669.
59. Alay Aksoy, S.; Alkan, C.; Tözüm, M.S.; Demirbağ, S.; Altun Anayurt, R.; Ulcay, Y. Preparation and textile application of poly(methyl methacrylate-co-methacrylic acid)/n-octadecane and n-eicosane microcapsules. *J. Text. Inst.* 2017, 108, 30–41.
60. Sarı, A.; Alkan, C.; Altıntaş, A. Preparation, characterization and latent heat thermal energy storage properties of micro-nanoencapsulated fatty acids by polystyrene shell. *Appl. Therm. Eng.* 2014, 73, 1160–1168.
61. Karaipekli, A.; Erdoğan, T.; Barlak, S. The stability and thermophysical properties of a thermal fluid containing surface-functionalized nanoencapsulated PCM. *Thermochim. Acta* 2019, 682, 178406.
62. Şahan, N.; Nigon, D.; Mantell, S.C.; Davidson, J.H.; Paksoy, H. Encapsulation of stearic acid with different PMMA-hybrid shell materials for thermotropic materials. *Sol. Energy* 2019, 184, 466–476.
63. Huo, X.; Li, W.; Wang, Y.; Han, N.; Wang, J.; Wang, N.; Zhang, X. Chitosan composite microencapsulated comb-like polymeric phase change material via coacervation microencapsulation. *Carbohydr. Polym.* 2018, 200, 602–610.
64. Hawlader, M.N.A.; Uddin, M.S.; Khin, M.M. Microencapsulated PCM thermal-energy storage system. *Appl. Energy* 2003, 74, 195–202.

65. Hawlader, M.; Uddin, M.S.; Zhu, H.J. Preparation and evaluation of a novel solar storage material: Microencapsulated paraffin. *Int. J. Sol. Energy* 2000, 20, 227–238.
66. Wu, B.; Shi, L.; Zhang, Q.; Wang, W.-J. Microencapsulation of 1-hexadecanol as a phase change material with reversible thermochromic properties. *RSC Adv.* 2017, 7, 42129–42137.
67. Machado, M.H.; Almeida, A.d.R.; Maciel, M.V.; Vitorino, V.B.; Bazzo, G.C.; da Rosa, C.G.; Sganzerla, W.G.; Mendes, C.; Barreto, P.L.M. Microencapsulation by spray drying of red cabbage anthocyanin-rich extract for the production of a natural food colorant. *Biocatal. Agric. Biotechnol.* 2022, 39, 102287.
68. Lu, W.; Yang, X.; Shen, J.; Li, Z.; Tan, S.; Liu, W.; Cheng, Z. Choosing the appropriate wall materials for spray-drying microencapsulation of natural bioactive ingredients: Taking phenolic compounds as examples. *Powder Technol.* 2021, 394, 562–574.
69. Borreguero, A.M.; Valverde, J.L.; Rodríguez, J.F.; Barber, A.H.; Cubillo, J.J.; Carmona, M. Synthesis and characterization of microcapsules containing Rubitherm®RT27 obtained by spray drying. *Chem. Eng. J.* 2011, 166, 384–390.
70. Arpagaus, C. Chapter Four—Production of food bioactive-loaded nanoparticles by nano spray drying. In *Nanoencapsulation of Food Ingredients by Specialized Equipment*; Jafari, S.M., Ed.; Academic Press: Cambridge, MA, USA, 2019; pp. 151–211.
71. Methaapanon, R.; Kornbongkotmas, S.; Ataboonwongse, C.; Sootitawatt, A. Microencapsulation of n-octadecane and methyl palmitate phase change materials in silica by spray drying process. *Powder Technol.* 2020, 361, 910–916.
72. Liu, H.; Wang, X.; Wu, D. Innovative design of microencapsulated phase change materials for thermal energy storage and versatile applications: A review. *Sustain. Energy Fuels* 2019, 3, 1091–1149.
73. Yuan, H.; Bai, H.; Lu, X.; Zhao, X.; Zhang, X.; Zhang, J.; Zhang, Z.; Yang, L. Effect of alkaline pH on formation of lauric acid/SiO<sub>2</sub> nanocapsules via sol-gel process for solar energy storage. *Sol. Energy* 2019, 185, 374–386.
74. Chai, L.; Wang, X.; Wu, D. Development of bifunctional microencapsulated phase change materials with crystalline titanium dioxide shell for latent-heat storage and photocatalytic effectiveness. *Appl. Energy* 2015, 138, 661–674.
75. Mandal, S.; Ishak, S.; Singh, J.K.; Lee, D.-E.; Park, T. Synthesis and application of paraffin/silica phase change nanocapsules: Experimental and numerical approach. *J. Energy Storage* 2022, 51, 104407.
76. Zhang, H.; Wang, X.; Wu, D. Silica encapsulation of n-octadecane via sol-gel process: A novel microencapsulated phase-change material with enhanced thermal conductivity and performance. *J. Colloid Interface Sci.* 2010, 343, 246–255.
77. Liu, H.; Wang, X.; Wu, D.; Ji, S. Morphology-controlled synthesis of microencapsulated phase change materials with TiO<sub>2</sub> shell for thermal energy harvesting and temperature regulation. *Energy* 2019, 172, 599–617.
78. Song, S.; Dong, L.; Qu, Z.; Ren, J.; Xiong, C. Microencapsulated capric–stearic acid with silica shell as a novel phase change material for thermal energy storage. *Appl. Therm. Eng.* 2014, 70, 546–551.
79. Tahan Latibari, S.; Mehrli, M.; Mehrli, M.; Indra Mahlia, T.M.; Cornelis Metselaar, H.S. Synthesis, characterization and thermal properties of nanoencapsulated phase change materials via sol-gel method. *Energy* 2013, 61, 664–672.
80. Ji, W.; Cheng, X.; Chen, S.; Wang, X.; Li, Y. Self-assembly fabrication of GO/TiO<sub>2</sub>@paraffin microcapsules for enhancement of thermal energy storage. *Powder Technol.* 2021, 385, 546–556.
81. Ghulam, M.; Zhang, J.; Wei, Q. Synthesis of a Novel Nanoencapsulated n-Eicosane Phase Change Material with Inorganic Silica Shell Material for Enhanced Thermal Properties through Sol-Gel Route. *J. Text. Sci. Eng.* 2017, 7, 292.
82. He, F.; Wang, X.; Wu, D. New approach for sol-gel synthesis of microencapsulated n-octadecane phase change material with silica wall using sodium silicate precursor. *Energy* 2014, 67, 223–233.
83. Pourmohamadian, H.; Sheikhzadeh, G.A.; Rahimi-Nasrabadi, M.; Tabrizi, H.B. Fabrication and characterization of microencapsulated PA with SiO<sub>2</sub> shell through sol-gel synthesis via sodium silicate precursor. *J. Mater. Sci. Mater. Electron.* 2017, 28, 9990–9997.
84. Zhang, Z.; Liu, Y.; Wang, J.; Sun, L.; Xie, T.; Yang, K.; Li, Z. Preparation and characterization of high efficiency microencapsulated phase change material based on paraffin wax core and SiO<sub>2</sub> shell derived from sodium silicate precursor. *Colloids Surf. A Physicochem. Eng. Asp.* 2021, 625, 126905.
85. Yu, S.; Wang, X.; Wu, D. Microencapsulation of n-octadecane phase change material with calcium carbonate shell for enhancement of thermal conductivity and serving durability: Synthesis, microstructure, and performance evaluation. *Appl. Energy* 2014, 114, 632–643.
86. Yu, S.; Wang, X.; Wu, D. Self-Assembly Synthesis of Microencapsulated n-Eicosane Phase-Change Materials with Crystalline-Phase-Controllable Calcium Carbonate Shell. *Energy Fuels* 2014, 28, 3519–3529.

87. Fang, Y.; Zou, T.; Liang, X.; Wang, S.; Liu, X.; Gao, X.; Zhang, Z. Self-Assembly Synthesis and Properties of Microencapsulated n-Tetradecane Phase Change Materials with a Calcium Carbonate Shell for Cold Energy Storage. *ACS Sustain. Chem. Eng.* 2017, 5, 3074–3080.
88. Jiang, Z.; Yang, W.; He, F.; Xie, C.; Fan, J.; Wu, J.; Zhang, K. Microencapsulated Paraffin Phase-Change Material with Calcium Carbonate Shell for Thermal Energy Storage and Solar-Thermal Conversion. *Langmuir* 2018, 34, 14254–14264.
89. Sari, A.; Saleh, T.A.; Hekimoğlu, G.; Tyagi, V.V.; Sharma, R.K. Microencapsulated heptadecane with calcium carbonate as thermal conductivity-enhanced phase change material for thermal energy storage. *J. Mol. Liq.* 2021, 328, 115508.
90. Jiang, Z.; Yang, W.; He, F.; Xie, C.; Fan, J.; Wu, J.; Zhang, K. Modified Phase Change Microcapsules with Calcium Carbonate and Graphene Oxide Shells for Enhanced Energy Storage and Leakage Prevention. *ACS Sustain. Chem. Eng.* 2018, 6, 5182–5191.
91. Wang, T.; Tong, J.; Li, X.; Wang, S.; Deng, J. Research on morphological control and temperature regulation of phase change microcapsules with binary cores for electronics thermal management. *Thermochim. Acta* 2021, 706, 179079.
92. Gao, F.; Wang, X.; Wu, D. Design and fabrication of bifunctional microcapsules for solar thermal energy storage and solar photocatalysis by encapsulating paraffin phase change material into cuprous oxide. *Sol. Energy Mater. Sol. Cells* 2017, 168, 146–164.
93. Cai, T.; Yang, W.; Chen, Z.; Yang, A.; Jiang, J.; Ding, B.; Zhu, L.; He, C.; Zhou, Y.; Zhang, K. Morphology-controllable tungstate microcapsules for gamma radiation shielding and thermal energy storage. *J. Energy Storage* 2022, 50, 104245.
94. Du, J.; Ibaseta, N.; Guichardon, P. Characterization of polyurea microcapsules synthesized with an isocyanate of low toxicity and eco-friendly esters via microfluidics: Shape, shell thickness, morphology and encapsulation efficiency. *Chem. Eng. Res. Des.* 2022, 182, 256–272.
95. Shi, T.; Hu, P.; Wang, J. Preparation of Polyurea Microcapsules Containing Phase Change Materials Using Microfluidics. *ChemistrySelect* 2020, 5, 2342–2347.
96. Fu, Z.; Su, L.; Li, J.; Yang, R.; Zhang, Z.; Liu, M.; Li, J.; Li, B. Elastic silicone encapsulation of n-hexadecyl bromide by microfluidic approach as novel microencapsulated phase change materials. *Thermochim. Acta* 2014, 590, 24–29.
97. Rahman, A.; Dickinson, M.E.; Farid, M.M. Microencapsulation of a PCM through membrane emulsification and nanocompression-based determination of microcapsule strength. *Mater. Renew. Sustain. Energy* 2012, 1, 4.
98. Akamatsu, K.; Ogawa, M.; Katayama, R.; Yonemura, K.; Nakao, S.-I. A facile microencapsulation of phase change materials within silicone-based shells by using glass capillary devices. *Colloids Surf. A Physicochem. Eng. Asp.* 2019, 567, 297–303.
99. Watanabe, T.; Sakai, Y.; Sugimori, N.; Ikeda, T.; Monzen, M.; Ono, T. Microfluidic Production of Monodisperse Biopolymer Microcapsules for Latent Heat Storage. *ACS Mater. Au* 2022, 2, 250–259.
100. Xing, J.; Zhou, Y.; Yang, K.; Chang, J.; Yu, Y.; Cai, L.; Shi, S.Q.; Huang, Z. Microencapsulation of fatty acid eutectic with polyvinyl chloride shell used for thermal energy storage. *J. Energy Storage* 2021, 34, 101998.
101. Salaün, F.; Devaux, E.; Bourbigot, S.; Rumeau, P. Influence of the solvent on the microencapsulation of an hydrated salt. *Carbohydr. Polym.* 2010, 79, 964–974.
102. Huang, J.; Wang, T.; Zhu, P.; Xiao, J. Preparation, characterization, and thermal properties of the microencapsulation of a hydrated salt as phase change energy storage materials. *Thermochim. Acta* 2013, 557, 1–6.
103. Cabeza, L.F.; Castell, A.; Barreneche, C.; de Gracia, A.; Fernández, A.I. Materials used as PCM in thermal energy storage in buildings: A review. *Renew. Sustain. Energy Rev.* 2011, 15, 1675–1695.
104. Hassabo, A.; Mohamed, A.; Wang, H.; Popescu, C.; Moller, M. Metal salts rented in silica microcapsules as inorganic phase change materials for textile usage. *Inorg. Chem. Indian J.* 2015, 10, 59–65.
105. Ushak, S.; Cruz, M.J.; Cabeza, L.F.; Grágeda, M. Preparation and Characterization of Inorganic PCM Microcapsules by Fluidized Bed Method. *Materials* 2016, 9, 24.