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Palacios, A.; Navarro-Rivero, M.E.; Zou, B.; Jiang, Z.; Harrison, M.T.; Ding, Y.

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## Review article

# A perspective on Phase Change Material encapsulation: Guidance for encapsulation design methodology from low to high-temperature thermal energy storage applications

A. Palacios<sup>a</sup>, M.E. Navarro-Rivero<sup>a,\*</sup>, B. Zou<sup>a</sup>, Z. Jiang<sup>a</sup>, M.T. Harrison<sup>b</sup>, Y. Ding<sup>a</sup>

<sup>a</sup> BCES Birmingham Centre of Energy Storage, University of Birmingham, United Kingdom

<sup>b</sup> National Nuclear Laboratory, Sellafield, Seascale, Cumbria CA20 1PG, United Kingdom



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## ABSTRACT

Encapsulation is one of the strategies that researchers have explored to improve the thermal performance of Thermal Energy Storage systems. Encapsulation can tackle some of the challenges that are currently hindering Phase Change Material utilisation. Encapsulation provides a protective layer that avoids the PCM from being in contact with the environment (in some cases the chemical stability of the PCM is affected by the environmental conditions), prevents corrosion of TES system components, and helps to control the volume change during the phase change. Although in the literature there are reviews about PCM encapsulation, no guidance about how to properly select one depending on the final application can be found.

In this paper, encapsulation has been categorized depending on the nature of the shell material into ceramic, metallic or polymeric capsules, and their encapsulation method into macro, micro or nano encapsulation techniques. Then, a thorough review of the different encapsulation techniques of PCMs, from low to high-temperature applications, has been carried out. The assessment of TES encapsulation methods has been used as the starting point for the creation of a flowchart that aims to give the research community a path to properly select and validate the encapsulation material and method depending on different application variables such as working temperature and PCM nature.

## 1. Introduction

Thermal Energy Storage (TES) refers to a collection of technologies that store thermal (heat or cold) energy for subsequent use either directly or indirectly through energy conversion processes. TES technologies are usually classified, according to the TES materials used for storing the thermal energy, into three categories [1,2]:

- Sensible heat storage (SHS, based on the temperature change of the TES materials)
- Latent heat storage (LHS, based on phase change of the TES materials)
- Thermochemical storage (TCS, based on adsorption/desorption, absorption/desorption, or reversible chemical reactions).

The fabrication and formulation of phase change materials (PCMs) aim to improve their performance by increasing heat transfer, avoiding

supercooling, accommodating the volume change during the phase change transition and minimizing the effects of chemical incompatibility with other components of the TES system. The fabrication routes that PCM materials can follow are shown in Fig. 1. Direct incorporation methods refer to those ones that do not require to manipulate the raw materials such as melting and dissolving processes and they are used as received, although grinding or sieving could be used to homogenize or achieve a specific particle size. Whereas impregnation, encapsulation and new routes go through steps that require the melting of the PCM to embed it into a matrix (impregnation), or chemical and/or physical complex processes to encapsulate the PCMs.

Some of the routes lead to thermal performance-enhanced PCMs, where properties such as specific heat capacity or thermal conductivity are increased [3]. Whereas others focus on achieving shape-stabilized PCMs (impregnation or encapsulation), where mainly leakage and volume expansion challenges are tackled, and other properties such as heat transfer can be enhanced. Some formulation routes, by modifying the

\* Corresponding author.

E-mail address: [h.navarro@bham.ac.uk](mailto:h.navarro@bham.ac.uk) (M.E. Navarro-Rivero).

PCM composition, have helped to improve the thermal properties and tackle PCM's challenges over the last decade. Thermal conductivity can be enhanced by dispersing nanosized materials such as metals [4], metal oxides [5], single-walled carbon nanotubes [6], multi-walled carbon nanotubes [7,8], carbon nanofibres [9], nanoplatelets [10] and graphene [11]. There are mainly two different methods used to disperse nanoparticles into PCMs [12]; sonication/ultrasonication or mechanical/magnetic stirrers via a one-step method or a two-step method. Fig. 2 shows the main advantages and disadvantages of adding nanoparticles.

Thermal conductivity enhancement of PCMs has been extensively studied as low thermal conductivity limits their use; low heat transfer results in slow charging and discharging processes. Thermal conductivity enhancement using nanoparticles is based on successful and stable particle dispersion. An example of PCM thermal conductivity enhancement is the study of Vivekananthan et al. [13], which prepared graphene nanoparticles dispersed in erythritol following a two-step method. The results showed that adding 1 wt% of graphene nanoparticles, increased the thermal conductivity by 53.1 %, although the latent heat decreased by 6.1 %. Besides thermal conductivity, graphene nanoparticles also diminished the subcooling, with the solidification temperature increasing by 18.76 % compared to pure erythritol.

Supercooling in PCMs, which happens when the crystallization temperature of materials is far below its melting temperature, can be a problem as the energy may not be available at the expected temperature, thus the heat cannot be released at the required temperature. The supercooling degree is the temperature range where the material remains liquid below its melting point. This behaviour is mainly seen in sugar alcohols, salt hydrates, salt solutions and fatty acids to a lesser extent [14]. To avoid this phenomenon, seeding is one of the strategies researchers studied, which led to new PCM formulations. Seeding is the use of solid particles to trigger the nucleation of the supercooled material. When using a different material, it can have the same crystal structure (<15 % variation in the unit cell dimension) or a different one, isostructural or non-isostructural, respectively. The particle dispersed into the PCM needs to be stable after charging and discharging cycles. Therefore, in some cases to assure the stability of the dispersion, surfactants and thickeners have been used. An example is the study of Zhang et al. [8], which used different surfactants (Tween-20, Tween-80, 1-decanol and SDS) to investigate the stability of prepared PCM/water

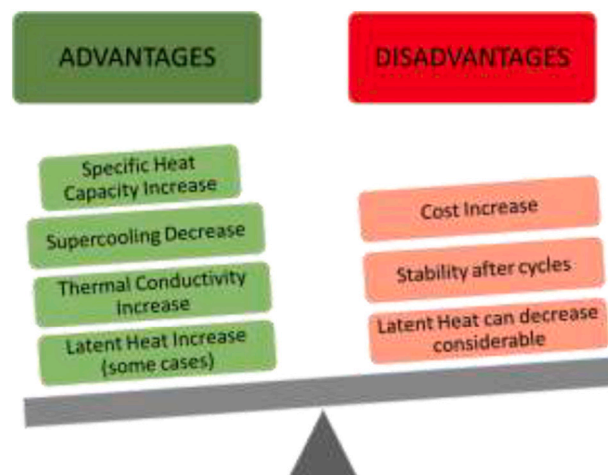


Fig. 2. Addition of particles - advantages and disadvantages.

emulsions. The authors assessed the minimum effective surfactant concentration and showed the size of the PCM droplets depending on the surfactant used. After being cycled, using Tween 20 offered a lower demulsification.

Encapsulation is one of the strategies that researchers have explored to increase the surface area between the PCM and the heat transfer fluid, thus improving the thermal performance of the TES system. Encapsulation also provides a protective layer that prevents the PCM from being in contact with the environment (in some cases the chemical stability of the PCM is affected by the environmental conditions), prevents or reduces the corrosion of other parts of the TES system and helps to control the volume change during phase change [15]. Encapsulation can be classified depending on the capsule size: macro encapsulation, for diameters from 1 mm to >1 cm; microencapsulation, for diameters from 1 μm to 1 mm; and nanoencapsulation, for a diameter of fewer than 1 μm.

PCM-containing microcapsules (microPCMs) have provided an alternative path for using PCMs in thermoregulated fibres, fabrics, foams, and building materials. For low-temperature PCMs, macro (>1mm), micro (μm) and nanoencapsulation (nm) particle sizes

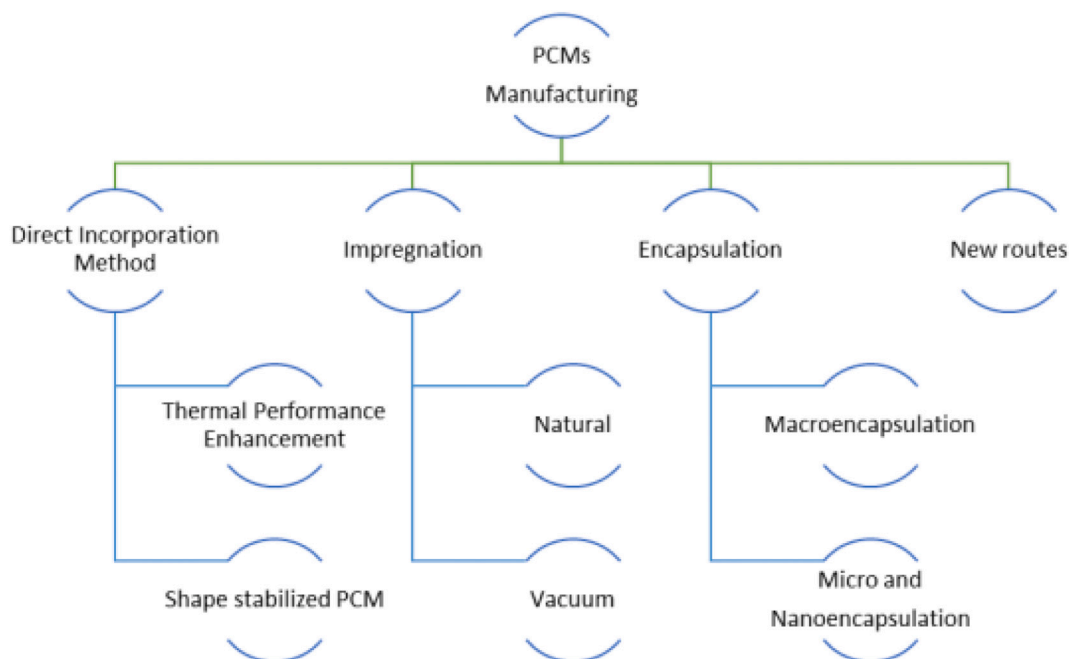


Fig. 1. Phase Change Material (PCM) fabrication.

synthesis strategies have been successfully developed and patented, mainly using polymeric shells. Currently, melamine-formaldehyde (MF) resin, urea-formaldehyde (UF) resin, and polyurethane (PU) are the most used shell materials for PCM microencapsulation at low-medium temperatures. However, there may exist ineluctable remnant formaldehyde after forming the shell through polymerisation, such as when using MF and UF resins, which causes environmental and health problems [16]. Besides, these materials cannot stand high-temperatures. For high-temperature applications, TES pilot installations have used macro-encapsulated inorganic salts such as Zn, NaNO<sub>3</sub>, MgCl<sub>2</sub>, and eutectic mixtures with melting temperatures higher than 300 °C. They used Ni, carbon or stainless-steel materials as shells in cylindrical containers ranging from mm to cm in size. Maruoka et al. [17], used the electroplating method to obtain 3mm diameter particles with a lead-nickel core-shell structure suitable for heat recovery of high-temperature waste heat. Other authors have proposed sol-gel processes using organic polymers with high melting temperatures (i.e. polyimide) or organic-inorganic hybrid shells for microPCMs. However, there are limited solutions for microencapsulating inorganic PCMs that can work in the temperature range between 300 and 500 °C, and meet the requirements for TES applications (e.g. cyclability). The main reasons are i) chemical incompatibility between the PCM-shell material-environment at high temperatures, ii) available high-temperature resistant shell materials that can withstand thermal stress, in terms of cyclability and mechanical strength to prevent PCMs to leak due to volume expansion during the solid to liquid phase transition., and iii) complex microencapsulation processes that increase energy needs and cost [18]. From an engineering point of view, encapsulation for high-temperature applications, such as solar thermal power plants, has always been challenging. Apart from the progress in sol-gel encapsulation, researchers have been continuously innovating to find stable and compatible encapsulating materials that can lead to excellent heat conductivity under high temperature and pressure conditions.

Overall this paper aims to provide a comprehensive and updated review of encapsulation techniques for thermal energy storage focusing on i) reviewing and updating the encapsulation status for low to high-temperature TES materials; ii) providing insights on encapsulation incorporation in industry sectors and construction materials; iii) summarise the practical challenges, advantages and innovation needs of PCM encapsulation at material and manufacturing level and iv) providing strategies and guidelines for material screening and characterisation. Finally, a flowchart to guide the selection of materials and production routes for the encapsulation of PCM has been designed, which highlights its dependence on temperature and application.

## 2. Scope and guidance

This paper is targeted at experienced researchers in the field, but also at those new to the topic who desire an updated view of the current phase PCM encapsulation landscape. This comprehensive review of encapsulated phase change materials (EPCM) is presented in two parts: Sections 3 and 4 comprise a literature review on EPCM, while Sections 5 and 6 cover the know-how of encapsulation. Section 3 focuses on EPCM fundamentals, discussing the kinds of PCM, kinds of encapsulation, encapsulation sizes as well as the advantages and disadvantages of the different material shells used. In Section 4, it has been included an extended literature review of EPCM for TES which is classified according to the encapsulation method used and the capsule dimensions (macro encapsulated, microencapsulated and nano encapsulated). Section 5 aims to provide insights into EPCM synthesis and characterisation. The first part of Section 5 targets the new trends and novel strategies for PCM encapsulation not just in TES but in other fields. Looking at other fields can help boost EPCM for TES, as the expertise can be translated to overcome the current limitations in TES. The last two parts of Section 6 are dedicated to providing a flow chart for EPCM selection and a detailed methodology to experimentally validate the synthesised salts.

Overall, this paper reviews the EPCM from the basic concepts of the technology to higher-level know-how guidelines.

## 3. Encapsulation basis

### 3.1. Encapsulation

Macro encapsulation involves the encapsulation of the PCM in a selected material container with the geometry designed for a specific application depending on the TES system. Macro encapsulation, compared to micro and nano, has a lower performance improvement due to lower thermal conduction within the capsule. Micro and nano-encapsulation, where PCM is surrounded and confined within a thin and sealed envelope (metallic/polymeric or ceramic) [19] can produce mononuclear, polynuclear, matrix or multiwall capsules, as can be seen in Fig. 3. Mononuclear micro/nano capsules have a shell around the core, polynuclear capsules have many cores enclosed within the shell, matrix capsules have core material distributed within the shell and multiwall capsules have a shell that consists of multiple layers. The capsules' external morphology and internal structure are strongly dependent on the formulation methods used and the shell material selected [20] They can be analysed by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM). While SEM and TEM are used to study their morphology, AFM is used to study the shell's roughness, compactness and surface imperfections. Microencapsulated PCMs (MEPCM) and nano-encapsulated PCMs (NEPCM), besides having the capability of adapting to volume change during the phase change process, also have a high surface area per unit volume, which leads to a better heat transfer and prevents the contact of the PCM with the environment or other parts of the system [21]. Their phase change temperature, besides being determined by the PCM itself; can be modified by altering some of the capsule's characteristics such as their average diameter (Da) [22]. Studies done by Sukhorukov et al. [23] showed the influence of particle size on the stability when going from microscale to nanoscale lead to an improvement in mechanical properties (microcapsules, 10 µm, experienced a higher deformation than nanocapsules, 10 nm), highlighting that nano encapsulated PCM could make capsules more suitable for long-term but higher pumping power than microcapsules. Nano-encapsulation can also provide a high cyclability and a faster heat transfer than micro-sized capsules, which has increased interest in it for further technological development [20].

When a PCM material is encapsulated inside small capsules, the specific surface area of the material increases, which allows the use of a heat transfer fluid directly in contact with the capsules, which increases the heat transfer between the storage material and the heat carrier. However, one of the drawbacks of encapsulated PCMs is that a void must be present inside the shell to accommodate the volume change during the melting occurs. Mathur et al. [24] investigated the creation of voids in sodium nitrate-encapsulated capsules to allow for the volume change of the PCM, see Fig. 4. The authors highlighted that the coating formulations (a binder, film former, inorganic filler, and surfactant) major factors for producing robust capsules were the binder composition and percentage, the polymer selection and the thickness of the shell coating.

#### 3.1.1. Encapsulation materials

The key properties of encapsulated materials in TES are their thermal properties (thermal conductivity, phase change temperature and the heat associated with the phase transitions). However, others such as stability, density, volatile organic compound emission, flammability, mechanical properties and permeability of the shell play a role when a specific application is considered. In the case of micro and nanocapsules, capsule size distribution and morphology, which greatly affect the PCM performance, are added to the list. The different shell materials that can be used for encapsulating PCMs, metallic, polymeric or ceramic, define the mechanical and thermal properties of the capsules, see Fig. 5.

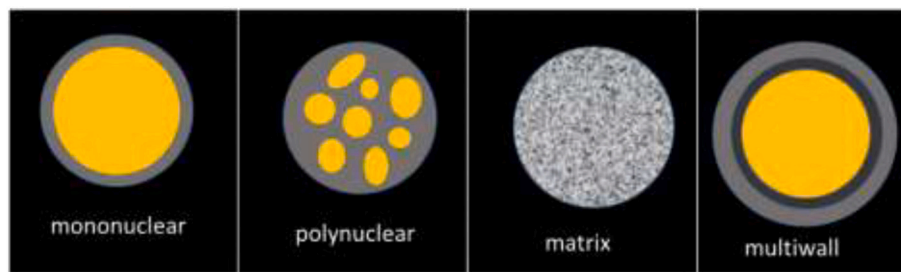


Fig. 3. Capsules type configuration; mononuclear, polynuclear, matrix and multiwall.

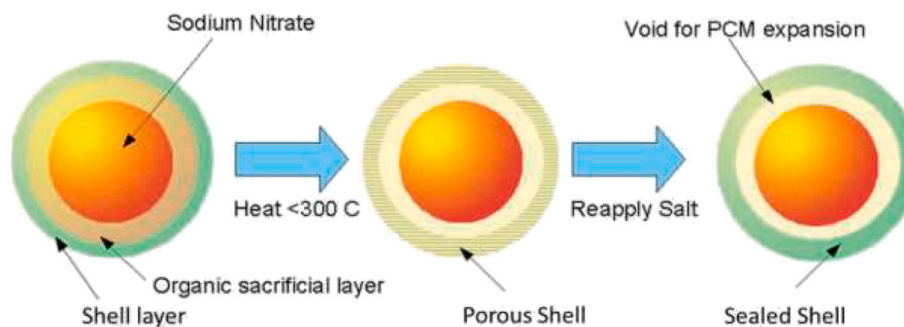


Fig. 4. Schematic of the investigated sodium nitrate encapsulated capsules [24].

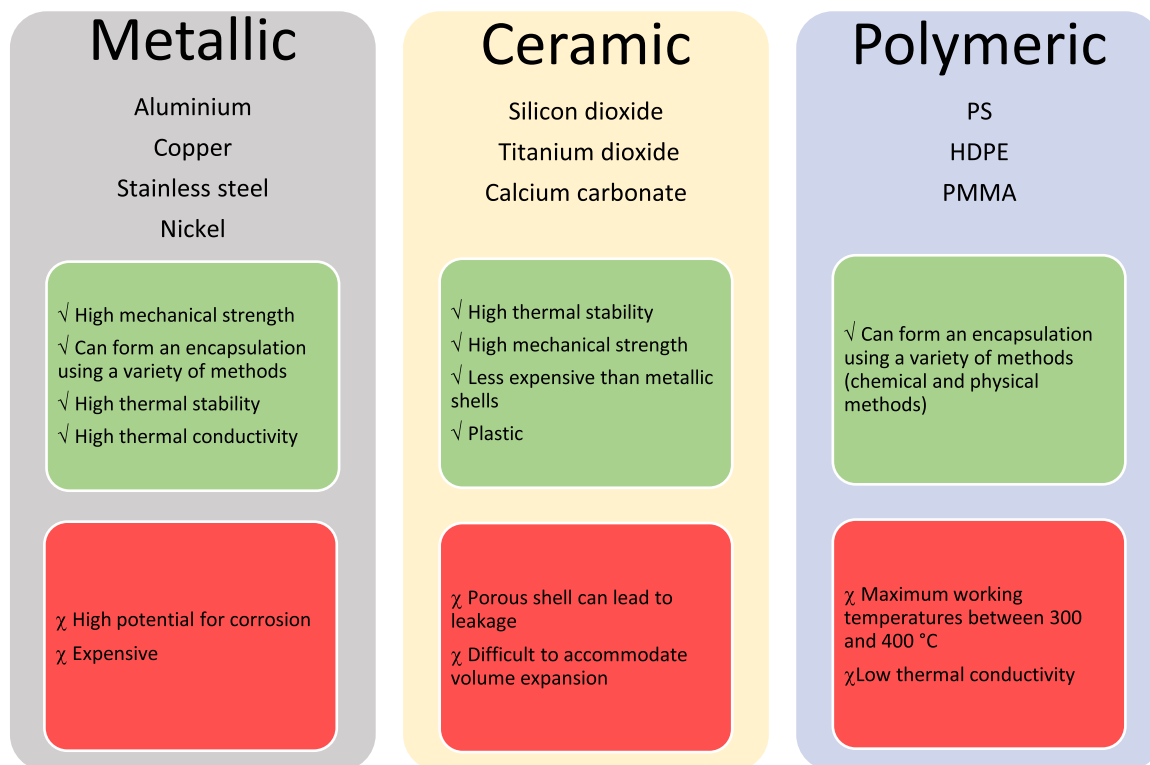


Fig. 5. Classification of PCM shell materials; advantages and disadvantages.

High-temperature applications increase chemical incompatibility and narrow down shell/PCM pair options. The majority of high-temperature macro encapsulations are fabricated using metallic shells. The shells have high mechanical strength and high thermal stability, despite possible corrosion problems. Metallic shells are easy to fabricate on a macro-scale, have a low cost, and their materials are abundant.

Steel shells are most commonly employed [15]. Although ceramic shells have also been studied and are cheaper, porous shells tend to be prone to leaking. Jacob et al. [15] reviewed and compared the thermal conductivity performance of encapsulated PCMs with different shell materials, such as metallic [25–27], plastic [28,29] and inorganic [30,31], for high-temperature energy storage applications (see Fig. 6). Among the



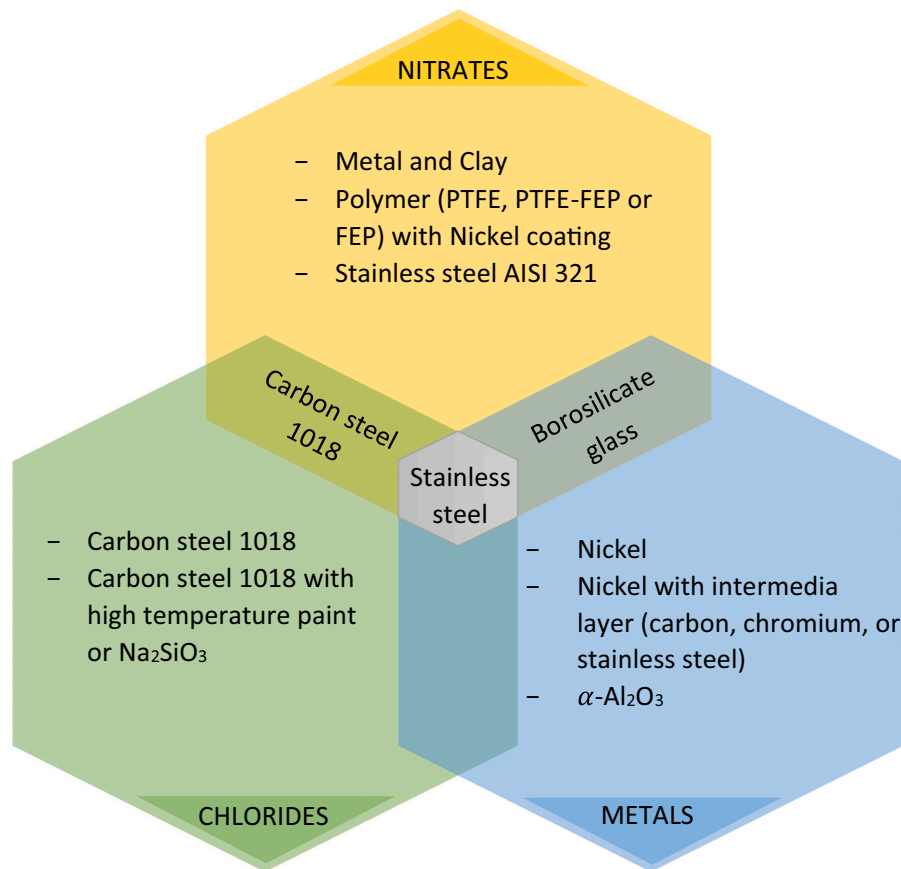


Fig. 6. Encapsulation shell materials for high-temperature applications [38].

shell materials evaluated, steel (carbon and stainless), nickel (and nickel alloy), sodium silicate ( $\text{Na}_2\text{SiO}_3$ ), silicon dioxide ( $\text{SiO}_2$ ), calcium carbonate ( $\text{CaCO}_3$ ) and titanium dioxide ( $\text{TiO}_2$ ) were the ones recommended for further research.

However, most attention has been paid to the preparation of organic shell materials, leading to >50 different known polymers being used as wall materials for microcapsules. This is despite polymeric shells having low thermal conductivity, slow thermal response, some chemical incompatibilities and an inability to work high temperatures [20]. This has made researchers look for new microencapsulated PCMs. One of the alternatives has been the use of inorganic materials that offer higher mechanical strength and thermal conductivity.  $\text{SiO}_2$ ,  $\text{CaCO}_3$  [32] and  $\text{TiO}_2$  [33] microcapsules shells, through interfacial or in-situ polymerisation, have been proposed.  $\text{SiO}_2$  is the most studied, with paraffin/ $\text{SiO}_2$  micro- and nanocapsules being prepared by spray-drying, interfacial polymerisation, interfacial polycondensation and emulsion polymerisation among other methods [34]. Other inorganic materials have also been used to a lesser extent such as  $\text{AlO}(\text{OH})$ . However, the use of inorganic shells is highly dependent on the core/shell encapsulation method. For high-temperature PCMs, involving molten salt and metals, little research has been carried out. Some studies can be found for molten salt encapsulation with perhydropolysilazane (PHPS), a ceramic precursor resin [35],  $\text{SiO}_2$  [36], or some alloys like zinc (shell organo-phosphorus based) and Al—Si ( $\text{Al}_2\text{O}_3$  shell) [37].

Also, bio-based and biodegradable microencapsulated PCMs are of great interest with potential in the food industry, textiles, bio-catalysts, pharmaceuticals and medical care. Therefore, interest has risen in the selection and study of new materials and the field is still trying to tackle the technological barriers.

### 3.1.2. Encapsulation methods

Micro/nanoencapsulation of PCMs can be achieved through different synthesis routes [22], see Fig. 7. The various methods aim to produce defined and uniform particle sizes, mechanical and chemical stability and a high core-to-shell ratio to make the energy storage capacity incorporated as high as possible. They can be divided into chemical and physical methods. Chemical methods form microcapsules through chemical reactions, whereas physical methods can either be physicochemical, where the materials that will form the shell do not undergo any chemical reaction and keep their original composition, or physicochemical, where the formation of the shell is due to both chemical and physical processes.

**3.1.2.1. Chemical.** The most common chemical methods for microencapsulation are the ones called in-situ polymerisation, where the polymerisation reaction and the microencapsulation occur in the same solution [40]. The in-situ polymerisation methods include emulsion, suspension and interfacial.

- *Suspension polymerisation* involves two phases; a continuous one with surfactants, and a discontinuous one, with a PCM-monomer mixture and initiator. Both phases are mixed under agitation and the polymerisation reaction takes place. Temperature, atmosphere, agitation speed and time are optimized for each PCM/shell process [41] as they determine the particle morphology and size.
- *Interfacial polymerisation* uses a set of two reactive monomers that react with each other at the interface; thus, they must be soluble in opposite solvent polarity to create the capsule. PCM interfacial polymerisation consists of the formation of an emulsion, in which one emulsified phase contains the PCM (the dispersed one), followed

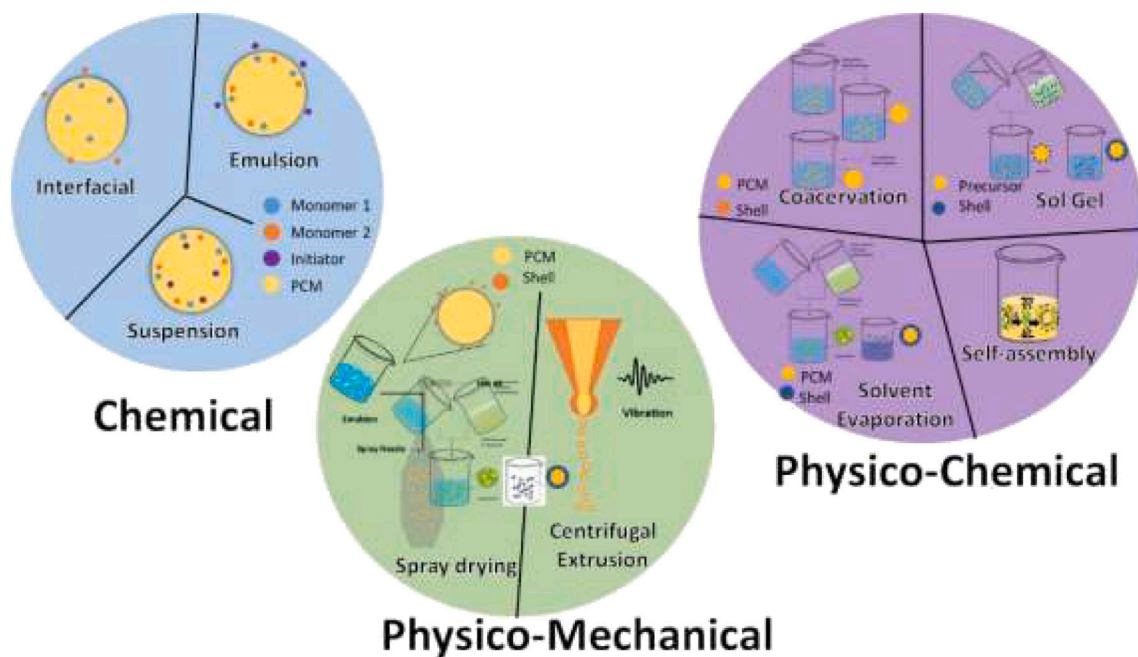


Fig. 7. TES polymerisation methods, adapted from [39].

by the polymerisation at the interface [42]. In this process, the polymerisation reaction is hard to control, thus, so is the quality of the membrane and the yield. The reaction conditions (monomer/oligomers concentrations, temperature, mixing rate and reaction time) are important parameters that affect the properties of the microcapsules obtained. Moreover, exhaustive washing is needed to completely remove the unreacted monomers, by-products, organic solvents and surfactants. The stirring rate modifies microcapsule size but also can modify the shell membrane formed [43].

- *Emulsion polymerisation* process consists of a dispersed phase composed of PCM and monomers in a continuous solution, which contains surfactants by vigorous stirring. Then the initiator is added in the continuous phase and the reaction starts at the interfaces. The microcapsule properties are affected by monomer concentration, temperature and the emulsification process. Methods that involve emulsification processes in general lead to polynuclear microcapsules [44] and are commonly used to encapsulate organic materials.

**3.1.2.2. Physical.** The most commonly used physical methods for microencapsulation include spray drying, solvent evaporation, centrifugal extrusion and fluidized bed processes. However, according to Jamekhorshid et al. [40], fluidised bed (air-suspension coating) methods are not suitable for MEPCMs production.

- *Physico-mechanical*-based processes include mainly spray-drying and centrifugal extrusion.

The *spray-drying* process involves the suspension of the PCM and the encapsulating agent by creating an emulsion or dispersion that afterwards is atomized into droplets in a heated chamber, where the solvent is evaporated. Thermoplastics are used as shell material [21]. In this process, the shell of the resulting dry particles always contains some of the core components. The capsules are usually polynuclear or matrix type [45]. However, high temperatures restrict the process to thermally stable shell/PCM materials, it is difficult to control the particle size, and the low yields are only suitable for small production [46].

*Centrifugal extrusion* is a liquid co-extrusion process where a liquid core material is pumped through the inner orifice of a nozzle and a liquid

coating material through the outer section. The result is a co-extruded rod where the core material (PCM) is surrounded by the coating material. Then, the extruded rod is broken into droplets that will become capsules [47]. The capsule load can be up to 80 % of the total weight.

- *Physico-chemical*-based processes include coacervation, sol-gel, solvent evaporation and self-assembly. Also classified among these methods, is the solvothermal technique where the chemical reaction takes place in a solvent at temperatures above the boiling point while employing a pressure of 1 bar [48].

*Coacervation* is the process where a phase separation from the initial solution of one or many hydrocolloids occurs. Then there is a subsequent deposition of the newly formed coacervate (aggregate of colloidal droplets due to electrostatic interaction forces) phase around a suspended or emulsified active ingredient, in our case, a PCM. Coacervation can be simple or complex, with the difference being due to the phase separation method [45]. In simple coacervation, the phase separation is induced by using an additive (e.g., alcohol or salt), or changing the temperature or pH of the solution; whereas complex coacervation uses an oppositely charged polymer. For the simple method, the solution is formed from 3 immiscible phases: the core material, the coating material and the solvent. Complex coacervation consists of liquid-liquid phase separation of two oppositely charged polymers through electrostatic interaction: a dense coacervate phase and a dilute one in equilibrium [49]. In both cases, the coating material is rigidized thermally, or by solvent evaporation. This process enables efficient control of the particle size and can work in a wide pH range; however, it is difficult to scale up and the removal of residual solvents is challenging and not suitable for low-range microparticles, or nanoparticles [46]. Hawlader et al. [19] compared two different paraffin microencapsulation methods; coacervation and spray drying. In general, the microcapsules formed using the coacervation method had higher energy storage and release capacity.

The *sol-gel method* starts with the preparation of the sol, a colloidal suspension or solution [50] of two immiscible phases, normally the PCM is in the discontinuous one. Then, a sol solution is prepared with the shell material precursors and added dropwise into the dispersed PCM solution. The gelation of the sol is obtained through low-temperature hydrolysis and condensation reactions on the surface of the

discontinuous phase. The key to this method is the self-assembly of the shell precursor on the droplets under elaborated conditions [51].

The *solvent evaporation* synthesis consists of the preparation of an oil-water emulsion where the polymer shell material is dissolved in an immiscible volatile solvent together with the core material, which is also dissolved or dispersed. During this process, the coating material shrinks around the core material. The hardening process of the polymer microcapsules happens with time and the removal of the solvent [52]. This method does not require elevated temperatures or phase separation-inducing agents. The nano- to microparticle size range can be controlled through the selection of the encapsulation conditions and materials [46].

The *self-assembly* technique has been a powerful tool for micro and nano-encapsulation. It can be defined as the spontaneous molecular arrangement of disordered entities of molecules into ordered structures. The process is due to specific local interactions among the components themselves. Besides this, the directionality and functionality of self-organized structures are determined by other functional interactions or forces (Fig. 8) [53].

Table 1 lists the main advantages and disadvantages of the most used encapsulation methods. Among these methods, physical methods cannot generally produce microcapsules smaller than 100  $\mu\text{m}$ , thus chemical methods are preferred for smaller sizes [54].

#### 4. Encapsulation in thermal energy storage technologies

In this section, a comprehensive literature review of PCM-encapsulation from low to high temperatures is presented. The following literature search has been conducted using the Scopus database by considering the most cited and influential papers under the keywords “phase change material and encapsulation”. >100 papers have been included in the compilation, which summarises both review papers and original scientific research papers. The outputs from the literature review are organized by the encapsulation method macro-, micro- and nano-. Macroencapsulation is subdivided depending on the shell material, whereas for micro and nano encapsulation by the encapsulation method. These include chemical polymerisation (suspension, interfacial and emulsion), physicochemical (sol-gel, solvothermal and coacervation) and physicomechanical (spray drying and self-assembly). A section on encapsulated materials in passive TES

systems has been added to emphasize EPCMs used in buildings and industrial applications, detailing the challenges and strategies which have led to the development of new composites using EPCMs to enhance materials performance and reduce energy losses.

##### 4.1. Macro-encapsulation

In this section, a literature review presenting some relevant examples of macro encapsulation of PCMs is included. Given that there are no specific synthesis methods for macro capsules, the research studies have been classified by the material shell: metallic shell, ceramic and glass shell.

###### 4.1.1. Metallic shell

Li et al. [57] theoretically and experimentally designed and studied a fixed-bed thermal energy storage system encapsulating  $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3\text{-Na}_2\text{CO}_3$  molten salt for solar power plant applications. The ternary molten salt was encapsulated in hollow stainless-steel balls (2 mm wall thickness). The metal balls were cut, filled with the molten salt up to 80 % of their volume, and then welded close to high-temperature working conditions to reduce the amount of air that remains in the capsule to avoid or diminish capsule deformation. No leakage was observed during the testing of the system. The theoretical analysis results indicated that the system charging efficiency increased with the decreasing diameter of the PCM capsules. The thermal behaviour of other encapsulated molten salts ( $\text{NaNO}_3$  and eutectic  $\text{NaCl-MgCl}_2$ ) was evaluated using a specific calorimeter designed for the capsules' size and working temperatures [58]. Both stainless steel (304) and carbon steel (1080) shell materials were assessed. Although all the tested capsules were thermally and physically stable across 50 thermal cycles (300–470  $^\circ\text{C}$ ) [58], further corrosion tests should be carried out to assure chemical compatibility to assess feasibility for long-term applications.

Alam et al. [59] conceived and studied an innovative technique for encapsulating spherical  $\text{NaNO}_3$  pellets ranging from 12.5 to 25.5 mm (Figs. 9 and 10). One of the advantages of this encapsulation approach was that it does not require sacrificial layers to accommodate the volumetric expansion due to PCM phase change. The PCM was encapsulated by a 0.5–0.7 mm layer of a non-reactive polymer, such as polytetrafluoroethylene (PTFE) and fluorinated ethylene propylene (FEP), by utilizing the jar-milling and compressing techniques. This was then



Fig. 8. Forces involved in self-assembly [53].



**Table 1**  
Advantages and disadvantages of mostly used PCM microencapsulation methods [21,40,45,46,49,55,56].

Techniques	Advantages	Disadvantages	Size range (µm)
Chemical	<ul style="list-style-type: none"> <li>• Easy control parameters</li> </ul>		
Interfacial polymerisation	<ul style="list-style-type: none"> <li>• Simple and reliable process</li> <li>• High active loading and tuneable delivery processes</li> <li>• Versatile and stable mechanical and chemical properties</li> <li>• System temperature up to 80 °C</li> <li>• Relatively low cost</li> <li>• Conductive to scale-up.</li> </ul>	<ul style="list-style-type: none"> <li>• Non-biocompatible carrier material organic solvents</li> </ul>	0.5–1000
Emulsion polymerisation	<ul style="list-style-type: none"> <li>• High MW polymer</li> <li>• Fast process</li> </ul>	<ul style="list-style-type: none"> <li>• Impurities from the surfactant</li> </ul>	0.05–5
Suspension polymerisation	<ul style="list-style-type: none"> <li>• Good heat control of the polymerisation reaction</li> </ul>	<ul style="list-style-type: none"> <li>• Few monomers are water-soluble.</li> </ul>	2–4000
Physico-chemical			
Sol-gel	<ul style="list-style-type: none"> <li>• Inorganic shell with high thermal conductivity</li> </ul>	<ul style="list-style-type: none"> <li>• Still under research</li> <li>• High working temperatures</li> <li>• Uncoated particles</li> <li>• Difficult to scale-up</li> <li>• Expensive</li> </ul>	0.2–20
Coacervation	<ul style="list-style-type: none"> <li>• Versatile</li> <li>• High encapsulation efficiency and mild processing conditions</li> <li>• Efficient control of the particle size</li> <li>• Simple: insensitive to water-soluble additives and has a wide pH working range</li> <li>• Low operating temperature</li> </ul>	<ul style="list-style-type: none"> <li>• Agglomeration</li> <li>• Polymer solvents are toxic</li> <li>• Residual solvents</li> <li>• Not suitable for producing low micrometre size range microspheres</li> </ul>	2–1200
Physico-mechanical			
Spray drying	<ul style="list-style-type: none"> <li>• Low cost</li> <li>• High yield of production</li> <li>• Equipment and know-how widely available</li> <li>• Versatile</li> <li>• Easy to scale-up</li> <li>• Free-flowing powders</li> </ul>	<ul style="list-style-type: none"> <li>• Agglomeration</li> <li>• High working temperatures</li> <li>• Uncoated particles</li> <li>• Small batches, moderate yields</li> </ul>	5–5000
Centrifugal extrusion	<ul style="list-style-type: none"> <li>• Suitable for bio-encapsulation</li> </ul>	<ul style="list-style-type: none"> <li>• High temperature</li> <li>• Clogging problems</li> </ul>	5–1500
Solvent evaporation	<ul style="list-style-type: none"> <li>• Low cost</li> </ul>	<ul style="list-style-type: none"> <li>• Lab-scale production</li> </ul>	5–5000 0.5–1000



**Fig. 9.** Polymer encapsulated  $\text{NaNO}_3$  (left), metal coated on polymer- $\text{NaNO}_3$  capsules at 356 °C after 50 cycles (middle), metal coated on polymer- $\text{NaNO}_3$  capsules at 356 °C after 2200 cycles (right) [59].

followed by the deposition of a thin layer of metal using electroless and electroplating methods. This novel encapsulation method avoids the metal corrosion caused by molten salt. The controllable metal coating process allows the capsules to reach an optimal core-to-shell ratio. Thermal cycling assessments showed that the encapsulated nitrate-based materials have superior thermal and chemical stability after 2200 thermal cycles (280–360 °C).

#### 4.1.2. Ceramic shell

Ceramic materials are also low-cost capsule materials. They have been proved to possess outstanding thermochemical stability under

molten salt conditions compared to metallic ones. However, the inherent microporous structure of ceramics can impact the compressive strength, thermal conductivity and leakage of PCM capsules [60,61]. To overcome this challenge, Wickramaratne et al. [62] focused on finding the optimal composition and sintering conditions to manufacture ceramic capsules. Researchers applied a wet pressing technique for the capsule fabrication, during which ceramic slurries were partially dried and shaped into a similar-sized spherical shape. After being left in the air for 24 h to dry, samples were sintered for 8 h at a certain temperature. The molten eutectic salt ( $\text{NaCl-KCl}$ ) was poured into the capsules via a preserved hole that was sealed up with different materials. The result

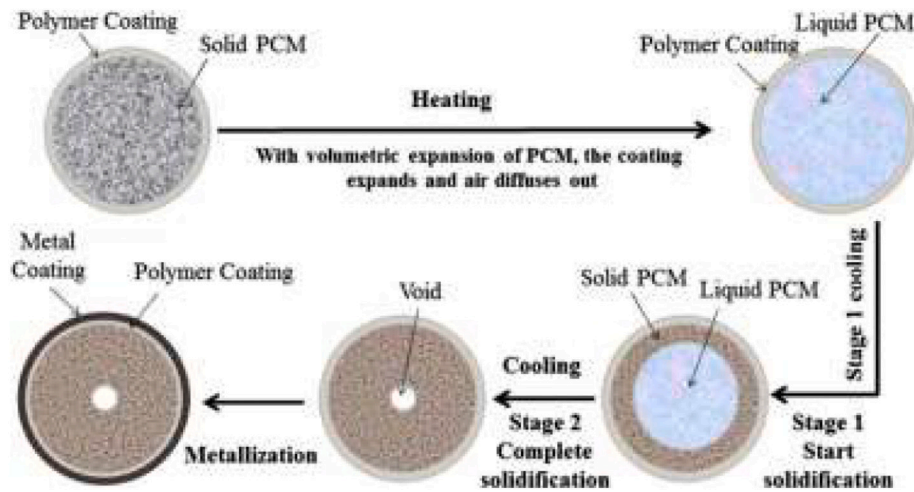


Fig. 10. Schematic of the metal-coated polymer investigated by [59].

showed that ceramics, with the same composition, sintered at 1190 °C had better stability than those sintered at lower temperatures. The molten salt capsules sealed with feldspar-sodium tetraborate (1:1) could withstand 150 thermal cycles between 580 and 680 °C without showing any degradation [63].

Hassan et al. [64,65] prepared geopolymer- and expanded clay-coated PCM (GP-L-PCM) macro capsules. PCM (PCM-RT31) was first infiltrated into lightweight expanded clay aggregate (LECA) and then coated with a geopolymer. The preparation process and the prepared GP-L-PCM capsules are shown in Fig. 11. Subsequently, the GP-L-PCM capsules were added to the geopolymer concrete (GPC) with volume ratios of 25 %, 50 %, and 75 %. The author investigated the thermal performance and mechanical properties of the GPC incorporated with GP-L-PCM capsules, finding that the GP-L-PCM slabs exhibit lower heat transmission. The front surface temperature decreased by 5.0 °C compared with the reference GPC slab, while the back-surface temperature decreased by 8.0 °C. However, the compressive strength decreased

from 65 MPa to 10.9 MPa after adding 75 % GP-L-PCM capsules into the GPC. Also, the thermal conductivity decreased from 2 W/m<sup>2</sup>•K to 0.9 W/m<sup>2</sup>•K with the addition of 75 % GP-L-PCM.

Carbon-based material is often used in shell formation to improve the system heat transfer. Ge et al. [66] compared the impact of a carbon-based thermal conductivity enhancer in a ceramic material shell (i.e. MgO) regarding its microstructure and stability of eutectic carbonate molten capsules. Results demonstrated that the eutectic molten salt (43 wt% Li<sub>2</sub>CO<sub>3</sub> and 57 wt% Na<sub>2</sub>CO<sub>3</sub>) encapsulated in the microstructure formed by the ceramic material after mixing, uniaxial compression and sintering performed well. This was attributed to the excellent wettability of the molten salt liquid phase on the ceramic surface. In contrast, the composite only consisting of PCM and carbon material exhibited a severe leakage and no mechanical integrity. Carbon materials have an undeniable effect on the increase in thermal conductivity of PCM composites. Thus, their use requires a trade-off when it comes to designing a composite PCM with desirable thermal properties.

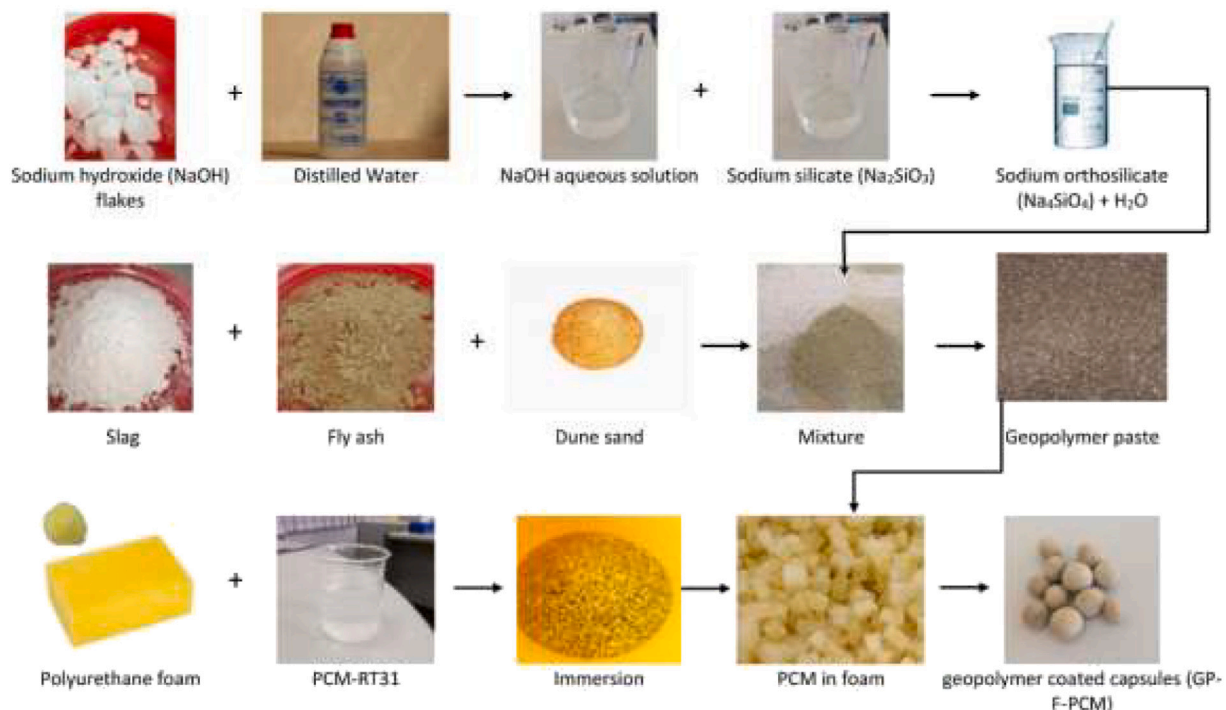


Fig. 11. The preparation process of the GP-L-PCM capsules [65].

#### 4.1.3. Glass shell

Some researchers chose borosilicate as the shell material to avoid potential chemical reactions (alloying or corrosion) between the PCM and the metallic shell. Compared to common metallic shells, borosilicate requires a relatively low temperature for sealing the capsules, which greatly reduces the chance of PCM degradation during the metal welding process. Pau Gimenez-Gavarrell and Sonia Fereres [38] designed a fabrication procedure for PCM-borosilicate encapsulation which is shown in Fig. 12. Both inorganic material ( $\text{NaNO}_3$ ) and metallic material (Pb) capsules were tested using a combination of visual and infrared images. Melting and freezing processes could be observed due to borosilicate material transparency, especially for the inorganic material. Infrared images showed a fast heat transfer across a single metal capsule. This macro encapsulation method is inexpensive. However, using borosilicate as capsule material has a few drawbacks, for instance, the low thermal conductivity of the shell material and the high risk of breakage. Also, the current fabrication process is not suitable for large-scale production.

Zhang et al. [67] aimed to tackle the hygroscopicity of some PCMs that leads to the narrowing of the application fields. Carbonate  $\text{K}_2\text{CO}_3$ - $\text{Na}_2\text{CO}_3$  eutectic salt was taken as the PCM material and  $\text{MgO}$  as the matrix. The CPCM surface was sealed (encapsulated) using a glass powder spray plating to avoid moisture. To encapsulate the molten salt composite, 1:4, 2:4 and 3:4 glass powder/anhydrous ethanol mixtures were studied. Then sprayed CPCM was placed in an oven and dried at  $60^\circ\text{C}$  for 2 h and then sintered at  $720^\circ\text{C}$  for 2 h. The authors concluded that the coating with the 3:4 ratio effectively reduced the moisture absorption of the composite. The MPCM capsules were tested at  $28^\circ\text{C}$  under 80 % RH in air for 96 h and observed that the moisture absorption rate of the coated CPCM was much lower than the one without the glass coating with no significant effect on the latent heat of PCMs (Fig. 13).

#### 4.2. Micro/nano encapsulation

##### 4.2.1. Chemical

Of the available chemical polymerisation techniques, this literature review focuses mainly on suspension polymerisation, interfacial polymerisation and emulsion polymerisation. Common features of the three methods are the surface-to-volume ratio, the shell-to-core ratio and the

synergies between those parameters. The development of easy, inexpensive and robust methods for the encapsulation of PCMs with suitably sized particles has been very important for textiles and similar applications [68]. In general, the authors observed that smaller capsules have a larger surface area to volume ratio that would contribute to heat transfer enhancement. For instance, it has been reported that enclosing PCMs in 20 mm capsules shortens the discharging time of a TES system by 50 % when compared to 60 mm capsules [69]. Theoretically, reducing the size would further promote this effect. One of the methods for creating small capsules is to produce emulsions with the desired droplet size followed by a shell formation on the surface of the droplets. Characteristics of different hetero-phase polymerisation systems are compared and compiled in microencapsulated paraffin wax through suspension-like polymerisation using a copolymer of methyl methacrylate (MMA) and styrene as the shell material. The copolymerisation process was greatly affected by the monomer ratio modifying the morphology and the average diameter of the microcapsules. The kinetics of the copolymerisation process was controlled by the monomer (MMA) due to high reactivity. In this way, as the number of MMA increased, the time required to reach the mean particle size decreased regardless of the amount of the core material. Al-Shannaq et al. [79] showed that homogeneous nucleation can be shell-induced by optimizing the shell composition and structure (no nucleating additives were needed), giving a strategy to minimise supercooling of PCMs by optimizing the shell composition and structure.

Table 2. Conventional homogenization is sufficient to form an emulsion containing droplets larger than  $1\ \mu\text{m}$ . Sonication methods have been proved to be efficient in achieving smaller droplets [70] and initiating low-degree polymerisation reactions during the capsulation process [71]. With the development of encapsulation techniques, capsules with multilayer and/or functional shells have been designed, which enable distinct components, such as polyelectrolytes [72], nanoparticles, or thermal enhancers [73] to be attached stepwise on the emulsion droplets surface [72].

Another parameter to consider when synthesising micro/nano-capsules is the core-to-shell ratio, which is discussed below. To achieve a high core-to-shell ratio, Seitz et al. [74] successfully enclosed PCMs with ultrathin layers of polymers. Emulsion droplets of icosane were prepared and alternately immersed in the oppositely charged

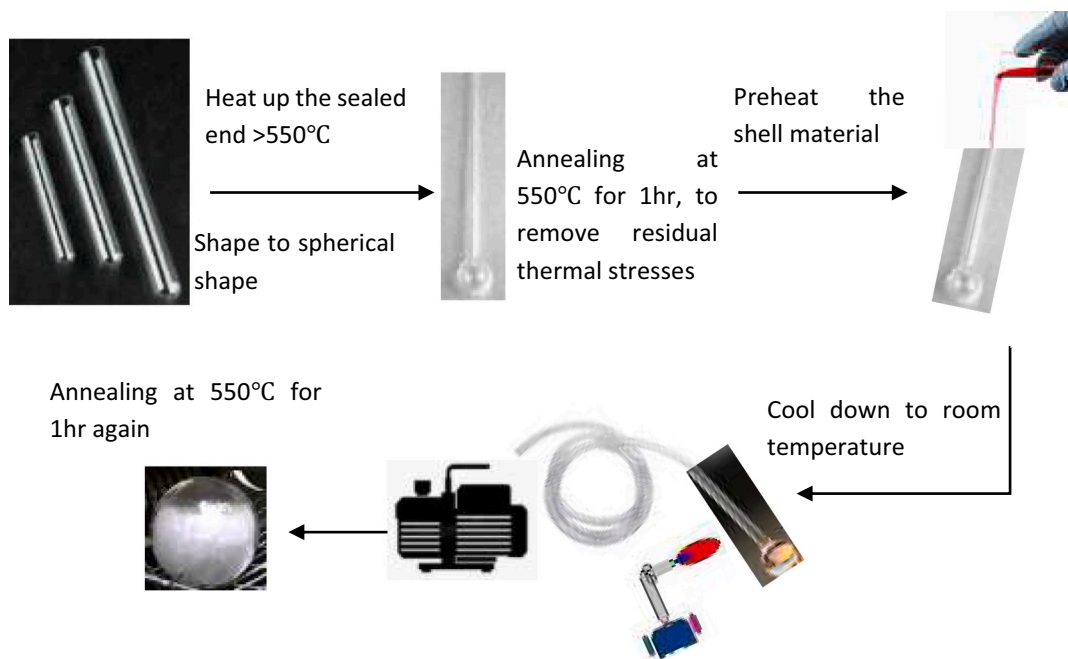


Fig. 12. Schematic diagram of PCM encapsulation using borosilicate as the shell material [38].



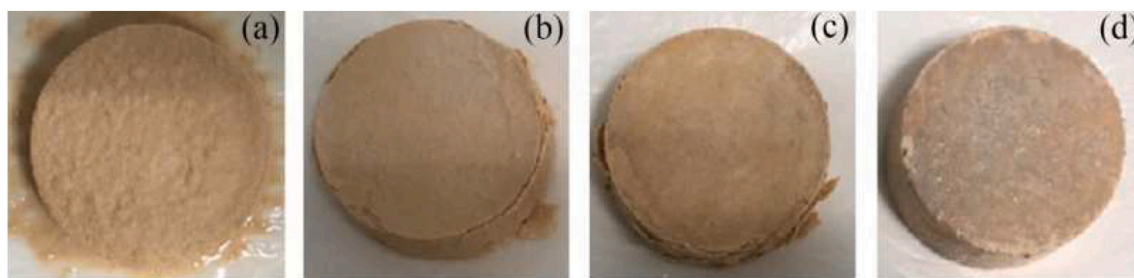


Fig. 13. The morphology of the samples with different concentrations of glass powder solution spraying after 96 h at 28 °C % R.H. [67].

Table 2

Characteristics of different types of emulsions [80].

Characteristics	Emulsion	Miniemulsion	Microemulsion
Thermodynamic stability	No	No	Yes
Stability lifetime	Seconds to months	Hours to months	Infinite
Droplet size range	1–10 $\mu\text{m}$	20–200 nm	10–100 nm
Polydispersity	Low	Very low	Very low
Typical particle size	1+ $\mu\text{m}$	100–300 nm	30–100 nm

polyacrylic acid and polyallylamine hydrochloride solutions for 10 cycles, then freeze-dried. The final product was determined to contain 88.6 % of core material, resulting in only a 10 % reduction in energy density compared with pure PCM. The encapsulated PCM withstood 100 thermal cycles with no leakage or thermal performance deterioration. The thermal degradation temperature indicates the EPCM could be used in broader applications than pure PCM. Researchers have applied this method to other types of organic PCMs. Yang et al. [75] and Zhang et al. [76] encapsulated tetradecane and octadecane using in-situ polymerisation and sonication methods, respectively. Both researchers observed a lower supercooling degree of the capsulated materials compared to the bulk material. Using sonication obtained smaller capsules (100–150 nm) with superior encapsulation efficiency (89.5 %). However, the capsule size did not decrease as a function of the sonication duration, perhaps because the elevated temperature of the solution due to the long processing time lead to particle aggregation [77]. Sanchez-Silva et al. [78] microencapsulated paraffin wax through suspension-like polymerisation using a copolymer of methyl methacrylate (MMA) and styrene as the shell material. The copolymerisation process was greatly affected by the monomer ratio modifying the morphology and the average diameter of the microcapsules. The kinetics of the copolymerisation process was controlled by the monomer due to high reactivity. In this way, as the number of MMA increased, the time required to reach the mean particle size decreased regardless of the amount of the core material. Al-Shannaq et al. [79] showed that homogeneous nucleation can be shell-induced by optimizing the shell composition and structure (no nucleating additives were needed), giving a strategy to minimise supercooling of PCMs by optimizing the shell composition and structure.

**4.2.1.1. Suspension polymerisation.** Suspension polymerisation is one of the most studied techniques, it is characterised by an immiscible reaction mixture, containing a suspension of droplets in a continuous phase (see Fig. 14). It is highly used for manufacturing polymers such as polyvinyl chloride (PVC), polymethyl methacrylate and polystyrene. Over time, suspension polymerisation has been also used to synthesise functional microspheres and recently, for micro PCM capsules [81]. Organic or water-insoluble PCM is desirable for this technique as it requires the formation of droplets. Further work has focused on the optimization of the shell by changing the shell material (inorganic, mono-polymer and co-polymer) and/or adding different crosslinking agents. Zhang et al. [82] prepared microencapsulated PCM based on paraffin

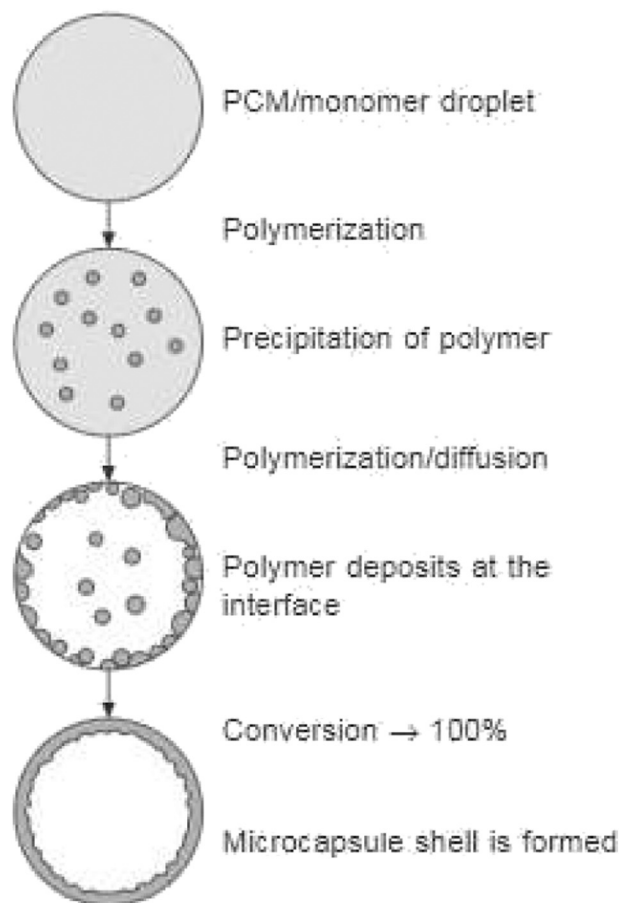


Fig. 14. Schematic of capsule formation during suspension polymerisation [81].

core and melamine-formaldehyde resin by the in-situ polymerisation method (Fig. 15), where graphene oxide (GO) was added. The obtained MEPCMs with GO were spherical with an average diameter of 6.32 to 15.89  $\mu\text{m}$  and were larger than MEPCMs without (5.63  $\mu\text{m}$ ). The novel MEPCMs exhibited better prevention of leakages (rate reduction of 93.1 % during 50 h tests) and a higher encapsulation rate of 93.9 wt%, which was considerably higher.

Konuklu et al. [83,84] in two different papers studied the microencapsulation of caprylic and decanoic acid, respectively. The authors encapsulated decanoic acid with polyurethane (PUF), polymer melamine foam (PMF), and phenol-melamine-urea-formaldehyde (PMUF) by in-situ polymerisation. The obtained decanoic acid/PUF microcapsules had a good thermal energy storage capacity, however, they did not have enough mechanical properties to avoid the decanoic acid leak from the core. The microcapsules broke during the charging process at 95 °C due to their thin wall shells. The authors recommended capric acid



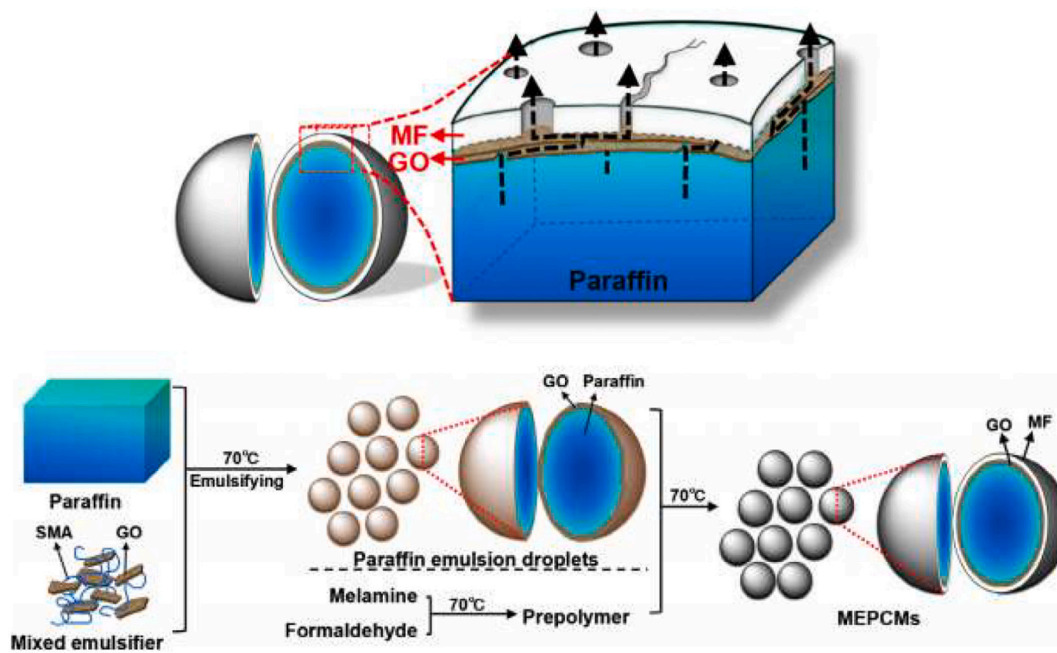


Fig. 15. Schematic for the MEPCM synthesis process in [82].

microencapsulated with PMUF, especially when synthesised with a binary surfactant system. A thermal storage capacity of around 88.75 J/g and 85.31 J/g was obtained and the microcapsules were thermally stable and leakage-free above 95 °C.

Li et al. [85] and Tyagi et al. [86] also reported microencapsulation methods for low-temperature PCMs (i.e. octadecane and paraffin kinds). Taguchi et al. [87] synthesised microcapsules absorbing n-pentadecane (PCM) and MMA (shell) into an oil-absorbable polymer. He investigated the effects of the volume of MMA absorbed and the soaking time on the formation of the PCM microcapsules and found out that the oil-absorbable polymer could absorb nine times the n-pentadecane weight and that the latent heat storage decreased from 107 J/g to 97 J/g, proportionally to the amount of MMA absorbed. Similar papers using poly-methylmethacrylate (PMMA) as the material shell for low-temperature encapsulation were reported in the following studies [88–91]. Chung chang et al. [92] encapsulated n-octadecane, by using PMMA network-silica hybrid as the shell material through the use of prepolymer solutions. The authors concluded that ageing conditions and the pH value in the aqueous phase affected the surface structure and the PCM content of the microcapsules. Following this, the most suitable outcome was achieved by adding 5 % of SiO<sub>2</sub> in microcapsules. Wang et al. [93] explored thermo-chromic properties as additional properties for microencapsulated capsules. The PMMA shells prepared by suspension polymerisation encapsulated n-octadecane, with both shell and PCM containing thermo-chromic pigments. The capsules presented a different colour depending on the temperature, which indicated either the thermal energy storage charge or discharge state. Qiu et al. [94] studied the microencapsulation of n-octadecane with different cross-linked MMA-based polymers (1,4-butylene glycol diacrylate (BDDA), divinylbenzene (DVB), trimethylolpropane-tri acrylate (TMPTA) and pentaerythritol tetra acrylate (PETRA) as different shell materials suspension-like polymerisation. They aimed to study the influence of the type and amount of crosslinking agent, the type of initiator and the polymerisation temperature on the properties of the EPCM. They concluded that by increasing the number of crosslinking agents and their cross-linkable functional moieties the heat storage capacity of the as-prepared microcapsules increased in. Nomura et al. [37] synthesised Al–Si alloy microspheres using Al<sub>2</sub>O<sub>3</sub> shells, obtaining high latent heat storage capsules with good durability. The MEPCM was prepared in two

steps, firstly, an AlO(OH) shell was formed shell on the PCM particles using a boehmite treatment, and then the shell was oxidated to form a stable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> by a heat-oxidation treatment in an O<sub>2</sub> atmosphere (see Fig. 16). Later on, they prepared the MEPCM with a void inside to allow for volume expansion during the solid-liquid phase transition, which resulted in a high-strength shell which show a high cyclability (300 cycles) [95]. The strength, physical. To produce PCM microcapsules by suspension polymerisation which were responsive to an external magnetic field, Lashgari et al. [96] added Fe<sub>3</sub>O<sub>4</sub> nanoparticles to the PCM. This study was done to give PCMs magnetic properties and allow a wider application scope.

Li et al. [97] used a similar procedure to encapsulate Al particles as PCM on a ceramic shell with a Cu outer layer shell. The synthesis contained three steps, starting with the formation of the boehmite shell around the Al particles, followed by a heating process to form Al<sub>2</sub>O<sub>3</sub> and finally, electroless plating to coat the MPCMs with Cu. The MPCMs reached a latent heat value of 223.4 J/g and after 10 cycles the shell surface showed a smooth and dense appearance. The performance after cycling was confirmed characterizing the melting point and latent heat, which kept constant.

**4.2.1.2. Interfacial polymerisation.** Interfacial polymerisation is another encapsulation method used, however, it is considered a more complex process than emulsion polymerisation. The wall formation is the result of the rapid polymerisation of generally hydrophilic and lipophilic monomers at the interface of an oil-in-water emulsion [40]. The droplets are first formed by emulsifying an organic phase (a core material and oil-soluble reactive monomers), which is usually isocyanate or acid chloride, in an aqueous phase. By adding then a water-soluble reactive monomer, the two monomers react at the interface of the droplets to form the polymer shell; the polymerisation reaction rapidly starts. Interfacial polymerisation or polycondensation is a commonly used method used for encapsulating a wide range of core materials such as oils.

Liang et al. [98] studied interfacial condensation, which is a kind of interfacial polymerisation method where polyurea, polyurethane, polyester, polyamide and amine resin were used as shell materials. In their study, they microencapsulated butyl stearate (PCM) by interfacial polymerisation with toluene-2,4-diisocyanate (TDI) and

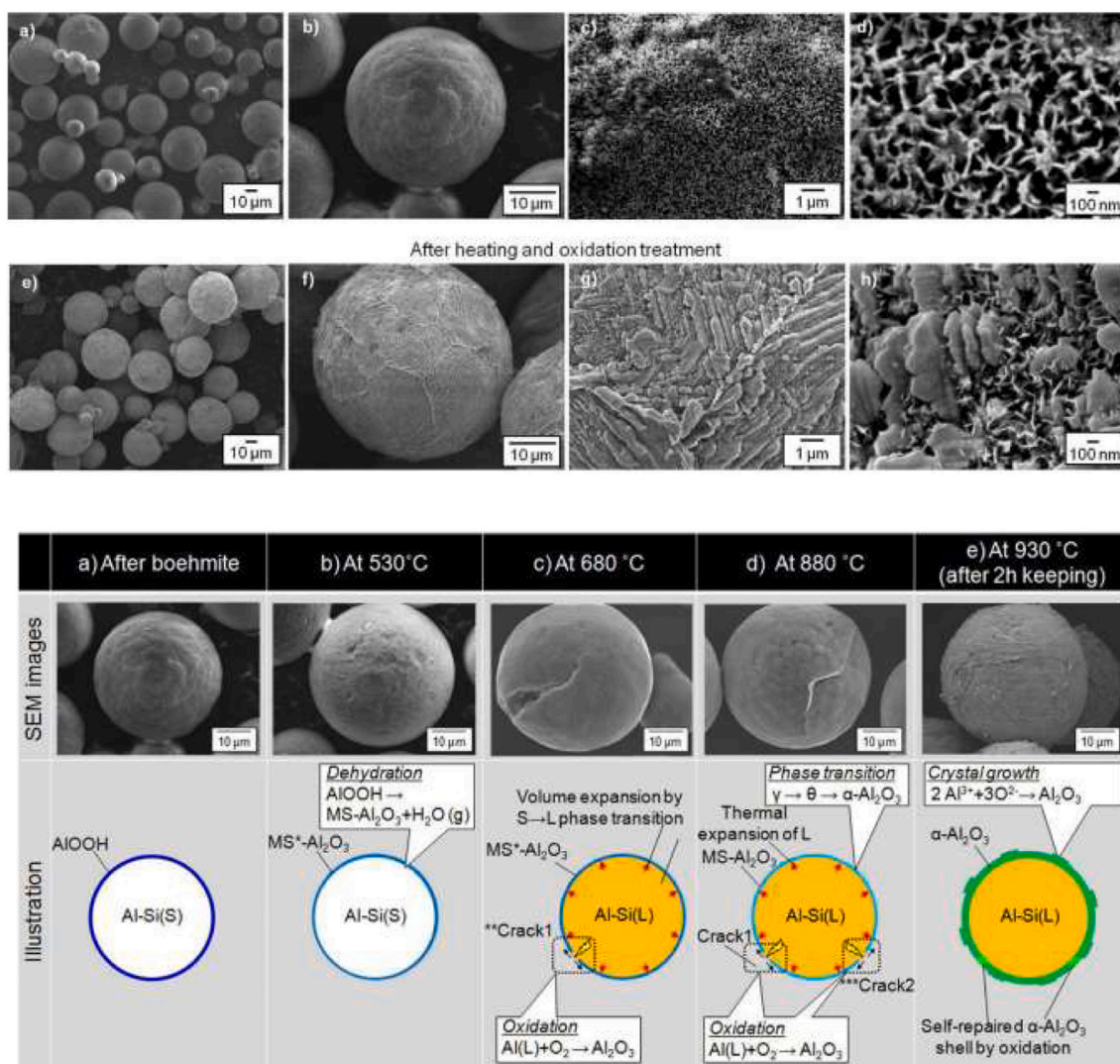


Fig. 16. Al–Si alloy synthesis process by [37] at different stages of the capsule's synthesis.

ethylenediamine (EDA) (monomers). The research showed that the micro-PCMs' phase change temperature was around 29 °C and the latent heat of fusion about 80 J/g. The particle size was in the range of 20–35 μm, and they had a good thermal performance when cycled.

Diamine water-soluble reactive monomers have also been used to produce shells to form PCM microcapsules using interfacial polymerisation. Park et al. [99] described the synthesis and characterisation of magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticle (NP)-embedded PCM nanocapsules (Mag-PCM) based on a paraffin core and polyurea shell (paraffin@polyurea), see Fig. 17. Both phases, hydrophobic and hydrophilic Fe<sub>3</sub>O<sub>4</sub> NPs were prepared for incorporation into the paraffin core and the polyurea shell, respectively. The magnetic-PCM nanocapsules were responsive to external magnetic fields due to the presence of the Fe<sub>3</sub>O<sub>4</sub> nanoparticles. The thermal conductivity of the nanocapsules increased with the amount of Fe<sub>3</sub>O<sub>4</sub> NPs incorporated, which resulted in the PCM nanocapsules displaying a smaller degree of supercooling.

Zhang et al. [100] synthesised microencapsulated n-octadecane using silica (TEOS) as the shell of different weight ratios modifying the pH through interfacial polycondensation. The microcapsules successfully confined the PCM while the thermal conductivity was improved and the phase change properties remained constant. The pH of the solution and the amount of the shell material during the interfacial condensation were controlled. Also, Fang et al. [101] studied the nanoencapsulation of n-tetradecane as PCM for thermal energy storage, see

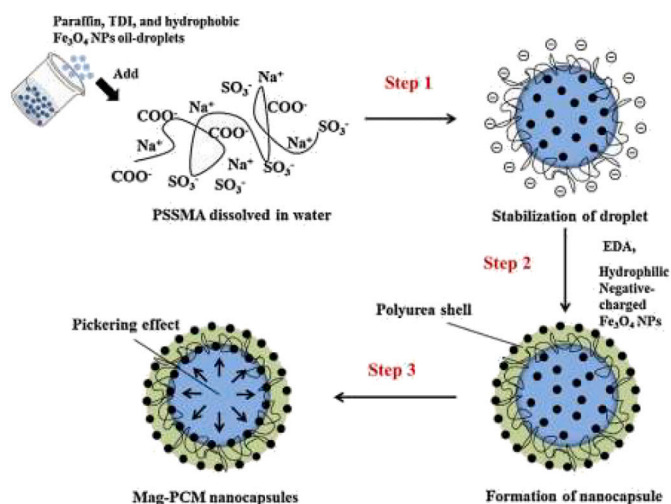


Fig. 17. Schematic illustration of the preparation of magnetic -PCM nanocapsules by interfacial polycondensation [99].

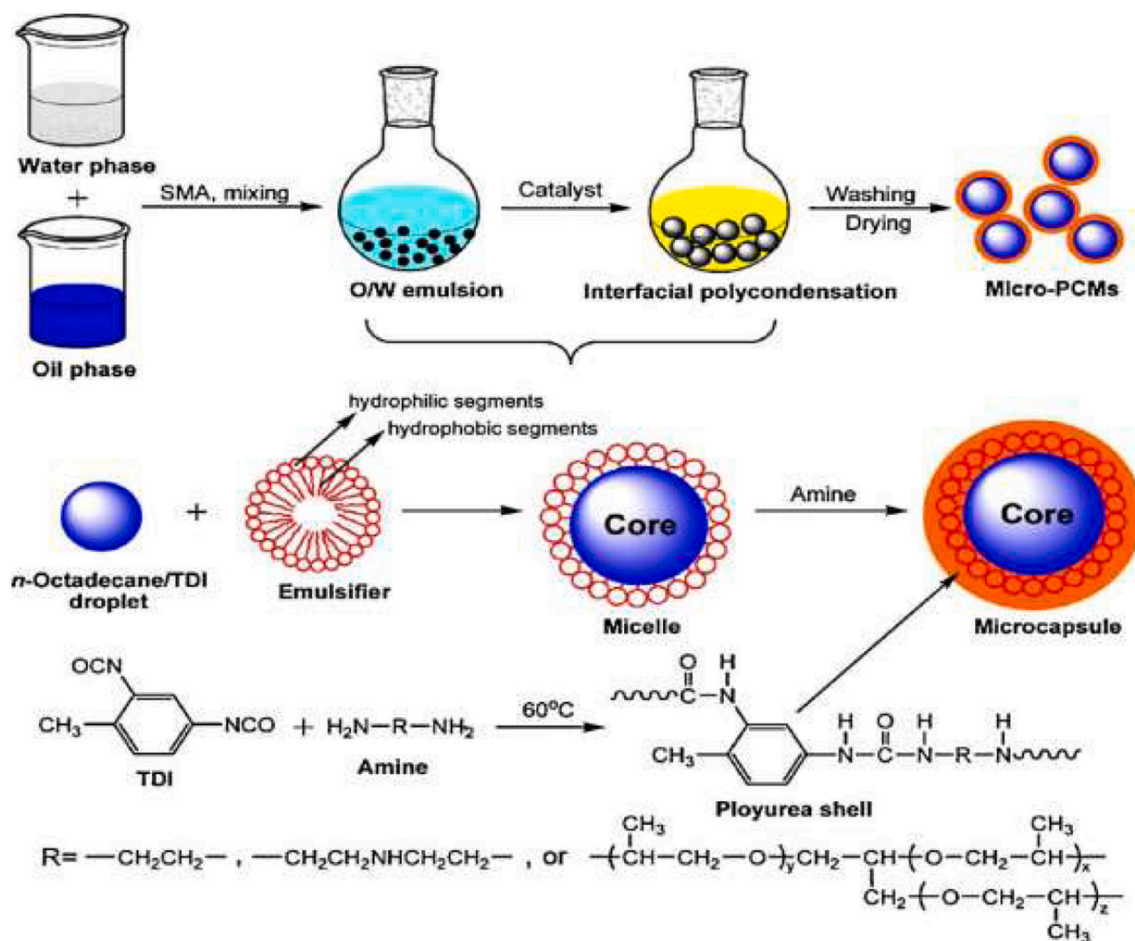


Fig. 18. Schematic of the formation of the microencapsulated n-octadecane with polyurea shells containing different soft segments through interfacial polycondensation [101].

Fig. 18 by in situ polymerisation. N-tetradecane was selected as the core material, urea and formaldehyde the precursors of the shell and sodium dodecyl sulphate as the emulsifier; resorcin was used as the system modifier. The authors controlled the size of the nanoparticles by stirring the solution at a constant 1500 rpm, a suitable rate to obtain nanoparticle size. The modifier increased, resorcin from 0.25 % to 5 %, which led to an increase in the mass ratio of n-tetradecane from 30.4 % to 61.8 %. The authors proposed this method to encapsulate different oil-phase organic compounds.

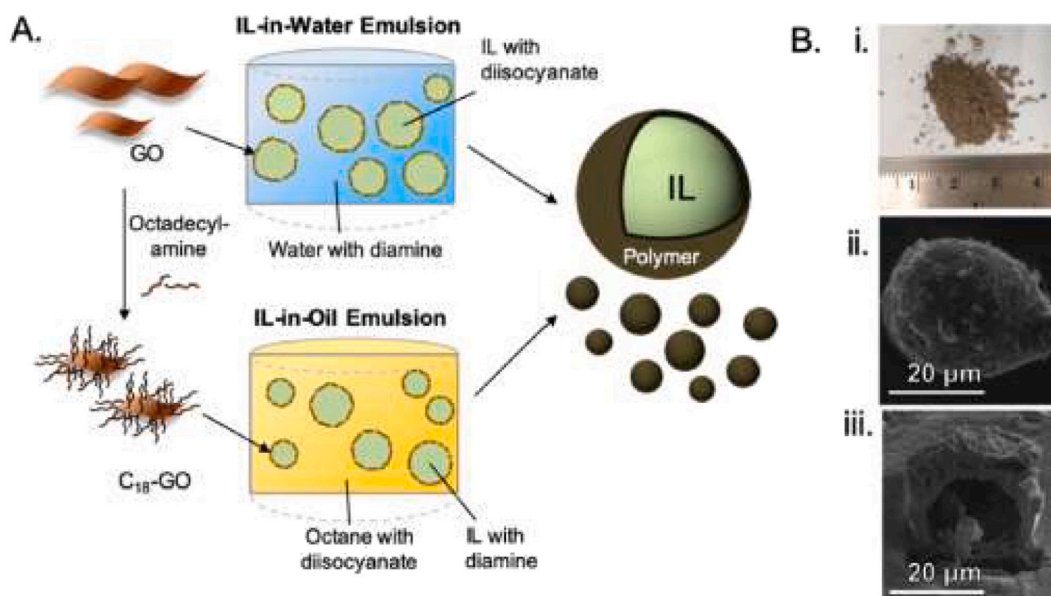
**4.2.1.3. Emulsion polymerisation.** Emulsion polymerisation processes have been widely used to manufacture a wide range of polymers such as adhesives, binders, paints (used for nonwoven fabrics), additives (used for textiles, paper and construction materials), impact modifiers (applicable for plastic matrices and diagnostic tests), drug delivery systems and so many other applications [102]. Emulsion polymerisation encompasses several different related processes which include conventional emulsion polymerisation, inverse emulsion polymerisation, dispersion polymerisation, micro-emulsion polymerisation, mini-emulsion and suspension polymerisation. This section is focused on the Pickering emulsion process, a specific type of emulsion polymerisation where stabilization is promoted by the adsorption of solid particles (for example colloidal silica) on the interface. Among emulsion polymerisation techniques, Pickering polymerisation has attracted increasing interest recently, because surfactants are replaced by solid particles. It is a simple and robust template for the preparation of micro-PCMs [103]. Compared to the above emulsification methods the formation of Pickering emulsions requires a considerably lower amount of

surfactant. The high material-to-surfactant ratio leads to no surplus surfactant remaining in the continuous phase. For quite a long time, several types of inorganic particles have been used to stabilise Pickering emulsions, such as ZnO, TiO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>. In recent years, GO has gradually been introduced as a stabilizer to fabricate colloidal particles based on Pickering emulsions.

Luo et al. [104] explored the encapsulation of ionic liquids using the Pickering emulsification method, choosing carbon nanosheet as the surfactant. The shell was formed by interfacial polymerisation of two reagents which are present separately in dispersed and continuous phases, for instance, di-isocyanates and diamines. This approach enables the formation of both material-in-water and material-in-oil emulsions, even if the encapsulated material is hygroscopic, see Fig. 19. The encapsulation is a one-step reaction with no formation of by-products. The capsules obtained were robust, showing no leakage after post-processing filtration and vortex. In addition, the encapsulated materials were in powder form and therefore easy to handle [104]. Researchers have successfully demonstrated this encapsulation technique to the field in applications such as energy storage [105], contaminant removal [106] and CO<sub>2</sub> sequestration [107].

Yin et al. [108] also confirmed Pickering emulsion polymerisation is a robust way of synthesising polymer-SiO<sub>2</sub>-coated microcapsules. Pre-modified SiO<sub>2</sub> was suspended in the oil phase with a ratio of 2:1 (v/v), and ultrasounds were then applied to obtain Pickering emulsions. 1 ml of NaNO<sub>2</sub> dilute solution was next added to the emulsion to prevent radical polymerisation. Capsules were separated from the suspension after conditioning at 60 °C for a day. The microcapsules produced contained a high proportion of PCM (62.8 %), the method was highly





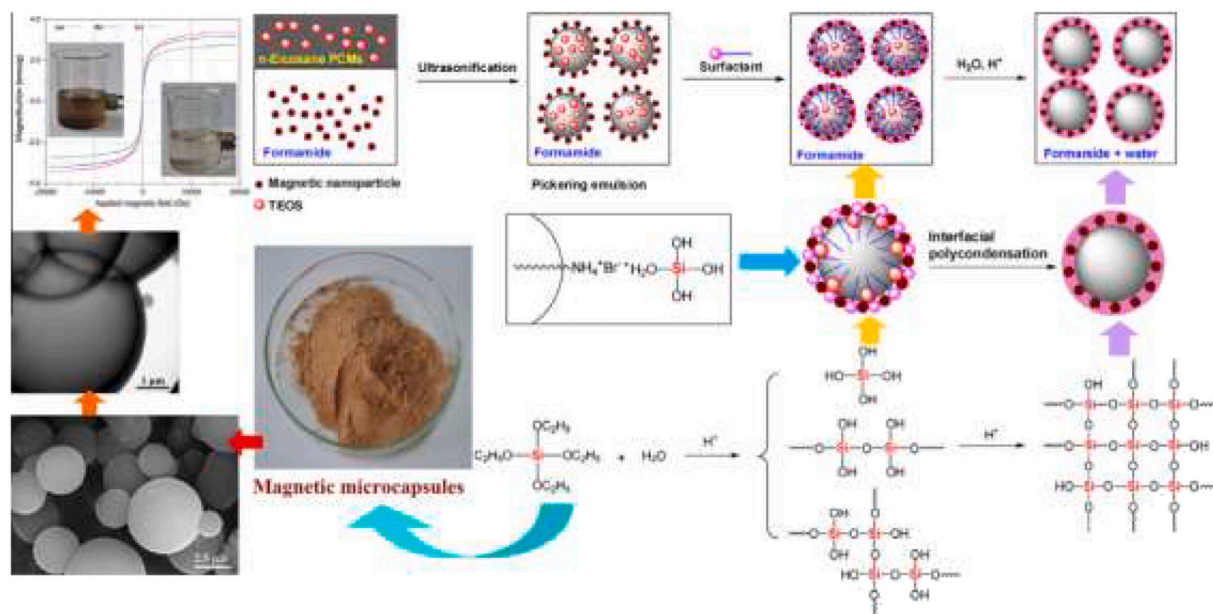
**Fig. 19.** (A) Illustration showing our preparation of IL capsules using IL-in-water and IL-in-oil Pickering emulsions and GO-based particle surfactants along with interfacial polymerisation. (B) (i) isolated IL capsules, (ii) SEM image of a IL capsule, and (iii) SEM cross-sectional image of a IL capsule [104].

efficient (94 %), and the microcapsules had outstanding thermal stability, which showed no chemical degradation after 2000 thermal cycles.

Zhang et al. [103] used Pickering emulsion templating to prepare a microencapsulated PCM (n-hexadecane) with double-walled shells (polystyrene/GO). GO nanosheets were modified by the polycondensate of diethanolamine and adipic acid. Using GO as the Pickering stabilizer, the authors successfully fabricated hollow microspheres, with a high relative encapsulation ratio (78 %) because of the efficient stabilization of modified graphene oxide. Jun-Feng Su et al. [109] prepared a series of PU-shell microPCMs containing n-octadecane. The particle size distribution was properly controlled by employing an emulsion-stirring rate of between 1000 and 4000 rpm. They concluded that the optimum emulsion-stirring rate was 3000 rpm as it does not significantly affect the thermal transmitting properties of the encapsulated PCM. Jiang et al.

[110] also used this polymerisation technique starting with the preparation of a Pickering emulsion stabilized with magnetic particles. The designed magnetic microcapsules are based on an n-icosane core and Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> hybrid shell as a new type of dual-function phase change material, see Fig. 20. They designed a two-step route to fabricate a Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> hybrid shell on the surface of the n-icosane core so that the magnetic Fe<sub>3</sub>O<sub>4</sub> domain could be protected by the silica matrix and avoid its transformation to hematite due to its oxidation when exposed to air.

**4.2.1.4. Self-assembly method.** Yu et al. [111] used calcium chloride (CaCl<sub>2</sub>) to microencapsulate n-octadecane forming calcium carbonate (CaCO<sub>3</sub>) shells through the self-assembly method, Fig. 21. The n-octadecane/CaCl<sub>2</sub> mass ratio used ranged from 30/70 to 50/50. The microcapsules obtained had a perfect spherical morphology with a well-



**Fig. 20.** Winterisation process of the Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> hybrid shell of magnetic microcapsules [110].



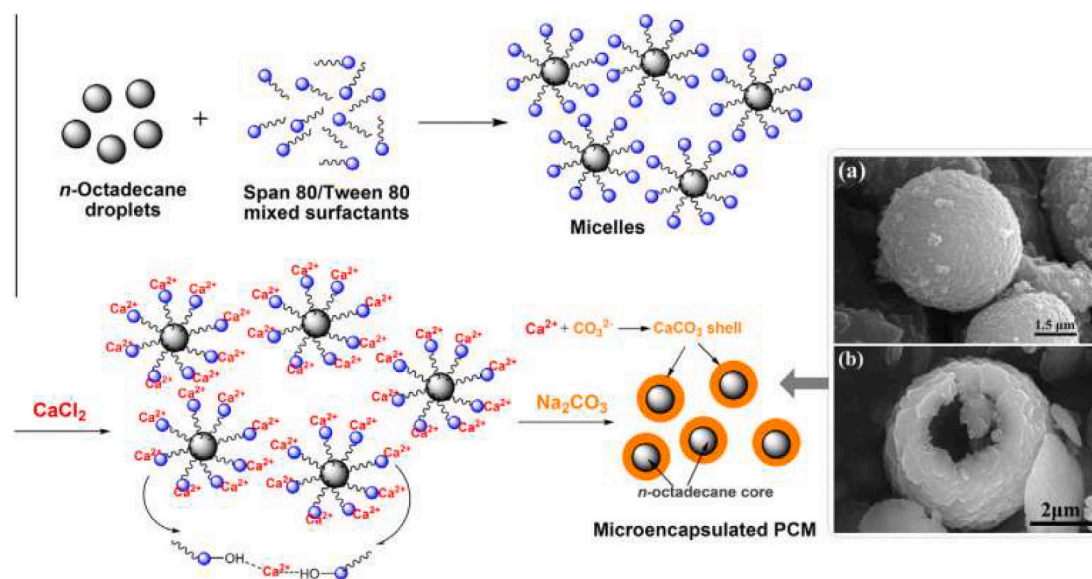


Fig. 21. Schematic for the synthesis of n-octadecane/ $\text{CaCl}_2$  microcapsules [111].

defined core-shell microstructure. The  $\text{CaCO}_3$  inner wall induced  $\alpha$ -form crystallization of n-octadecane by heterogeneous nucleation achieving a higher crystallinity. The process achieved high encapsulation efficiency and the microcapsules had good phase-change performance and high thermal storage capability. The  $\text{CaCO}_3$  shell leads to high thermal conductivity, a good anti-osmosis property, and long-term serving durability.

Also, Wang et al. [112] successfully synthesised micro-PCMs with binary cores using  $\text{CaCO}_3$  as the shell by the self-assembly method. The phase change temperature of the microcapsules could be adjusted from 25 to 50 °C by changing the weight ratio of the binary core. DSC results indicated that the microcapsules' binary core content was in the range of 55.7–59.4 %. TGA showed that the mass loss of the microcapsules was between 5 % and 28 % when heated to 400 °C.

#### 4.2.2. Physico-chemical

**4.2.2.1. Sol-gel encapsulation.** The sol-gel method can be used to prepare microcapsules, by forming a solid shell through the gelation of a colloidal suspension. This suspension, which is often a solution, is prepared, to begin with from a molecular precursor, such as a metal alkoxide [113]. Microencapsulation technologies utilizing the sol-gel method have been used for silica or other inorganic materials shells. During the encapsulation method, an oil-in-water (O/W) emulsion route has been shown to offer an easy way to control the spherical morphology and size distributions [114]. Wang et al. [50] are some of the first researchers to apply the sol-gel technique to prepare microcapsules for energy storage studies. A fixed ratio of PCM n-pentadecane/TEOS was added slowly over half an hour to a solution that contained emulsifier and HCl (different concentrations), and then the mixture was continuously stirred for 2 h before the ageing step (5 h). The particles were separated, filtrated, and dried at room temperature. The results suggested that cationic emulsifiers should be chosen for encapsulation in acidic conditions. Yu et al. [115] also studied the impact of different types of emulsifiers on the encapsulation process of an n-dodecanol-emulsifier-melamine-formaldehyde (MF) system but using the mechanical emulsification method. A conflicting result was obtained. The anionic emulsifier was preferred in their encapsulation process conditions. And Chai et al. [116] investigated a novel bifunctional microencapsulated PCM (n-eicosane) with a crystalline titanium dioxide ( $\text{TiO}_2$ ) shell through in-situ polycondensation in a sol-gel process. In Chai's work, tetrabutyl titanate (TBT) was used as the titania precursor,

they successfully synthesised the microcapsules with a well-defined shell structure. The thickness of the shell could be controlled by the weight ratio of n-eicosane/TBT added during the synthesis, see Fig. 22.

To further expand the sol-gel encapsulation technique to high-temperature applications, an intermediate sacrificial layer is required for fabricating the sol-gel capsules, which prevents interactions between the PCM and the sol-gel. The materials applicable for forming the sacrificial layer are often polymers that decompose to gas below the phase change temperature of the core material, such as PMMA and polyethyl methacrylate (PEMA). Fig. 23 demonstrates the procedure of sol-gel encapsulation of NaCl that was designed by Arconada et al. [117]. The researchers selected an inorganic PCM and organic binder, which were mixed with a fixed proportion of water and compressed by a stainless-steel pelletizer. Afterwards, the PCM pellets underwent a thermal treatment and fast cooling to ambient temperature. Then, the pellets were impregnated in a homogeneous mixed polymer solution following a filtration process. A layer of pre-prepared sol-gel was then deposited onto the dried polymer layer of the pellet. Finally, the encapsulated PCMs were heat-treated in the air at a suitable high temperature to burn off the polymer layer. Experimental results illustrated a structural deformation of the  $\text{SiO}_2$ -encapsulated PCM capsules after five

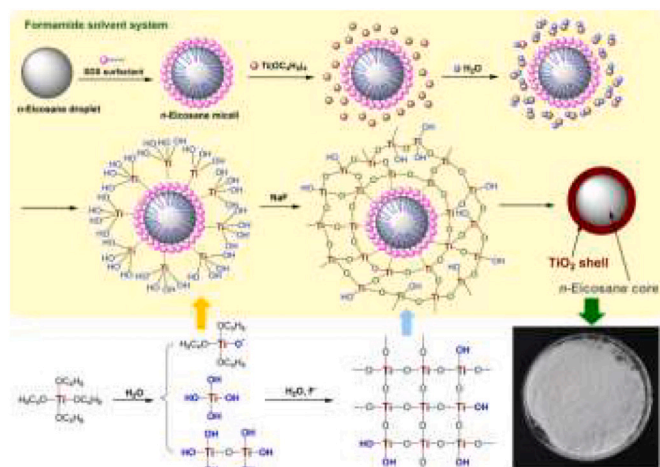


Fig. 22. Schematic of the novel bifunctional microencapsulated PCM [116].

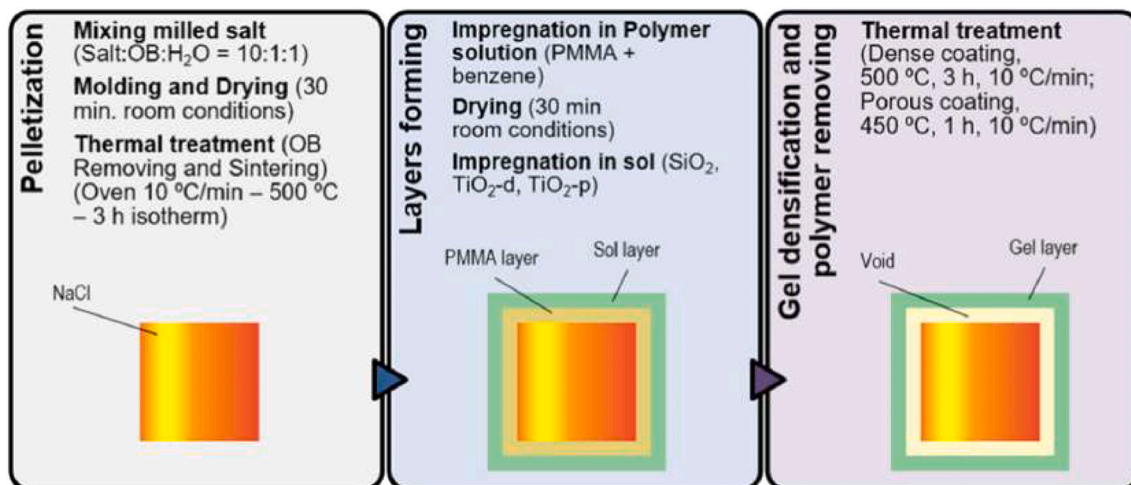


Fig. 23. Experimental procedure for NaCl macro encapsulation [117].

thermal cycles (25–850 °C). An energy density reduction in both TiO<sub>2</sub> and SiO<sub>2</sub> encapsulated PCM was noticed during the thermal cycling but proved less significant for the former. The authors believe with further optimisation of the encapsulated structure, this method will have great potential. Encapsulation of KNO<sub>3</sub> took place following a similar process concept (Fig. 23). The author aimed to complete 10 thousand thermal cycles (250–400 °C) which is equivalent to a 30-year lifespan, but stopped after 25 % of this goal was achieved [24].

Zhang et al. [118] reported the microencapsulation of LiNa and SiO<sub>2</sub> using polyvinylpyrrolidone (PVP) as the surfactant, see Fig. 24, targeting their use as a passive thermal storage medium for CSP applications. The authors concluded that the microcapsules were thermally stable for 10 cycles with an encapsulation ratio of 61.2 % and a latent heat of over 220 J/g at 498 °C. The LiNa microcapsules showed an enhanced effective heat capacity of 134.4 % compared to the best-commercialized product.

Zhang et al. [119] used a eutectic salt (Na<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub>) with MgO as the matrix material and tetraethyl orthosilicate and tetrabutyl titanate as precursors of the sol-gel method. They prepared two different solutions with TiO<sub>2</sub> and SiO<sub>2</sub>. The eutectic salt (Na<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub>) was added to the previously prepared sol solutions using PVP as the surfactant and dried in a vacuum drying chamber for 12 h before finally being given 20 min of ultrasonic vibration. They studied different concentrations, 1.5 wt% and 3 wt%, for both SiO<sub>2</sub> and TiO<sub>2</sub>. The main outputs of the study were regarding the thermal conductivity and the latent heat storage; the

former increased by 10 % for the SiO<sub>2</sub> solutions and 16 % for the TiO<sub>2</sub> solutions; while the latent heat loss was around 4.10 %.

Romero Sanchez et al. [36] synthesised sodium nitrate (NaNO<sub>3</sub>) microcapsules with SiO<sub>2</sub> shells using two different surfactants: hexadecyltrimethylammonium bromide (CTAB) and Span 80. The authors concluded that the maximum working temperature affected greatly their thermal stability depend, alongside other factors, on. Temperatures higher than 400 °C led to the dissociation of NO<sub>3</sub><sup>-</sup> to NO<sub>2</sub><sup>-</sup> and therefore to a modification of the NaNO<sub>3</sub> TES properties. This study showed sol-gel as a feasible method for the microencapsulation of NaNO<sub>3</sub> using SiO<sub>2</sub> as shell material, although the SiO<sub>2</sub> shell may affect the NaNO<sub>3</sub> crystal growth. During the microcapsule formation, parameters such as concentration, temperature, time, etc. greatly affected the effectiveness of microencapsulation. On account of this, further work has to be done to analyse the influence of the NaNO<sub>3</sub> crystal phase on the energy storage capacity of SiO<sub>2</sub> shell microcapsules.

Another alternative to sol-gel encapsulation is to avoid the use of a surfactant. Although encapsulation using surfactants is a simple technique, the low thermal conductivity of the surfactant results in an increase in thermal resistance, thereby reducing thermal transport efficiency. Lee and Jo [120] studied the surfactant-free microencapsulation of NaNO<sub>3</sub>@SiO<sub>2</sub> microcapsules synthesised by the sol-gel method without using surfactants, see Fig. 25, reaching high encapsulation rates (89 % on average).

Park et al. [121] also developed a synthesis route to avoid

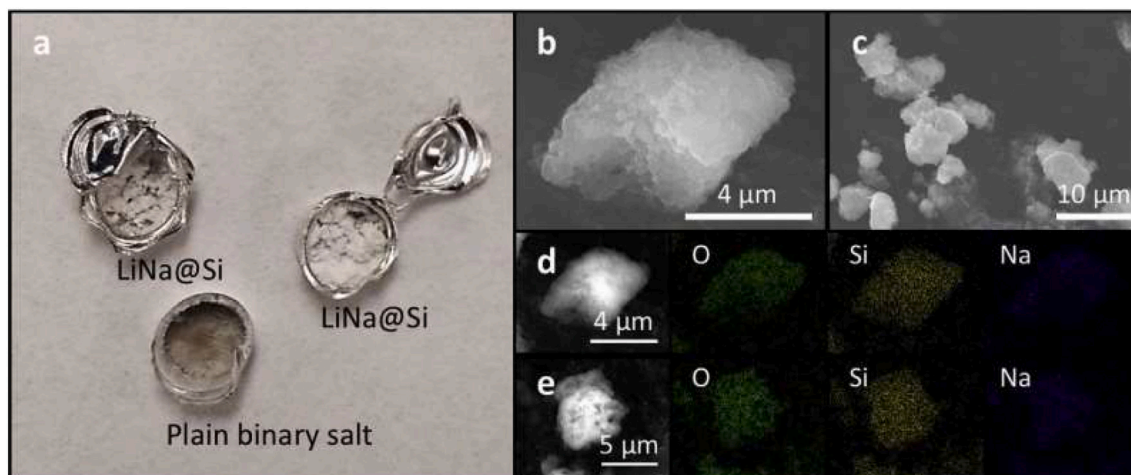


Fig. 24. Thermal stability of MEPCM after 10 cycles a) photos of DSC pan opened immediately after thermal cycling; b-c) SEM images and d-e) X-ray mapping [118].

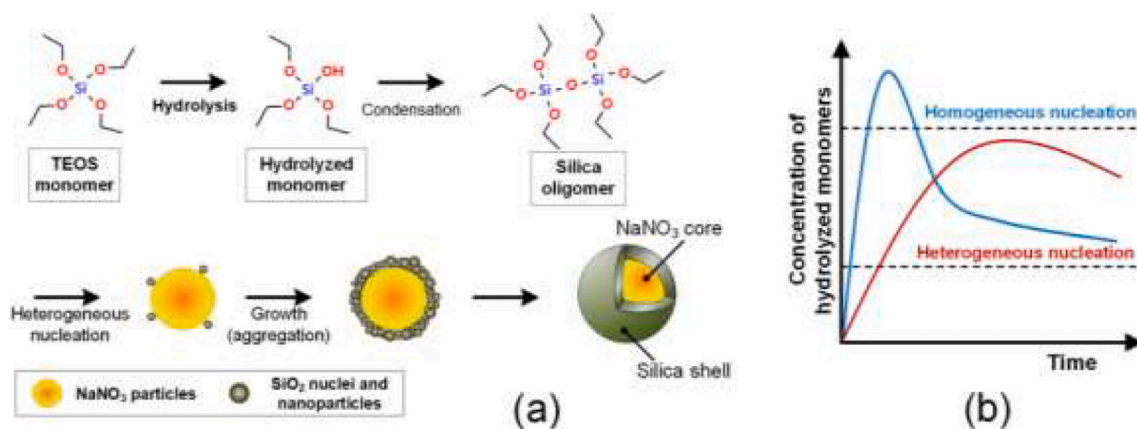


Fig. 25. Schematic diagram showing (a) NaNO<sub>3</sub>@SiO<sub>2</sub> microcapsule synthesis by heterogeneous nucleation, and (b) plots of different nucleation behaviours [120].

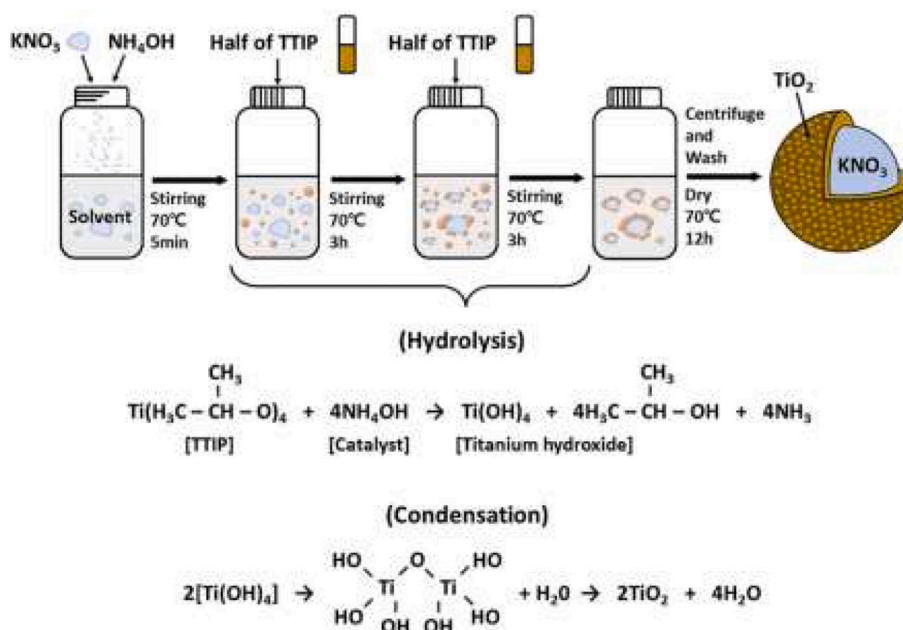


Fig. 26. Schematic diagram of KNO<sub>3</sub>@TiO<sub>2</sub> microcapsule synthesis by sol-gel without surfactant [121].

surfactants, which have lower decomposition temperatures than high-temperature PCMs, see Fig. 26. When surfactants remain at the surface of the shell, they can affect their cyclic stability by creating porous on the capsule, which deteriorates the capsules' mechanical integrity and makes them more prompt to break (PCM leakage). Their study used different solvents (acetone, ethanol, and isopropanol) to produce KNO<sub>3</sub>@TiO<sub>2</sub> microcapsules with an enhanced thermal conductivity than the pure salt. The size of the MPCMs depended on the solvent, with the largest particles (437 ± 70 nm) using ethanol and the smallest ones (188 ± 24 nm) using acetone as solvent. The cyclability study with 100 cycles showed no decrease in latent heat (around 70 J/g).

**4.2.2.2. Complex coacervation.** Coacervation is the most widespread technique for preparing microcapsules for textiles [1]. This approach is based on the decrease of solubility of the coating polymer by the addition of a third component to the organic solvent solution, then a coacervate is formed around an active core between oppositely charged polymers. Complex coacervation is based on the interaction of two oppositely charged polyelectrolytes, the dispersed core material is added to the polymer solution over a narrow pH range, and the mixture is then suspended in an aqueous phase containing a surface-active agent. In

general, complex coacervation is initiated by a change in pH or temperature and the addition of a non-solvent or electrolytic compound that forms two-phase coacervates that precipitate due to the repulsion with the solvent. Hawlader et al. [19] compared complex coacervation and spray drying for paraffin wax microencapsulation. From the study, they concluded that the microcapsules had high energy storage and release capacities (145–240 J/g) when following the coacervation method. SEM profiles showed that the microcapsules were spherical with a uniform size distribution. The microcapsules showed an energy capacity dependence with the core-to-coating ratio and a microencapsulation efficiency dependence with the process parameters (core-to-coating ratio, emulsifying time and the amount of cross-linking agent). Onder et al. [122] also encapsulated three types of paraffin waxes (n-hexadecane, n-octadecane and n-nonadecane) using complex coacervation methods achieving microcapsules with high heat storage capacities. The coacervates of n-hexadecane, made at low, medium and high percentages; and n-nonadecane, made at medium percentages, performed well in terms of energy absorption, as DSC analysis showed. The achieved enthalpies were found to be proportional to those of the pure PCMs. FT-IR results proved successful complex coacervation of PCMs.



**4.2.2.3. Solvent evaporation.** Wang et al. [18] modified a solvent evaporation method by adding a heating curing step to obtain AL-Si@SiCn microcapsules, see Fig. 27. The shell material encapsulating the metallic Al–Si PCM was achieved using a polysilazine binder (OPSZ), which is able to adhere strongly to metals, glass, ceramic or organic surfaces. When heated, polysilazane forms a cross-link and transforms into a solid inorganic shell. Using organic polysilazine (OPSZ), a SiCN ceramic layer with ultra-high heat resistance (up to 1800 °C) is formed. The microcapsules formed had a diameter ranging from 5 to 500  $\mu\text{m}$ , a melting point around 575 °C and an enthalpy of 200–290 J/g. Although losing thermal storage properties compared to the pure PCM, cyclability was improved reaching just 3–5 % thermal storage performance instead of 13–19 % in some formulations after 50 cycles.

#### 4.2.3. Physico-mechanical

**4.2.3.1. Spray drying.** Spray drying is another widely used technique in many sectors, as it provides rapid evaporation of the solvent and maintains a low particle temperature during the process. Spray drying consists of the atomization of an emulsion or suspension of a shell and core material mixture. The preparation of the emulsion or suspension is done through intense homogenization [2]. This technique produces dry powder from a liquid or slurry, which makes it ideal for thermally-sensitive materials that may require extremely consistent, fine particle size. The spray-dry process has been utilized extensively in food and pharmaceutical technology but not in thermal energy storage, although at an industrial scale, it offers lower production costs, limited loss of raw materials and process waste, and ease of control and scalability to large continuous processes [123]. In general, polymers are normally the preferable materials utilized as shells; however, for spray drying stable and non-toxic inorganic materials are preferred, such as silica. Methapanon et al. [123] studied the microencapsulation via sol-gel emulsion and spray-drying of methyl palmitate and n-octadecane using silica as the shell. The material had the potential to be used as a thermal energy storage material for passive cooling applications. The authors concluded that the surfactant concentration influenced the size of the emulsion droplets and the encapsulation efficiency, for both PCMs. The highest PCM encapsulation efficiency was achieved with a PCM/silica weight ratio of 0.25; additional PCM did not remain inside the capsules.

Zhang et al. [25] considered using metals as PCMs for high-temperature energy storage due to their excellent thermal conductivity and good energy density. Copper was pre-treated with a strong acid to remove the oxidised surface. Chromium and nickel were then sequentially electrodeposited onto the cleaned copper with two different periodic-barrel electroplating instruments. The bilayer electroplating process took >200 h, and the thickness of the shells was time-dependent. SEM-EDS revealed the bilayer shell was uniformly and firmly coated to the outside of the PCM and no porosity was found in the shell structure. The encapsulated copper had a 53.2 J/g energy density which could be altered by adjusting the weight percentage of the coating layers. After 1000 thermal cycles, no leakage occurred. However, after cycling, the outer Ni layer decreased in thickness due to the gradual growth of a NiO layer, the Cr layer cracked and additionally, there was the formation of a brittle ternary Cu-Cr-Ni alloy during the high-temperature period. That ternary layer could not accommodate the volume change and so a gap formed between the shell layers, see Fig. 28.

Prior to spray drying, the green solvothermal technique can be introduced as an additional step, where the temperature is the main parameter that influences the phase composition of the microencapsulated powder. Romero-Sanchez et al. [124] prepared a microencapsulated  $\text{KNO}_3$  with solvothermal technology using ZnO as the inorganic shell material (see Fig. 29).  $\text{KNO}_3$  was dissolved in water (solubility 31.6 g  $\text{KNO}_3$ /100 mL water) and spray dried in a LabPlant system through a 0.5 mm nozzle using a hot air jet at 200 °C, to transform the acicular shape crystals into spherical particles with average sizes of 50  $\mu\text{m}$ . The spherical particles were dispersed in ethyl alcohol by mechanical stirring at a concentration of 0.16 g  $\text{KNO}_3$ /100 mL. The Zn  $(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  powder was then dispersed in the ethyl alcohol solution at the desired mass ratio. The solution pH was adjusted by adding  $\text{KNO}_3$  solution in ethyl alcohol, and then the suspension was poured into the Teflon vessel of an autoclave (Berghof, Germany) and solvothermal treated for 2 h at different temperatures, under 40 atm Ar pressure. The main conclusions of this study are that  $\text{KNO}_3$  particles were covered by ZnO microcrystals and displayed thermal properties during the phase transition similar to those of raw  $\text{KNO}_3$ , thus indicating the feasibility of  $\text{KNO}_3$ -ZnO microencapsulation by the solvothermal method. It was concluded that by increasing the solvothermal temperature up to 250 °C, the formation of the metastable phase zinc hydroxinitrate with different  $\text{NO}_3$ : $\text{H}_2\text{O}$  ratios was suppressed. It was observed that the microcapsules

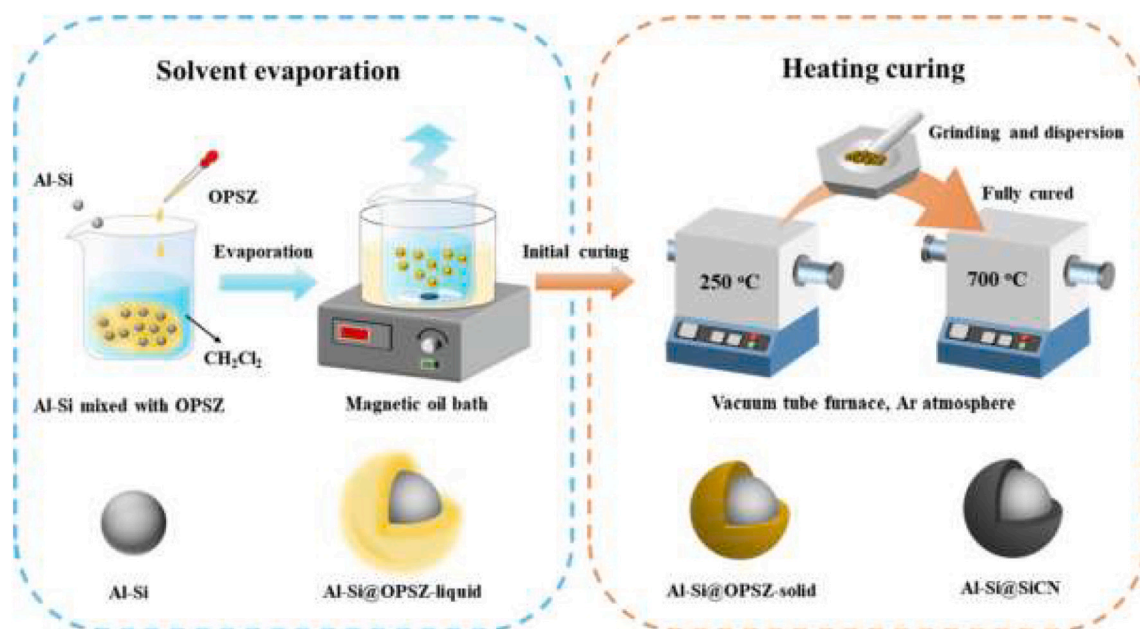
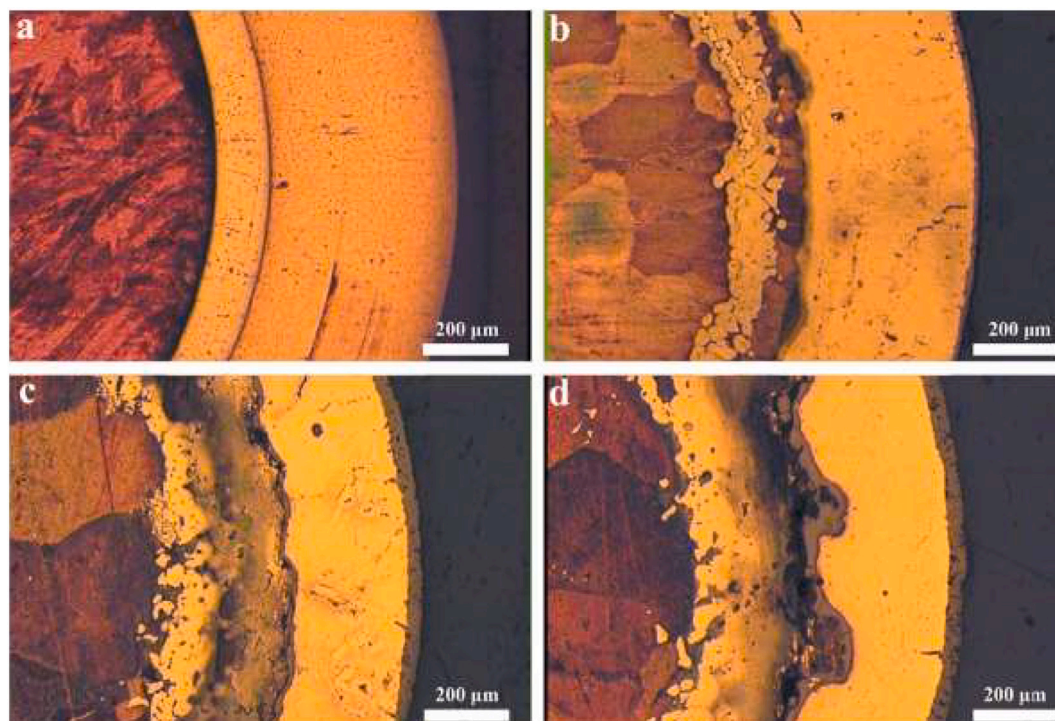
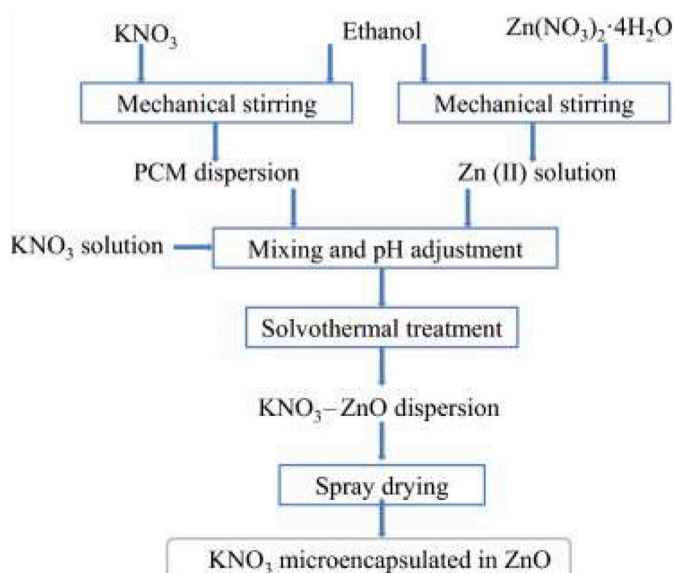


Fig. 27. Modified solvent evaporation method to produce metallic-PCM microcapsules [18].





**Fig. 28.** Cross-sectional morphology changes of capsules after different numbers of charge-discharge cycles between 1050 °C and 1150 °C: (a) 0 cycles, (b) 10 cycles, (c) 50 cycles and (d) 100 cycles [25].



**Fig. 29.** Experimental procedure for green solvothermal-spray drying [124]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

obtained by spray drying using a 1 mm nozzle size had the highest flow speed and so therefore all further microcapsules were prepared to employ these conditions.

#### 4.2.4. Multi-functional MPCMs

In this section, the authors have gathered modified encapsulation strategies that fall outside the categories provided in previous sections, e.g. a modified route or novel material choices from the ones considered above. Micro and nanoencapsulation allow complex compositions to be obtained where the PCM capsules, besides storing thermal energy, can

extend their range of possible applications through other features. Some different PCMs with increased functionalities are those that present magnetic properties, convert solar radiation into heat, have thermochromic or antibacterial properties [22], or provide microcapsules with fire-retardant properties [125]. Demirbağ et al. [125] prepared microcapsules with fire-retardant properties as additives for thermal comfort in textile applications by the coacervation method. During the process, clay nanoparticles were added to the solutions to provide flame-retardant properties. The microcapsules had good thermal stability during the textile manufacturing process and significantly better flame-retardant properties than the ones without fire-retardant.

Different researchers use multi-functional micro/nanocapsules to produce materials with thermoregulating (PCM) and radiation-related functions. Wang et al. [126] prepared nano-encapsulated PCMs with silicon carbide nanoparticles that increased the thermal conductivity and the capacity of the nanocapsules to convert NIR light to heat. Ma et al. [127] also prepared microencapsulated PCMs with photo-thermal conversion and thermal energy-storage capabilities. TiO<sub>2</sub> shells with modified GO) were used to encapsulate paraffin by in-situ polymerisation. The latent heat of the composite was 74.99 J/g and the encapsulation efficiency was 37.93 %. The microcapsules had better thermal stability than pure paraffin and higher thermal conductivity than water. It was possible to improve their properties even further improved by modifying the GO present in the TiO<sub>2</sub> shell. The resulting microcapsules became a promising candidate for solar energy storage in direct absorption solar collectors. And Du et al. [128] selected long-chain curing agents to form microcapsules based on the increased flexibility of the epoxy shells. The methyl palmitate PCM MPCMs were synthesised using in-situ polymerisation and photochromic dyes possessing UV absorption ability and photochromic performance were added, see Fig. 30. The energy storage capacity of the capsules ranged from 175 to 120 J/g with a melting-solidification ranging from 27 to 40 °C.

Other researchers like Tsuneyoshi et al. [129] prepared microcapsules with magnetic applications. Specifically, they formed metal-coated microcapsules, which contained metallic shells with tuneable magnetic properties. The microcapsules were prepared by phase separation and

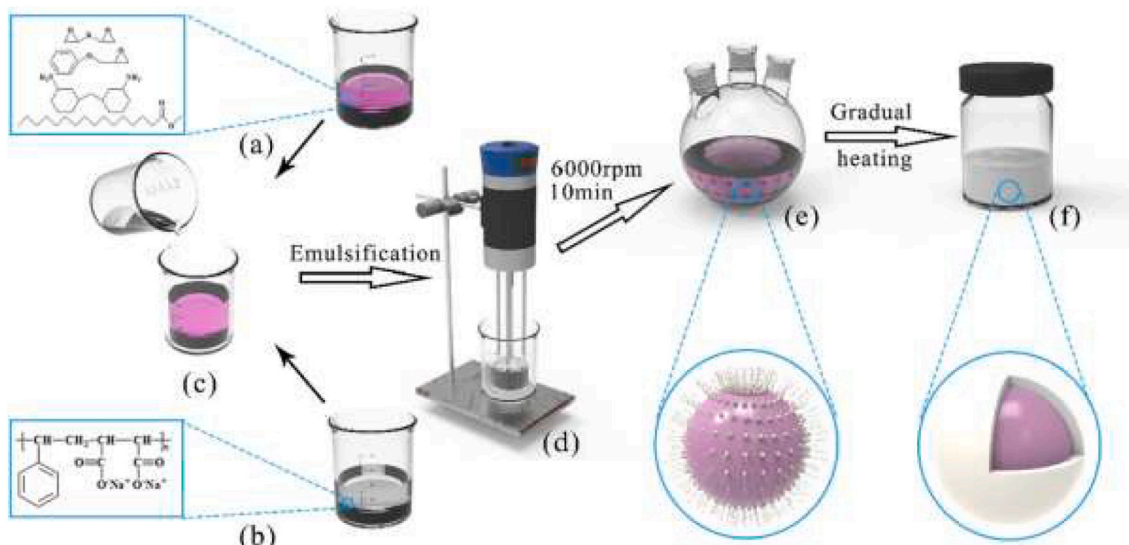


Fig. 30. In-situ polymerisation of multi-functional (TES/UV absorption) microcapsules [128].

then were metal coated using electroless plating to obtain a Ni–P shell. The alloy shell's magnetic properties switched from superparamagnetic to ferromagnetic due to the changes in the Ni crystal size.

Besides the examples mentioned above, new trends for the formation of micro/nanocapsules are moving towards encapsulation routes have employed more environmentally friendly processes, such as the use of biomaterials for both the shell and the PCM, or new routes that avoid surfactants, which are harmful to the environment.

#### 4.3. EPCM in passive thermal energy storage

Attempts have been made by both academic and industrial communities to combine EPCMs with various energy sectors, hence adding commercial value to the PCMs. One of the most followed approaches has been to incorporate EPCMs into a building envelope for higher energy efficiency and better thermal comfort. Furthermore, latent heat-based TES can potentially shift the peak energy loads to the non-peak hours or low tariff hours. Currently, more than one-third of the world's total energy is consumed by the residential and commercial building sectors, with the major portion of the energy being used for space cooling and heating [136], which has provided a great motivation to combine TES technology with the building sectors. Besides the building sector, the incorporation of EPCMs with industrial sectors is also tempting, as a large amount of waste heat is released in many industrial plants, such as coal-fired plants, iron and steel-making plants, non-ferrous producing plants, etc. Hence, EPCM-based refractories could be a solution to preserve and recycle excess energy, where in some cases their waste by-products can be used in the EPCM as the containment material. The utilisation of these solid wastes by effectively converting them into revalorized products with the incorporation of PCM would not only offer economic benefits but also contribute to sustainable development and lower CO<sub>2</sub> emissions. In this section, the potential methods to incorporate EPCMs into the building and industrial sectors are reviewed.

##### 4.3.1. Incorporation of PCMs in building materials

There is a wide range of building materials in which to incorporate EPCM, for instance, cement, mortar and concrete, gypsum, plasters, geopolymer, etc. According to different applications, these materials are manufactured with different properties due to different working requirements needed. For example, concrete is considered a structural material that requires good mechanical properties, such as high compressive strength and good resistance to thermal stress. Whereas, mortars and plasters are building materials that do not strictly require

high mechanical strength. Therefore, the properties of building materials together with the application requirements need to be considered carefully while incorporating EPCM. The incorporation of PCMs into the building sector has been classified according to the constructive materials used in the buildings; for example, concrete or mortar.

**4.3.1.1. Concrete.** Concrete is one of the most used construction materials for buildings. Over several decades, many attempts have been made by researchers to add PCM to achieve a good thermal mass and lower the fluctuation in temperature.

Pilehvar et al. [130] incorporated micro-encapsulated PCMs with geopolymer concrete (GPC) and Portland cement concrete (PCC). The PCM employed was a paraffin wax (Rubitherm®RT27), which was used as the core material coated with low-density polyethylene (LDPE) and ethyl-vinyl-acetate (EVA) (EVA/LDPE = 0.5). The authors measured the compressive strength of both GPC and PCC incorporated with the PCM capsules and found the compressive strength decreases with the increasing amount of PCM at temperatures below and above the melting point (20 and 40 °C). By the microstructural study of the concretes, a weak connection between solid particles was observed, as well as air voids. This explained the strength reduction of concrete after EPCM incorporation. However, the authors considered that the compressive strength was acceptable and still sufficient for specific applications and a better thermal storage capacity was obtained. Afterwards, the authors compared two types of PCMs with GPC: one type of PCM capsules used paraffin wax coated with LDPE and EVA, while the other type of PCM was coated with styrene (St) and divinyl benzene (DVB) [131]. To avoid interaction during the hydration process and to reduce the water affinity of the shell surface, both shells were designed to have a hydrophobic surface. The St-DVB shell was more hydrophobic than the PE-EVA shell, which contained some polar groups. It was found that the PE-EVA shell tended to agglomerate due to the polar groups on the surface, which lead to a higher reduction in the compressive strength than displayed by the St-DVB shell in the GPC.

**4.3.1.2. Mortar.** Mortar is a building material or bonding agent that typically holds bricks, tiles and other masonry units together. Mortar is typically a matrix that contains cement or other cementitious material (e.g. lime, alkali-activated binders), fine aggregates (e.g. river sands, rock powder) and adequate water [138]. Sometimes, superplasticisers or viscosity-modifying agents are added. Among the different types of mortars, cement mortar is the most popular one selected to incorporate PCMs; see Fig. 31 [132].

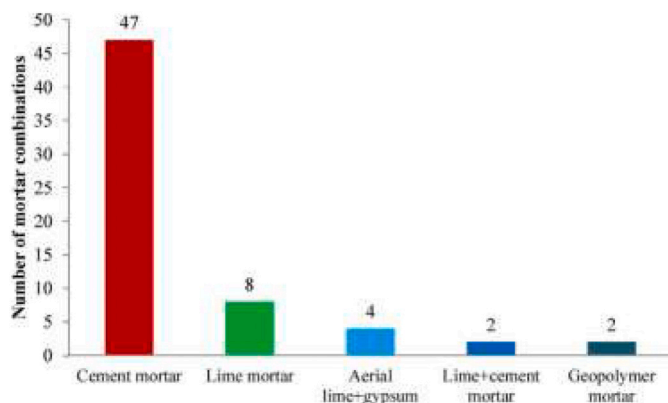


Fig. 31. Different types of mortar with incorporated PCM [132].

Leakage and chemical compatibility are regarded as the main challenges for the incorporation of PCM into mortars. Sharifi et al. [133] used lightweight aggregate (LWA) and rice husk ash (RHA) as matrixes to impregnate with PCMs and added them into a Portland cement-based mortar. Although these matrixes are porous, a leakage of PCM into the bulk cement mortar was still observed. Measurement of the compressive strength showed a reduction of 10 % and 35 % obtained for the LWA-PCM-based mortar and the RHA-PCM-based mortar, respectively. Despite the compressive strength reduction, the material could be used in most construction applications. In addition, the authors also found that using LWA as the matrix can prevent PCM from interfering with the hydration reaction.

Wang et al. [134] prepared a PCM-based clay geopolymer mortar by vacuum absorption method. Geopolymers are amorphous to a semi-crystalline polymeric material that shows excellent properties, such as high compressive strength, low creep, good acid resistance and low shrinkage. In their work, the authors impregnated the expanded perlite with paraffin by vacuum impregnation. Then, the obtained PCM composite was coated with calcium silicate and compared with the one without coating. Results showed that the coated PCM did not present any leakage, whereas, the one without coating did display it when the temperature increased. Besides these findings, the authors also found that the inclusion of PCM in the clay geopolymer mortar can effectively reduce the transported heat and allow a milder temperature variation compared to traditional mortar materials.

#### 4.3.2. Incorporation of EPCMs in industrial sectors

This section explores the use of EPCMs in the industrial sector through two approaches: refractory bricks and by-product waste materials.

**4.3.2.1. EPCM refractory brick-based.** Refractory bricks can withstand high temperatures and also tend to have a low thermal conductivity that reduces heat transmission and thus enables higher energy efficiency. These properties are employed by high-temperature industries to produce products such as combustion chambers, lining furnaces, kilns, fireboxes, etc. Incorporating PCM into refractory bricks can enhance their heat storage capacity and also enable the stabilization of the internal temperature, which is especially favourable for processes that require a consistent temperature.

Ceramic is a prevalent containment material for the PCM due to its high-temperature stability and sluggishness, see formulated a  $\text{Na}_2\text{CO}_3\text{-Li}_2\text{CO}_3\text{/MgO/graphite}$  composite PCM with up to ~50 wt% of PCM. The prepared PCM composite can be used at temperatures of up to 500 °C with good mechanical and chemical stability.

However, ceramics are brittle materials, and their tensile strength is much lower than their compressive strength, see Table 3. Magro et al. [135] proposed that the thermal expansion coefficient of the

Table 3

Properties of ceramics used as containment materials for PCM [135].

Ceramic	Young's modulus	Coefficient of thermal expansion	Thermal conductivity	Flexural strength
	E (GPa)	CTE ( $10^{-6}/\text{K}$ )	K (W/m•K)	MOR (MPa)
AlN	330	4.5	160	320
$\text{Al}_2\text{O}_3$	300	8.2	25	345
Mullite	151	5.4	6	180
Sialon	288	3	17.5	760
SiC	410	4.0	120	550
$\text{Si}_3\text{N}_4$	310	3.3	29	689

containment materials should ideally be consistent with the PCM. The mismatch of the thermal expansion coefficients could lead to non-negligible thermal stress. When the thermal stress exceeds the modulus of rupture, the PCM brick is expected to fail. Thus, the authors simulated the mechanical stress generated when using aluminium as the PCM incorporated within different ceramics. Six favourable ceramics were investigated for use as refractory bricks by the authors, including aluminium nitride (AlN), aluminium oxide at 96 % purity level ( $\text{Al}_2\text{O}_3$ ), mullite, sialon, silicon carbide (SiC) and silicon nitride ( $\text{Si}_3\text{N}_4$ ). The properties of these materials are shown in formulated a  $\text{Na}_2\text{CO}_3\text{-Li}_2\text{CO}_3\text{/MgO/graphite}$  composite PCM with up to ~50 wt% of PCM. The prepared PCM composite can be used at temperatures of up to 500 °C with good mechanical and chemical stability.

In their study, the distribution of the first principal stress around the PCM was obtained, as well as the first principal stress versus temperature; see Fig. 32. It was found that ceramics with a low coefficient of thermal expansion and high Young's modulus (i.e. AlN, SiC,  $\text{Si}_3\text{N}_4$  and Sialon) generate the highest thermal stress, while ceramics with low coefficient of thermal expansion and low Young's modulus (i.e. mullite) or with a high coefficient of thermal expansion and high Young's modulus (i.e.  $\text{Al}_2\text{O}_3$ ) generate the lowest thermal stress. Furthermore, it was found that the maximum filling ratio of the PCM and the energy density of the PCM brick can be determined by considering the maximum first principal stress to be equal to 90 % of the rupture modulus. The maximum filling ratio of the PCM with different ceramics is shown in Table 4.

Apart from detailed modelling work conducted to investigate the feasibility of PCM-based refractory bricks, some authors have also experimentally validated high-temperature PCM-ceramic-based composites. Wilk et al. patented the impregnation of a molten PCM into a porous refractory material [136]. The refractory material was mainly composed of alumina-silica fibres, colloidal silica and an inorganic/organic binder. In addition to this, Qin et al. [137,138] successfully formulated a composite PCM using diatomite and  $\text{Na}_2\text{SO}_4$  as matrix and PCM, respectively. The prepared PCM composite showed excellent high-temperature thermal stability up to 980 °C. Ge et al. [66,139] formulated a  $\text{Na}_2\text{CO}_3\text{-Li}_2\text{CO}_3\text{/MgO/graphite}$  composite PCM with up to ~50 wt% of PCM. The prepared PCM composite can be used at temperatures of up to 500 °C with good mechanical and chemical stability.

**4.3.2.2. EPCM by-products or waste materials based.** The utilisation of industrial by-products or waste materials not only contributes to the environment but can also continue sustainable development at a low cost. There are major generators of industrial solid wastes such as thermal power plants producing coal ash, integrated iron and steel mills producing blast furnace slag and steel melting slag, but also others such as non-ferrous industries (aluminium, zinc, iron and copper) producing wood ash, red mud and tailings, and the cement industry producing cement kiln dust, silica fume, etc. [140]. Some of the waste materials even present some TES-related useful properties e.g. slag usually has excellent high-temperature stability and fly ash has a porous structure. Replacing cement or other cementitious materials with these industrial solid wastes has been one of the main approaches for recycling and some



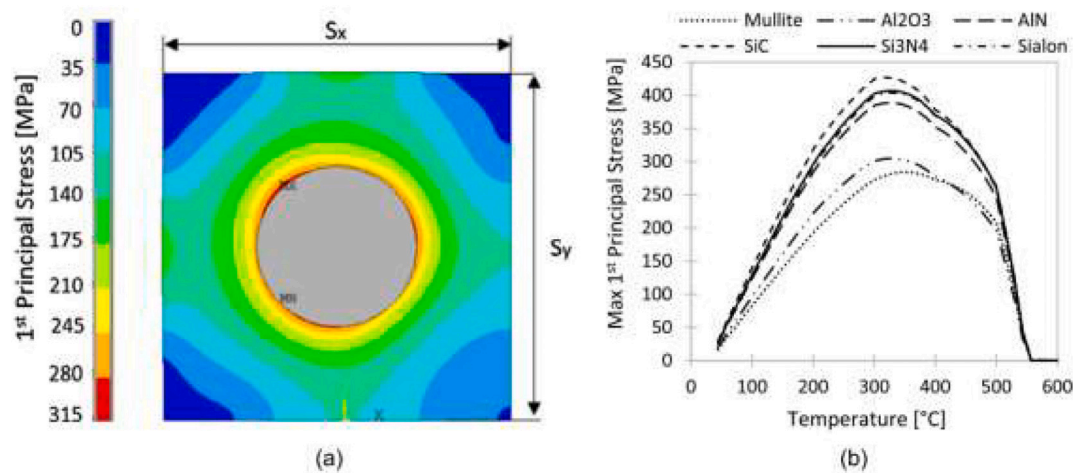


Fig. 32. First Principal stress distribution around the PCM (a); the maximum first principal stress versus temperature (b) [135].

Table 4

PCMs maximum filling ratio and energy density [135].

Ceramics	PCM filling ratio (%)	Energy density, (MJ/m <sup>3</sup> )
Mullite	1	8.55
AlN	6	69.82
Al <sub>2</sub> O <sub>3</sub>	16	168.95
SiC	21	224.93
Si <sub>3</sub> N <sub>4</sub>	33	356.00
Sialon	39	421.20

researchers have considered incorporating these materials with PCMs.

Memon et al. [141]. impregnated ground granulated blast furnace slag (GGBS) with dodecyl alcohol (DA) to get a form-stable PCM composite. The GGBS that was used is a by-product of the iron and steel-making industry that is produced in blast furnaces, and it is also a well-known substitute in construction materials. Through vacuum impregnation, the authors found that GGBS was able to retain 11 wt% of PCM without leakage. Cui et al. also [142]. used the GGBS to produce the alkali-activated slag (AAS) and then incorporated it with graphite-modified PCMs inside microencapsulates. The authors used the AAS to replace ordinary Portland cement (OPC), as studies showed that AAS possess similar properties and performance. In addition, carbon fibre (CF) was used to reinforce the mechanical strength of the PCM composite and also to improve its thermal conductivity. Studying the mechanical properties of the composites, the authors found that the AAS-PCM composite showed an even better compressive strength than the OPC-PCM composite, showing a 30 % increment in compressive strength.

Fly ash (FA) is a solid waste mainly generated in coal-fired plants, which is composed of oxides of Si, Al, Fe, etc. FA often has a high porosity and thus a large specific area [143]. Jiang et al. [144] impregnated expanded fly ash with paraffin and capric acid. It was found that the porosity of the composite is about 30 % and that it can retain 27.2 % and 26.2 % of the paraffin and the capric acid by volume fraction.

#### 4.3.3. EPCM challenges and new research strategies

Despite the sustainable benefits and thermal comfort, the incorporation of PCM into the building and industrial sectors can result in detrimental effects on both its fresh and hardened properties. This has created considerable debate in the research community concerning the proper selection of the EPCMs, especially concerning key points such as fire safety, PCM leakage and mechanical strength, which are still under study, as reported by Adesina [145]. These challenges still need to be addressed before the large-scale deployment of EPCM-based building

materials [146].

- Inconsistent phase change

PCM theoretically should have congruous melting and solidification processes. However, many PCMs suffer severe supercooling, phase segregation and chemical degradation issues that lead to inconsistent phase change [147–149]. This means that the PCM cannot solidify back to its original state from the melting phase to complete the energy charging and discharging cycle, and as a result, the ability of the PCM to store latent heat can be ineffective. To address these issues, there are several potential solutions: 1) selection of PCMs with low supercooling and phase segregation issues; 2) employing a nucleating agent and thickening agent to trigger the solidification process and to suppress the phase segregation; 3) proper encapsulation or incorporation to mitigate supercooling or phase segregation.

- Resistance to alkali environment

Containment materials in the construction sector tend to be alkali in nature, which can lead to chemical incompatibility with the PCM. Therefore, the selection of the PCM needs to consider the alkali resistance of the PCM for its survival in the host materials. Paraffin wax PCMs are stable in alkali environments; hence, it is one of the most popular PCMs employed for incorporation into building materials. Other PCMs such as polyethylene glycol (PEG) should be avoided. Hawes et al. [150,151] investigated the alkalinity of various concretes and found that autoclaved concrete blocks had the lowest alkalinity, followed by regular concrete blocks, pumice concrete and lightweight concrete prepared with expanded shale aggregate (EXSL). For pumice concrete blocks, there is a strong need to reduce their alkalinity or use pozzolans to reduce it. To address the chemical incompatibility between the PCM and the host materials, the most effective approach is to encapsulate the PCM with non-reactive shell material to avoid direct contact.

- Leakage of PCM

Leakage can be found when the PCM is incorporated by the immersion method or the direct incorporation method [65]. In the immersion method, some large pores exist in the matrix, which cannot retain the melted PCM and prevent leakage due to the weak capillary force. Also, the outer layer of the matrix tends to leak as the PCM on the surface is not sealed completely. In terms of the direct mixing method, leakage can occur due to the breakage of the PCM capsules while in the mixing process or after certain thermal cycles. To prevent leakage, PCM capsules with good mechanical properties that can withstand



mechanical mixing and thermal expansion are vital. Li et al. [152]. found that the use of a hydrophobic modifier can prevent leakage when the PCM is directly incorporated with the cement.

- Loss of strength

A loss of compressive strength is often observed when incorporating EPCMs into host materials, which has a considerable effect when the application is in structural materials. There are several reasons responsible for it: 1) the replacement of sand or cementitious particles of high stiffness and strength by EPCMs can lead to a reduction in the strength, which is more obvious in the melting state of the PCM; 2) weak bonds between the cementitious particles due to the interference of the PCM in the hydration process [21,130]; rupture of the PCM capsules during mixing or compression may cause leakage of the PCM and hence the loss of strength [130]. There is currently no widely recognised method to improve the mechanical strength of EPCMs incorporated into building materials. Methods to prevent the leakage of PCM and also the rupture of PCM capsules could be one of the approaches. Another option would be the selection of a PCM that does not interfere with the hydration process of the building material and could potentially mitigate the reduction of compressive strength.

- Fire safety

Fire safety is an important aspect of building materials that needs to be considered rigorously in practical applications to meet strict construction laws. Organic PCMs have been widely studied for incorporation with building materials despite their presenting a highly flammable nature. Hence, the inclusion of PCM in host materials can be a threat to fire safety. To reduce the flammability of PCMs, the addition of fire retardants to the PCM composite has been considered. Encapsulation of PCM with flame-resistant shell or matrix materials could also be a potential solution. Ling et al. [150] reported that BASF demonstrated that a paraffin/magnesium oxide-based matrix could improve its flame-resistant properties. This material has passed the Euro-class B fire rating.

### 5. Flow chart for EPCM design method

In this section, a selection methodology and flow chart are presented to explain the steps and sequence to follow to obtain encapsulated PCMs that can meet the requirements of a specific application.

Material assessment for chemical processes has always been a complex topic with no unique solution. No selection strategies have thus far been proposed for encapsulated PCMs, as shown in the literature review

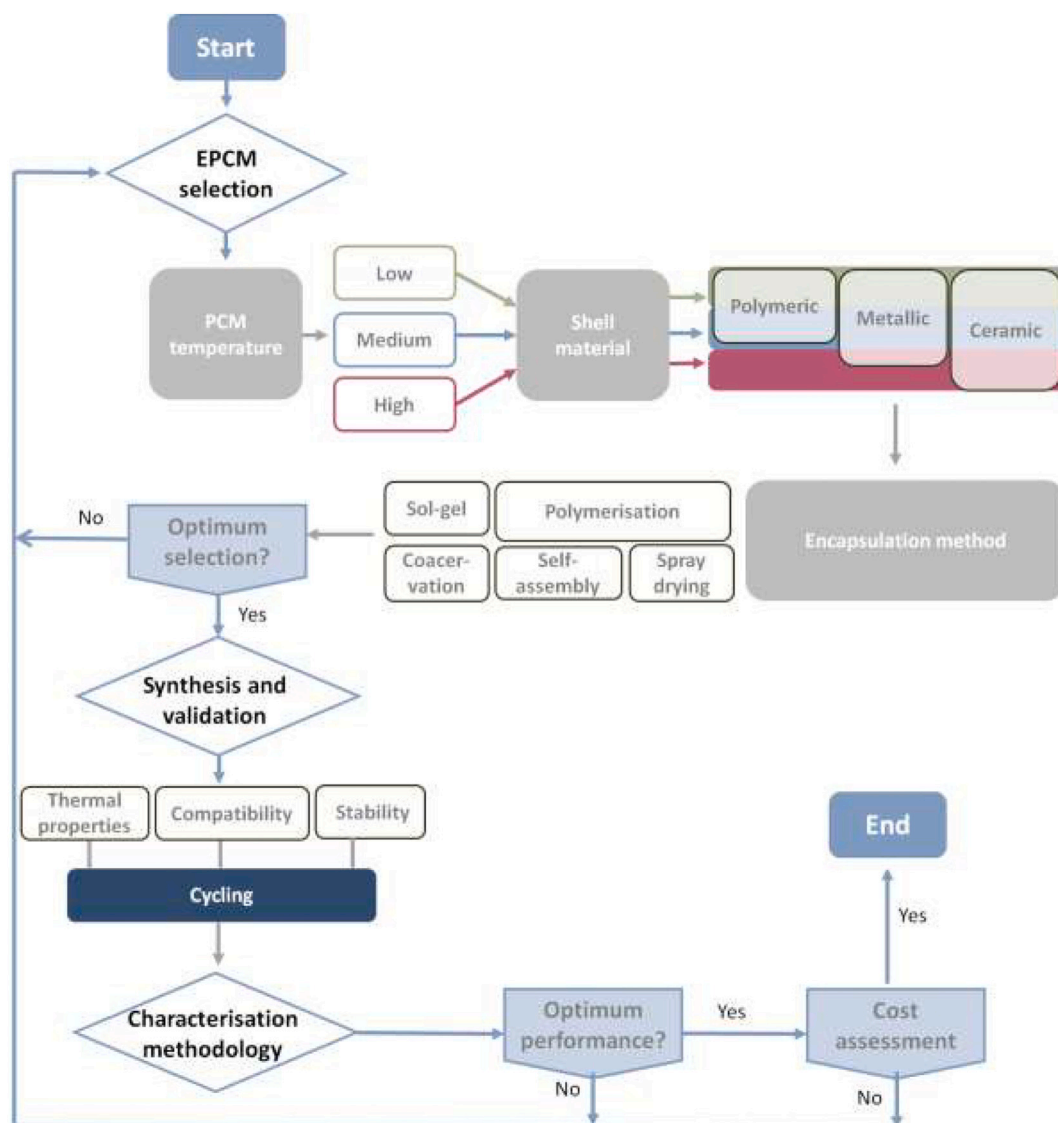


Fig. 33. EPCM selection flow chart.

section. In this paper, the authors propose a flow chart selection process to establish a standard procedure to translate the material requirements into suitable/optimum formulation performance. The methodology proposed consists of the following steps (as illustrated in Fig. 33).

5.1. EPCM components selection

In this selection step, the priority is to identify the main components of the EPCM; the PCM, shell material and encapsulation method. Previous sections have highlighted the different PCMs (low, medium and high temperature), shells (ceramic, polymeric and metallic), and lastly, the encapsulation methodology, which is dependent on the previous two. The selection of these components has a substantial influence on the performance of the EPCM as detailed below:

- The nature of the PCM material dictates the selection of the shell material (material compatibility) and the encapsulation methodology, as shown in Table 5. The operational temperature of the PCM influences the shell material selected. Polymeric shells are implemented in low to medium applications, while metallic and ceramic can be used for low to high temperatures, with ceramic being the most resistant to high temperatures as metallic shells can suffer from corrosion or incompatibilities.
- The shell material plays an important role in the heat transfer and the mechanical strength of EPCMs. A shell with a high-strength material and high thermal conductivity not only will improve the performance of the TES system but also increase the number of thermal cycles that the EPCM will have optimal performance. According to Salunkhe et al. [153], an ideal shell material should have (1) sufficient structural and thermal strength to withstand the phase change process; (2) maintain all the thermophysical properties at the micro and nano-level size; (3) be leak-proof; (4) unreactive with the enclosed PCM; (5) a good water diffusion barrier; (6) and high thermal conductivity to facilitate the heat exchange between the PCM and its surrounding.

The encapsulation methodology has a significant influence on the geometry of the EPCM as well as the encapsulated material output. It has been observed that the geometry has a large effect on the heat transfer characteristics of the PCM [153]. Commonly used encapsulation geometries are shown in Fig. 34.

The correct choice of suitable PCM, shell material, encapsulation preparation method and size selection vary according to the application. If the selection is optimal, in the sense that it meets the operational requirements and constraints, we can move to the following step.

5.2. Synthesis and validation

Once the PCM, shell material and encapsulation methodology have been selected, the EPCM can be synthesised and experimentally validated. Three main aspects of the EPCM performance must be studied;

**Table 5**  
Classification of encapsulation methods for the core-shell material. Adapted from [154].

Method		Organic	Inorganic
Chemical	Suspension polymerisation	Yes	No
	Emulsion	Yes	Yes
	Interfacial polymerisation	Yes	Yes
Physicochemical	Coacervation	Yes	No
	Sol-gel process	Yes	Yes
Physical	Physico-mechanical	Yes	No
	Centrifugal extrusion	Yes	Yes
	Solvent evaporation	Yes	No

- Thermal properties: the performance of a PCM-based thermal system is significantly affected by the melting and solidification characteristics of the PCM. For that reason, the thermal properties of the PCM must be measured after cycling to determine the effect of the shell and geometry on the thermal attributes of the PCM. Additionally, the phase change latent heat of the EPCM likely decreases with the increase in the number of thermal cycles, which may be caused by crystal structural changes in PCM. This phenomenon must be studied and predicted for optimal performance of the EPCM. Also, the thermal conductivity of shell material plays an important role in the heat exchange of the EPCM. Metallic shell materials provide higher heat transfer rates, which can also be useful in high-temperature PCM applications, although their microencapsulation is currently a challenge [154].
- Stability: the thermal and structural stability of the microcapsules are important for performing multiple thermal cycles. The thermal stability of EPCMs at high temperatures is strongly influenced by the PCM content in the capsule and the surface roughness [155]. Smooth and dense shells maintain a better core/shell integrity across many thermal cycles to prevent leakage of the liquid core. The leakage behaviour must be studied in this step to analyse this phenomenon.
- Compatibility: chemical compatibility between PCMs and the shell material used restricts the application temperature. Thus, material compatibility must be studied to avoid side reactions over operational temperatures. Both PCM phase segregation and supercooling are considerable challenges. Inorganic PCMs are more prone to these phenomena, although these challenges are also present in some organic PCMs. These problems can be alleviated by the addition of suitable enhancement materials. The incorporation of such materials has an impact on the latent storage capacity and phase change temperature as well as playing a role in the compatibility synergies of the EPCM.

5.3. Characterisation methodology

If the outputs of the characterisation methodology are optimal and within the range of desired performance, then the characterisation methodology can be applied to the EPCM after being cycled. To determine the thermal stability of EPCMs a minimum number of cycles ranging from 50 to 100 is advised, in some studies 2000 cycles have been reported [59]. Highly dense EPCMs have shown a higher strength of the polymer shell and better cyclability [154]. When the performance has been optimized, the cost of the process and material should be considered via a cost assessment study, as shown in Fig. 33 flow chart.

6. Summary and overview

This review paper gives a detailed and comprehensive summary of the encapsulation techniques, methods and progress of PCMs for TES applications. State-of-the-art Encapsulated PCMs (EPCMs) synthesis and encapsulation techniques are presented. The main conclusions are that EPCM is still costly to produce, particularly for large-scale thermal storage applications, and the main challenges are related to the manufacturing routes and cycling stability in operational conditions. Although EPCMs have had an impact and they stand as a feasible solution to overcoming some of the inherent drawbacks of PCM, the technology is still at the development stage and is likely to branch into other sectors. The knowledge gained in the use of encapsulation in the TES field can certainly be useful and could be transferred to other sectors depending upon their requirements.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.



Fig. 34. Different geometries for EPCMs (a) spherical (b) tubular (c) cylindrical and (d) rectangular [153].

## Data availability

No data was used for the research described in the article.

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