The micro-/nano-PCMs for thermal energy storage systems: A state of art review

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Summary
With advancement in technology—nanotechnology, various thermal energy storage (TES) materials have been invented and modified with promising thermal transport properties. Solid-liquid phase change materials (PCMs) have been extensively used as TES materials for various energy applications due to their highly favourable thermal properties. The class of PCMs, organic phase change materials (OPCMs), has more potential and advantages over inorganic phase change materials (IPCMs), having high phase change enthalpy. However, OPCMs possess low thermal conductivity as well as density and suffer leakage during the melting phase. The encapsulation technologies (ie, micro and nano) of PCMs, with organic and inorganic materials, have a tendency to enhance the thermal conductivity, effective heat transfer, and leakage issues as TES materials. The encapsulation of PCMs involves several technologies to develop at both micro and nano levels, called micro-encapsulated PCMs (micro-PCM) and nano-encapsulated PCMs (nano-PCM), respectively. This study covers a wide range of preparation methods, thermal and morphological characteristics, stability, applications, and future perspective of micro-/nano-PCMs as TES materials. The potential applications, such as solar-to-thermal and electrical-to-thermal conversions, thermal management, building, textile, foam, medical industry of micro- and nano-PCMs, are reviewed critically. Finally, this review paper highlights the emerging future research paths of micro-/nano-PCMs for thermal energy storage.

KEYWORDS
encapsulation technologies, micro-encapsulated, micro-PCM, nano-PCM, nanotechnology, nano-encapsulated, phase change materials, thermal energy storage

1 | INTRODUCTION

After the energy crisis of the 1970s, the world is facing a shortage of energy resources. Researchers are looking to different energy storage technologies based on renewable and sustainable resources to meet the future energy requirements.\(^{3}\) Phase change thermal energy storage (TES) technology using phase change materials (PCMs) ensures the storage, transportation, and wider domestic and industrial applications of thermal energy. TES technology has high heat capacity and enthalpy of fusion with the capability of absorbing and releasing extensive amounts of thermal energy during phase transition. The thermal performance of phase change TES technology employing PCMs, which are also known as latent heat storage materials (LHSMs), solely depends on the properties
of PCMs. On the basis of chemical composition, PCMs are classified into two major categories: organic phase change materials (OPCMs) and inorganic phase change materials (IPCMs). The advantages of PCMs and especially OPCMs, which includes paraffins (n-alkanes) and non-paraffins (n-alkenes) materials, are higher stability, high energy storage density, no segregation, nontoxic, self-nucleation (supercooling), noncorrosiveness, and nonreactive.2 Con-}


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ally high thermal conductivity, and flame retardancy. In spite of this, IPCMs possess subcooling and phase separation, which reduce their instant release and utilisation of thermal energy for large-scale TES applications. OPCMs have lower thermal conductivity3 and also suffer leakage problem and subcooling phenomenon during phase transition.4 The lower thermal conductivity of OPCMs reduces the rate of heat transfer, which causes increase in temperature gradient and insensitivity to temperature changes across the system boundaries. OPCMs, with potential advantage as TES materials, are being developed for applications including air conditioning, ie, natural air cooling;5 cold thermal storage and absorption refrigeration;6,7 solar energy storage;10,11 thermal regulating fabric;12,13 passive heating of building,14-17 heat pipes,18 desalination,19 thermal management of electronic devices and electric vehicle batteries,20-30 spacecraft,31,32 and other integrated thermal control systems such as trombe wall, PCM-filled wallboards, shutter, concrete, under floor heating systems, ceiling boards, and hot water supply.33,34 However, the leakage issue and lower thermal conductivity of OPCMs causes harm with interacting medium and results in energy efficiency losses of the thermal system.

Efforts have been made to solve the aforementioned challenges related with both types of PCMs. Various conventional approaches such as the addition of more water, nucleating agents, thickeners, and stirring of the salt solution have been employed to control the predicaments of IPCMs in their constant dissolution and crystallisation procedure.35 In contrary, the addition of conductive fillers and flame-retardants has reduced the disadvantages of OPCMs. However, these efforts would certainly lessen the energy storage density of PCMs due to the presence of inactive mass.36 At present, nanoconfinement technologies have attracted a lot of interest and present a new opportunity for considerable refinement in the thermophysical properties of PCMs while sustaining their energy storage capacity.37,38 There are several advantages associated with nanoconfinement like small domain size, large surface area, diverse surface functionalities, controlled volume expansion, reduced reactivity with the external environment, and high heat transfer rate.

Confinement is the procedure of enclosing liquid or solid PCMs within supporting materials to fabricate a type of composite PCM. The main function of confinement is to stop the contact of the liquid phase of PCMs with the surrounding environment.39 The surface chemistry occupied at the interfaces of two phases such as solid-liquid or liquid-gas has a considerable effect on the thermodynamic properties of composite PCMs. Confinement technology can be applied to control the phase change parameters by a new mechanistic way by heterogeneous nucleation, large contact area, and associated surface energy in a confined environment. For example, the confinement of salt hydrates inside packaging materials not only restrains the loss of water of crystallisation during the phase transition to resolve the phase dissociation and supercooling phenomena but also enhances the heat transfer duration. Depending on the size, confinement technology can be classified into macro-confinement, micro-confinement, and nano-confinement. Different kinds of physical properties like adhesion forces, Van der Waals interactions, capillary actions, and surface chemistries are more effective at the nanoscale of confinement. For that reason, nano-confinement technology has proven to more valuable than macro- and micro-confinement.40,41 Additionally, nano-confinement provides better heat transfer, and accommodates dimensional changes related with the phase transition of PCMs. According to material designs and dimensions, confinement strategies can be classified as:

1. Core-shell confinement (0D)
2. Longitudinal confinement (1D)
   - Tubular confinement
   - Fibrous confinement
3. Interfacial or layer confinement (2D)
4. Porous confinement (3D)

In core-shell confinement, a small particle of liquid or solid PCMs is coated with shell material and exhibits the zero-dimensionality. Longitudinal confinement is also similar to core-shell confinement, but is one-dimensional (1D). According to shell materials, longitudinal confinement is further achieved either by infiltrating the melted PCM into the inner cavity of nanotubes (tubular confinement) such as CNTs, or by restraining the PCMs within the internal diameter of nanofibres (fibrous confinement) employing coaxial electrospinning technique. Interfacial or layer confinement technology covers the confinement of PCMs at the interface of nanomaterials by the interaction between PCM molecules and the surface of nanomaterials such as graphene oxide. In nanoporous confinement, the PCMs are impregnated into the nanopores of the supporting materials through a
vacuum developed infiltration method, shown in Figure 1. In term of size, the term core-shell nanoconfinement is used if the size of the capsules varies between 1 and 1000 nm, and for longitudinal confinement, the diameter of nanotubes or nanofibres should vary from 1 to 1000 nm.

Here, in the current study, the core-shell confinement of PCMs is further reviewed in detail. PCMs are encapsulated in a capsule of a core-shell composite construction called encapsulated phase change materials (EPCMs).43-45 The EPCMs are tiny capsules or containers, consisting of two parts: (a) core of PCMs and (b) shell of polymer or inorganic materials, which may have core-shell, multi-shell, and polynuclear structure depending on the synthesis technique, as shown in Figure 2. These capsules are in both regular (e.g., spherical, tubular, and oval) and irregular shapes. Additionally, the structural arrangement of the capsule depends on the core material and deposition process of the shell.44 The material of the coating shell has significant importance in terms of providing structural integrity and stability. In particular, to enhance heat transfer rate, the encapsulated PCMs need mechanically strong and thermally conductive shell materials. The proportion of core and shell materials therefore is a key parameter to enhance the TES capability and structural stability, applied in both non-flow and flowing systems. Weight percentage of both core and shell materials are relatively dependent on each other and defines TES performance. A high weight percentage of shell material reduces the heat storage capacity of core PCM, but alternatively increases the structural stability and vice versa.47-49 Therefore, the mass of coating material needs to be optimised to obtain the desired thermophysical properties. Various coating materials such as organic polymers, silica, metal oxides, and hydroxides have been utilised. Furthermore, the selection of the shell material is based on encapsulation technique and type of PCM. Generally, polymers are used as a traditional coating materials for encapsulation of PCMs. The positive features of using polymers as shell materials are that they are cheap, lightweight, mechanically stable, easily processed, and compatible with PCMs.50 In addition, the polymers are flexible, which allows the expanded volume of PCM during phase transition resulting in ease of melting while keeping the shape and stability of prepared nanocapsules. Such promising physical properties of polymers makes them preferable to use as shell material for PCM encapsulation. Heretofore, polystyrene (PS), polyurea (PU), poly(urethane), polycyraclates, poly-amide (PA), polymethyl methacrylate (PMMA), polyethyl methacrylate (PEMA), and formaldehyde resins have been utilised as shell materials to encapsulate OPCMS. So far, many encapsulation technologies have been introduced as (a) micro and

**FIGURE 1** Confinement strategies and potential applications of PCMs. Reused from Aftab et al.42 with permission from The Royal Society of Chemistry [Colour figure can be viewed at wileyonlinelibrary.com]

**FIGURE 2** A, Synthetic illustration of phase change EPCMs and B, various structures. Reused from Aftab et al.42 with permission from The Royal Society of Chemistry [Colour figure can be viewed at wileyonlinelibrary.com]
nano encapsulation, (b) shape-stabilised composite, and (c) intercalation. The encapsulation of the PCMs

- Macro-encapsulated PCM (macro-PCM) (1 mm)
- Micro-encapsulated PCM (micro-PCM) (1-1000 μm)
- Nano-encapsulated PCM (nano-PCM) (1-1000 nm)

OPCMs with temperature range of -10 to 80°C are mostly under development with various encapsulation techniques into microcapsule and nanocapsule.51 The encapsulation techniques depend on the physical and chemical properties of shell and core materials as well the method of encapsulation.51-53 From 50 years of developments in nanotechnology, macro and micro encapsulation technologies of PCMs have improved by increasing the thermal performance and stability of encapsulated PCMs. As the stability of the EPCM capsules relies on the size of particles, micro-PCMs can increase the viscosity of the fluid54-56; they can also fracture in the fluid flow resulting in a fluid flow obstacle. To overcome this issue, nano-PCMs of small particle size, large surface area, low leakage, uniform fluid flow, and suspension stability have gained attention as new TES materials for energy storage applications.55 Additionally, nano-PCMs have volume and surface effect, are easily dispersed in fluid and steadily flow in slurry make them favourable in thermal energy storage and thermal management applications.57,58

To date, a few studies have summarised the progress on preparation of micro-PCMs59,60 and nano-PCMs.41 However, this review critically summarises research in the area of novel energy storage materials for the applications of TES systems. Initially, ideal characteristics of EPCMs are elaborated, which are potentially necessary to enhance thermal storage and heat transfer performance. Further, a detailed discussion on preparation technologies to encapsulate PCM into macro-, micro-, and nano-sized capsules are presented using physical-mechanical, physical-chemical, chemical-mechanical, and chemical encapsulation methods. Thermophysical properties of these novel EPCMs are summarised representing their enhancement in thermal conductivity, latent heat of fusion, and encapsulation efficiency. Additionally, a detailed discussion on characterisation techniques to evaluate the chemical, thermal, physical, morphological, and thermal reliability and thermal cyclic properties of EPCMs is presented. The stability, which is a real challenge of PCM capsules, is discussed with respect to chemical and thermal properties to explore the functionality and thermodynamic nature as energy storage materials. Potential applications such as solar-to-thermal and electrical-to-thermal conversion, thermal management, building, textile, foam, and medical industry of micro- and nano-PCMs are reviewed critically. Finally, this review highlights the emerging future research directions of EPCMs in the area of TES.

2 IDEAL CHARACTERISTICS OF EPCM

Ideal characteristics of EPCM include the ability to significantly influence thermal systems while performing as a TES material, especially at varying operating conditions. Thus, for an ideal EPCM, it is necessary to meet specific criteria and environmental conditions for longer duration operation. Figure 3 presents the ideal characteristics of EPCM, which are necessary for utilisation in thermal applications. The ideal characteristics of EPCMs depend on their fundamental chemical, physical, thermal, and economics properties, which are as follows61:

- Sufficient phase-transition temperature: Suitable phase change temperature of EPCM is essential and must match the operating conditions of specific application at melting and solidification temperature points.
- High latent heat of fusion: Latent heat of fusion, also called enthalpy of fusion, of the EPCM is the most desirable thermal property pertaining to ability to absorb large amount of heat with least amount of volume, especially to reduce the size of the TES system. EPCMs based on organic PCMs as core materials and polymeric materials as a shell have the tendency to absorb higher latent heat.
- High thermal conductivity: Higher thermal conductivity provides the additional capability to store thermal energy, while sensible heating phase results in shorter charging and discharging phases. Inorganic material coated EPCMs have more potential to increase the thermal conductivity, resulting in transmission of heat at higher rate. However, the increase in thermal conductivity of EPCMs causes lower absorption of latent heat fusion.
- Durability: EPCM must withstand damage from friction and wear and tear. The strength of the coated shell of an EPCM has to sustain its mechanical properties while flowing through system.
- High density and small volume change at phase transition: High density of the EPCM helps to reduce the size of the encapsulated container. The small volume change undertaken in phase transformation helps to minimise the complexity of the EPCM storage container.
- Congruent melting: helps the EPCMs to prevent irreversible segregation, reducing the loss of storage capacity while recycling.
- Favourable phase equilibrium: Favourable or suitable phase equilibrium temperature ensures heat
storage and extraction at constant temperature in a TES system.

- Long-term chemical stability: The continuous charging and discharging of EPCMs, water loss, decomposition or chemical interaction with storage container can undergo degradation in EPCMs. So it is highly preferred that EPCMs should maintain their long-term chemical stability and corrosion resistance when interacting with other materials.
- Nonhazardous: For safety measures, EPCMs should be nontoxic, nonflammable, and nonexplosive.
- High nucleation rate: An ideal EPCM should have a high nucleation rate and good crystallisation rate.
- Low supercooling or subcooling: Low subcooling, also called supercooling, ensures melting and cooling at the same temperature, which is due to metastable condition of the EPCM during solidification. This means that during cooling, the EPCM is not in a thermodynamic equilibrium state. The supercooling particularity occurs in salt hydrates, which prevents the extraction of thermal energy.
- Low vapour pressure and adequate crystallisation rate: Low pressure and rapid crystallisation of EPCM help to reduce the design complexity of EPCM storage system.
- Low cost and availability: The cost and availability of EPCM have a major significance on the overall cost of the thermal system. As the development of EPCMs require high precision and clean environment, so it may increase their cost.

3 | THE PREPARATION TECHNOLOGIES FOR EPCMS

The encapsulation techniques of PCMs are usually categorised into four different methods, (a) physical-mechanical, (b) physical-chemical, (c) chemical-mechanical, and (d) chemical, which are based on synthesis of the EPCMs. Table 1 highlights a brief summary of the abovementioned methods, their subrelevance techniques, and the resulting size of capsules formed for the relevant type of PCMs.

3.1 | Physical-mechanical methods

Generally, the physical-mechanical methods do not involve any chemical reaction resulting in the formation of microcapsules of relatively large size. Table 2 summarises the properties of each technique of the physical-mechanical method. The advantages and disadvantages of physical-mechanical methods are summarised in Table 3. The physical-mechanical methods include the
following techniques forming microcapsules.

- Pan coating
- Air-suspension coating
- Centrifugal extrusion
- Vibration nozzle
- Spray drying
- Solvent evaporation/extraction
- Vacuum impregnation

encloses the core of the capsule (eg, PCMs) and is solidified by a cooling medium. The alternative method is to gradually apply or spray the coating material onto the core material or particles into the tumbler machine/vessel, which reduces the processing time as well energy and material consumption.\textsuperscript{62} In this technique, the melting temperature of the core material must be higher than the shell material; otherwise, PCM encapsulation will not be eventuated effectively.

### 3.1.1 Pan coating

The pan coating process is the oldest and most widely used, especially in pharmaceutical industries, to form small-coated particles and pellets. The solid particles are mixed with a dry coating material then heated to a set temperature, thus melting the coating material, which

### 3.1.2 Air-suspension coating

 Adopting air-suspension technique for micro-encapsulation gives more control and flexibility in comparison with pan coating, by charging operation times of core material into the coating zone while processing.\textsuperscript{63} Solid particles are suspended in an upward air stream

### TABLE 1 Summary of encapsulation methods, techniques, formed capsules, and type of PCMs

| Methods               | Techniques                        | Formed Capsules | PCMs     |
|-----------------------|----------------------------------|-----------------|----------|
| Physical-mechanical   | Pan coating                       | Micro           | Organic  |
|                       | Air-suspension coating            | Micro           | Organic  |
|                       | Centrifugal extrusion             | Micro           | Organic  |
|                       | Vibration nozzle                  | Micro           | Organic  |
|                       | Spray drying                      | Micro           | Organic  |
|                       | Solvent evaporation/extraction    | Micro           | Organic  |
|                       | Vacuum impregnation               | Micro           | Organic  |
| Physical-chemical     | Ionic gelation                    | Micro           | Organic  |
|                       | Coacervation                      | Micro           | Organic  |
|                       | Sol-gel method                    | Micro/nano      | Organic/inorganic |
| Chemical-mechanical   | Microfluidic method               | Micro           | Organic  |
|                       | Melt-coaxial electrospray method  | Micro           | Organic  |
| Chemical              | Interfacial polymerisation        | Micro/nano      | Organic/inorganic |
|                       | Suspension polymerisation         | Micro           | Organic  |
|                       | Emulsion polymerisation           | Micro/nano      | Organic/inorganic |
|                       | Miniemulsion polymerisation       | Nano            | Organic/inorganic |
|                       | In situ polymerisation            | Nano            | Organic/inorganic |

### TABLE 2 Advantages and disadvantages of physical-mechanical methods

| Techniques             | Advantages                          | Disadvantages                           |
|------------------------|-------------------------------------|-----------------------------------------|
| Pan coating            | Low-cost production                 | High skilled manpower required          |
|                        |                                     | Difficulty in control                    |
| Air-suspension coating | Low-cost                            | High skilled level required             |
|                        | large production volume             | Agglomeration of particles              |
| Centrifugal extrusion  | Suitable for encapsulation          | High temperature range                  |
| Vibrational nozzle     | Large volume of production          | High temperature range                  |
|                        | Easily scaled-up                    |                                         |
| Spray drying           | Easily scaled up                    | High temperature range                  |
|                        | Easy availability of equipment      | Agglomeration of particles              |
|                        | Controllable to produce             | Uncoated particle                       |
| Solvent evaporation    | Economical                          | Limited for lab production              |
|                        | Feasible to remove moisture         |                                         |
|                        | Low cost                            | Limited for large-scale production      |
| Vacuum impregnation    |                                     |                                         |
### 3.1.3 Centrifugal extrusion

Southwest Research Institute (SwRI)\(^6\) developed a mechanical process to produce microcapsules on the principle of centrifugal force in which the core material, which is in liquid phase, flows through inside a tube. The coating or shell material, which should be immiscible with core material, flows through the annular around the tube. The key parameters that influence the process are rotational speed of cylinder, flow rate of core and shell materials, concentration, viscosity, and surface tension of the core material. With rotation or vibration of the tube, the core and coating materials extrude from the orifice making spherical capsules due to surface tension forces. The coated capsules are then solidified by heat or chemical reactions in a bath.\(^{46,67}\) There is no study found of PCM encapsulation using this method.

### 3.1.4 Vibration nozzle

There are several studies available but without vibration, in which microgranulation or matrix encapsulation is normally carried out through a vibrating nozzle under laminar flow regime. The uniform capsules are formed due after coating and drying in the solutions with both water and volatile organic solvents. During a cyclic process in the coating zone, the shell material (usually polymer or inorganic material) is repeatedly sprayed on the core particles up to the required level of thickness for encapsulation. This encapsulation technique was employed for pharmaceutical,\(^{64}\) food,\(^{65}\) and cosmetic industries,\(^{66}\) and it is not suitable for PCM encapsulation. Figure 4 shows the typical operating principle of air-suspension particle operation with two growth mechanism of interparticle agglomeration and surface layer.

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**TABLE 3** Summary of prepared micro-PCMs using physical-mechanical methods

| Reference | Method | Core | Shell | Particle size, μm | EE, % | Tm, °C | Latent heat, J/g |
|-----------|--------|------|-------|------------------|------|--------|-----------------|
| Borrego et al.\(^7\) | Spray drying | RT-27 | LDPE, EVA, Gelatin and gum arabic | 3.9 | 49.32 | 28.40 | 98.1 |
| Hawlader et al.\(^8\) | Spray drying | Paraffin wax | Gelatin and gum arabic | ~0.2 | 86 | 62.3-95.7 |
| Carvalho et al.\(^9\) | Spray drying | N-octadecane | Lecithin and chitosan | 0.1-5 | 62.3-95.7 | 145 |
| Carneiro et al.\(^10\) | Spray drying | Flaxseed oil | Lecithin and gum arabic | 1.35-5.70 | 62.3-95.7 | 145 |
| Rajam and Anandharasan\(^11\) | Spray drying | Lactobacillus plantarum | Methyl cellulose | 5 | 62.3-95.7 | 145 |
| Yang et al.\(^12\) | Spray drying | Poppyseed oil | Gelatin and gum arabic | ~0.2 | 86 | 62.3-95.7 |
| Memon et al.\(^8\) | Vacuum impregnation | Paraffin wax | LWA | ~2 x 10\(^5\) (macro) | 70 | 96.8 | 185 |

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to vibration\textsuperscript{68}, however, this method has been carried out for PCM encapsulation. Some studies reported the uniform stable PCM composites prepared by this method but without vibration.\textsuperscript{69-75}

### 3.1.5 Spray drying

The spray drying encapsulation technique is economical, easily scaled-up, and controllable to produce homogeneous microsize capsules with efficient design of the atomizer.\textsuperscript{76-78} The spray drying process is the most commonly used technique in the food and pharmaceutical industries\textsuperscript{79-82} due to the suitability of encapsulation of heat-sensitive materials. This technique involves four major steps.\textsuperscript{83} Figure 5 presents the flow process of typical spray drying encapsulation technique.\textsuperscript{67}

- Preparation of the dispersion/emulsion of wall material.
- Homogenisation of the dispersion/emulsion.
- Atomization of the in-feed dispersions.
- Dehydration/evaporation of the atomized particles.

The produced microcapsules are usually polynuclear or matrix type, and with increasing production rate or flow rate, agglomerated and uncoated particles are obtained.\textsuperscript{46}

**FIGURE 5** Flow diagram of spray drying encapsulation technique.\textsuperscript{67} Reused with permission from John Wiley and Sons license number 4385841192579

### 3.1.6 Solvent evaporation/extraction

Solvent evaporation or extraction is a liquid-liquid emulsification system that is extensively used in the pharmaceutical industry. This technique is carried out in liquid manufacturing vehicle (LMV) and emulsification of polymer in a volatile solvent in water followed by solvent removal. The basic steps of micro-encapsulation by solvent evaporation are shown in Figure 6.\textsuperscript{84} There are different methods of micro-encapsulation of drugs by solvent evaporation, which depends on the hydrophilicity or the hydrophobicity of the core material. The detail procedure of the solvent evaporation technique can be found in Li et al.\textsuperscript{84}

### 3.1.7 Vacuum impregnation

Vacuum impregnation technique is frequently used to remove air from the encapsulation materials and is widely used in the food industry. The process of macro-encapsulation carried out by Memon et al\textsuperscript{85} used paraffin as a core material and light weight aggregate (LWA) as a shell material for TES. Figure 7 illustrates the

**FIGURE 7** Flow process of a macro-encapsulated TES LWA. Schematic image of PCM-LWA preparation process; A, LWA; B, paraffin-LWA; C, paraffin-LWA coated with a mixture of epoxy graphite powder; and D, paraffin-LWA graphite powder sample coated with silica fume.\textsuperscript{85} Reused with permission from Elsevier license number 4385850945845 [Colour figure can be viewed at wileyonlinelibrary.com]

**FIGURE 6** Basic step of micro-encapsulation by solvent evaporation.\textsuperscript{84} Reused with permission from Elsevier license number 4385850567033 [Colour figure can be viewed at wileyonlinelibrary.com]
preparation process of PCM (paraffin) and LWA using the vacuum impregnation technique.

### 3.2 Physical-chemical methods

Generally, physical-chemical methods include physical reactions such as phase separation, condensation, boiling, and complexation. These include the following three main methods. The advantages and disadvantages of physical-chemical methods are summarised in Table 4. Table 5 enumerates the thermophysical properties of prepared capsules under different types of physical-chemical methods.

- **Ionic gelation**
- **Coacervation**
- **Sol-gel method**

#### 3.2.1 Ionic gelation

This method is generally used in the pharmaceutical industry, especially in drug supply systems, but it has not been used for the encapsulation of PCMs. In this method, the gel forming solution is put into droplet form in a gelation bath resulting in the formation of hydrogel beads. The gelation process occurs due to the ionic bonding between the polymer chain, due to when the alginate solution is dropped in a calcium bath, which leads to the calcium alginate microcapsules, or by cooling such as an agarose solution.

#### 3.2.2 Coacervation

The coacervation word is derived form the Latin word *acerus* meaning “heap.” Generally, the coacervation method is classified under two methods: (a) *simple coacervation* and (b) *complex coacervation*. In the simple coacervation method, the low-molecular substance is interacted with dissolved polymer. In complex coacervation method, the interaction happens between two polymers who have opposite charges. The complex coacervation method involves the mixture of two polymers and complexation processes such as cross linking, desolvation and thermal treatment, which requires extra cost and a more unyielding operation as compared with simple coacervation. However, the complex coacervation method produces more smaller size microcapsules of spherical shape with greater stability. Figure 8 represents the typical flow diagram of complex coacervation. The complex coacervation method consists of three stages: (a) the preparation of the oil-water emulsion by adding the core material (usually oil) dispersed in water forming a phase separation coacervation with aqueous polymer solution; (b) the deposition of the shell material onto the core particles by adding second aqueous polymer solution of opposite electric charge followed by adjusting the pH number, temperature, or by dilution of the medium; (c) and, finally, the mixture is cooled down forming micro-encapsulation with stabilisation by cross-linking and harvesting of the micro-PCMs or thermal treatment.

From complex coacervation, Konuklu et al produced micro-PCM using caprylic acid (octanic acid) using various wall materials (UF resin, MF resin, and UMF resin) suitable for TES applications. The schematic of flow process and SEM image of produced particle size of micro-capsules is shown in Figures 9 and 10.

#### 3.2.3 Sol-gel method

“Sol-gel” is the abbreviation of “solution-gelling” and is largely used to synthesise inorganic materials. The sol-gel process is a familiar physical-chemical technique to develop nanocapsules with an inorganic shell. It has captured attention in recent years as it is inexpensive and needs mild processing conditions. The sol-gel process followed as the polycondensation reactions of a molecular precursor in a liquid phase to form a colloidal solution (sol), which is subsequently converted to an oxide network (gel). Figure 11 shows the typical process of the sol-gel method. In the sol-gel method, the processes are as follows: (a) The precursor (usually alkoxides and inorganics) is mixed uniformly with the solvent, catalyst, and complex agent; (b) a stable and transparent colloidal solution is formed after hydrolysis and condensation chemical reactions. At this step, the condition of dispersion changes
| Reference   | Method                  | Core              | Shell                      | Particle size, µm | EE, %  | T_m  | Latent heat, J/g |
|-------------|-------------------------|-------------------|----------------------------|-------------------|--------|------|-----------------|
| Lazko et al 111 | Simple coacervation   | n-Hexadecane     | Soy glycmin                | ~ 101.7           | 65     |      |                 |
| Sutaphanit and Chiprasert 112 | Simple coacervation   | Holy basil essential oil (HBEO) | Gelatin | 392.30 | 44.65-100.09 |      |                 |
| Konuklu et al 148 | Complex coacervation | Octanic acid     | UF, MF, UMF                | 0.2-1.5           | 59.29  | 13.90| 93.9            |
| Hawlader et al 113 | Complex coacervation | Paraffin wax     | Gelatin and gum arabic    | 50-100            | 9.43-94.26 |      | 20-90           |
| Hawlader et al 114 | Complex coacervation | Paraffin wax     | Gelatin and gum arabic    | 50-100            | 79.43-94.26 |      | 20-90           |
| Hawlader et al 116 | Complex coacervation | Paraffin wax     | Gelatin and gum arabic    | ~ 0.5             | ~60    | 213  |                 |
| Santos et al 94 | Complex coacervation   | Xylitol           | Gelatin and gum arabic    | 78.45-109.31      | 31-71  |      |                 |
| Piacentini et al 116 | Complex coacervation | Sunflower oil    | Fish gelatin and arabic gum | 40-240          |      |      |                 |
| Alvando et al 117 | Complex coacervation   | n-Tetradecane    | Gelatin                    | 90-125            | 5.30  | 192  |                 |
| Özonur et al 118 | Complex coacervation   | Coco-fatty acid   | Gelatin and gum arabic    | 1 mm              | 29-31  |      |                 |
| Onder et al 119 | Complex coacervation   | n-Hexadecane, n-octadecane, n-nonadecane | Gelatin-gum arabic mixture | ~                  |       | 11-38| 19.70-165.80   |
| Bayès-García et al 120 | Complex coacervation | RT-27            | Sterilised gelatine/arabic gymn, agar agar/arabic gum | 9.12 | 48.49 | 298.3-301.3, 299.5-302.5 | 79.78 |
| Butstraen and Salaün 121 | Complex coacervation | TMiglyol 812N     | Chitosan and gum arabic   | 5-10              |      |      |                 |
| Shin et al 122 | Complex coacervation  | n-Eicosane       | MF                         | 1.89              | 53    | 36.9 | 134.3          |
| Jiang et al 123 | Sol-gel method        | n-Eicosane       | Fe₂O₃/SiO₂                 | ~4-6              | 71.78 | 39.15| 170.20         |
| Wu et al 124 | Sol-gel method        | Tris             | SiO₂                       | ~100-200          | 67.90 | 110-155 | 146           |
| Cao et al 125 | Sol-gel method        | Paraffin wax     | TiO₂                       | ~50               | 85.5  | 58.8 | 161.1          |
| Cao et al 126 | Sol-gel method        | Palmitic acid (PA) | TiO₂                     | 200-400 nm        | 30.4  | 61.7 | 63.3           |
| Chen et al 127 | Sol-gel method        | Stearic acid (SA) | SiO₂                      | 20-30             | 90.7  | 52.6-53.5 | 162.0-171.0 |
| Chen et al 128 | Sol-gel method        | Paraffin wax     | SiO₂                       | 40-60             | 82.2  | 57.96 | 156.86         |
| He et al 129 | Sol-gel method        | n-Octadecane     | SiO₂                       | 2-4               | 41.45 | 27.96 | 87.46          |
| Wang et al 130 | Sol-gel method        | n-Pentadecane    | SiO₂                       | 8-15              | 69.1-87.5 | 57.84-58.37 | 130.82-165.68 |
| Fang et al 131 | Sol-gel method        | Paraffin wax     | SiO₂                       | 7-16              | 86.4  | 27.1 | 184.9          |
| Zhang et al 132 | Sol-gel method        | n-Octadecane     | SiO₂                       | 7-16              | 183.7 nm, 466.4 nm, 722.5 nm | 82.53, 84.28, 88.32 | 61.06, 60.92, 61.6 | 168.16, 172.16, 180.91 |
| Latibari et al 133 | Sol-gel method        | Palmitic acid (PA) | SiO₂                     | 183.7 nm, 466.4 nm, 722.5 nm | 82.53, 84.28, 88.32 | 61.06, 60.92, 61.6 | 168.16, 172.16, 180.91 |
| Latibari et al 134 | Sol-gel method        | Stearic acid (SA) | TiO₂                      | 317.6-946.4 nm    | 30.36-64.76 | 58.23-59.14 | 58.12-123.96 |
| Chai et al 135 | Sol-gel method        | n-Eicosane       | TiO₂                       | 1.5-2             | 49.90-77.97 | 42.73-43.88 | 97.60-152.50 |
| Hong et al 136 | Sol-gel method        | Indium           | SiO₂                       | 200 nm            |      | 155.3 | 19.6           |
| Li et al 137 | Sol-gel method        | RT 28            | SiO₂, EG                   | 5-20, 1-5         | 27.53, 27.72 | 112.84, 104.41 |                 |
| Chang et al 138 | Sol-gel method        | n-Octadecane     | PMMA/SiO₂                  | 10                |      |      | 178.9          |
from solution to gel; hence, why this method is known as the sol-gel method; (c) the formed sol is further processed by ageing to make three-dimensional network structure; (d) finally, micro- and nano-PCM is formed after drying, sintering, and curing processes. Additionally, the sol-gel method is mixed with the miniemulsion polymerisation method to gain better thermophysical properties. For instance, Zhu et al. prepared the nano-PCM using n-octadecane as PCM with organosilica shell via interfacial co-hydrolysis and co-polycondensation of functional SiO2 precursors adopting the miniemulsion technique. The authors obtained the nanocapsules of organosilica from 200 to 693 nm of precise core-shell structure. Using mesoporous particles, the interfacial contact of EPCM with solid support enhances the nucleation sites in comparison with core-shell particles resulting reduced the supercooling. Thus, due to mesoporous confinement and heterogeneous nucleation sites, a thick shell is more promising to lessen supercooling than a thin shell.

Considering the inflexibility of shell materials, some authors follow a track for enhancing the energy storage performance of hybrid systems. Zhang et al. confined stearic acid with a SiO2 nanoshell with controlled shell density and improved the energy storage capacity of the EPCM by 36.9% compared with that of unconfined stearic acid, as shown in Figure 12. This improvement in latent heat is attributed to the formation of a various stable hydrogen bonds network in highly superimposed stress on the encapsulated SA core from the SiO2 shell, which considerably decreases the intermolecular spacing of the SA core.
in contrast to its unconfined state. Hence, collapsing and reshaping of these tightly packed stable hydrogen bonds contribute to the latent heat of SA while experiencing phase transition. Further, this strong hydrogen bonding causes the rise of phase transition temperature of confined SA. Despite the merits of the rigid shell, there are also some disadvantages. Rao et al. investigated the melting mechanism of NEPCM of confined $n$-octadecane with free and constrained SiO$_2$ shell using molecular dynamic simulation method. The results showed that the encapsulated $n$-octadecane was restrained with constrained SiO$_2$. Further, the soft shell can increase the fluidity and eventually improve the heat transfer speed of the TES systems. Compared with organic-based PCMs, IPCMs have also been confined within the SiO$_2$ shell. Zhang et al. synthesized Na$_2$SO$_4$10H$_2$O encapsulated SiO$_2$ nanobowls via synchronous hydrolysis reactions of SiO$_2$ precursors. The authors proposed, as well as validated, that the microstresses inside the liquid particles or nanodroplets was responsible for the formation of solid nanostructures. Furthermore, the SiO$_2$ wall, acting as a heterogeneous nucleator, reduces the degree of supercooling to a minor extent, however, it is immense and unsuitable for actual life applications. Moreover organic and inorganic PCMs, metallic PCMs including indium, tin and alloys have also been confined by a SiO$_2$ shell. Higher crystallinity and thermal conductivity was reported in metallic PCMs. The silica shell can further reduce the corrosion and stop leakage. Wu et al. suspended bare indium and SiO$_2$ encapsulated indium nanoparticles in a base liquid, poly-$\alpha$-olefin (PAO), for high-temperature heat transfer applications using the colloid method. In contrary of prediction, they established the fact that the coalescence of indium particles within a single-phase fluid is not a big issue. Thus, indium nanoparticles can be employed without encapsulation.
Metal-based compound materials are also investigated by scientists to use as shells other than SiO₂. In comparison with SiO₂, metal-based materials have greater value of thermal conductivity and mechanical strength, and they also provide a compact and rigid structure. The formation of a metal compound shell involves the condensation of a metal hydroxide precursor during in situ sol-gel and emulsion polymerisation, similar to SiO₂ shell formation. Until now, very few metal-based compounds have been utilised for encapsulation of PCMs. Latibari et al.⁹⁹ utilised TiO₂ to prepare nanocapsules of SA using TiO₂ as a shell and found that the nanocapsules present higher thermal conductivity and encapsulation efficiency up to 64.76% for NC of sizes 583.4 nm and 946.4 nm. Pan et al.⁹⁸ used the boehmite (γ-AlOOH) shell to encapsulate the SA, and it had been discovered that the phase transition temperature of SA was lowered by 50°C due to the confinement effect, as shown in Figure 13. The heat storage density of the prepared nanocapsules was about ~ 140 kJ/kg, which is lower than that of the pristine PCM but still higher than that of the mostly room temperature PCMs. Therefore, boehmite coating technology can be utilised to alter the phase transition temperature of high-temperature PCMs having high-energy storage performance to room temperature. Sol-gel method is usually suitable for encapsulation of both micro- and nano-enhanced PCMs. The summary of different studies adopting sol-gel method is enumerated in Table 5.

### 3.3 Chemical-mechanical methods

In chemical-mechanical methods, mechanical machine is used to accomplish the chemical reaction to encapsulate the PCMs. It generally includes the following two methods. The detail summary of these two techniques are provided in Table 6.
3.3.1 Microfluidic technique

In microfluidic technique, widely used in the medical and pharmaceutical fields, the capillary microfluidic device is utilised to form the monodisperse double emulsion droplets following the flow motion geometry. Figure 14 illustrates the complete process of formation of monodisperse double emulsion droplets developed by Sun et al. The authors used the water-oil-water (W-O-W) double emulsion template and produced the outer phase of materials (water, glycerol, and polyvinyl alcohol [PVP]) and middle phase of materials (oils included Suppocire AIM oil, paraffin, nonadecane, and eicosane) in co-flowing channels with different flow rates. The micro-PCM is obtained following washing and drying processes. Fu et al prepared the silicone/n-hexadecyl bromide microcapsules by microfluidic technique selecting n-hexadecyl bromide as an inner fluid and poly(dimethylsiloxane) vinyl terminated and poly(methylhydrosiloxane) as outer fluids. The optical and SEM images of produced micro-PCMs are shown in Figure 15.

3.3.2 Melt-coaxial electrospray technique

This encapsulation technique is the further modification of spray drying technique introducing a chemical reaction during process. It was first introduced by Loscertales et al who proposed a method to generate steady coaxial jets of immiscible liquids having micrometre/nanometre diameter in size. The schematic diagram of melt-coaxial electrospray technique used by Moghaddam et al is shown in Figure 16. The authors first time produced the
microcapsules using \( n \)-nonadecane and sodium alginate as core and shell materials, respectively.

### 3.4 Chemical methods

The chemical method ensures the production of smaller sizes such as nanocapsules using organic and inorganic materials as shell material or precursor to build the shell. Following are the most used techniques under chemical methods to produce PCM encapsulations. Table 8 represents the different approaches and properties of micro-/nano-encapsulated PCMs prepared by various chemical methods. The advantages and disadvantages of chemical methods are summarised in Table 7.

- Interfacial polymerisation
- Suspension polymerisation
- Emulsion polymerisation
- Mini-emulsion polymerisation
- In situ polymerisation

#### 3.4.1 Interfacial polymerisation/polycondensation

In interfacial polymerisation, the first process is the preparation of oil-water (O/W) or water-oil (W/O) emulsions by adopting appropriate emulsifier. The next step is the formation of polymer capsules in the surface of the core materials (ie, OPCMs) by interfacial polymerisation at an interface between two phases with each of them containing a suitable reaction monomers. The final step is the separation of the capsule from oil phase or water phase. Figure 17 shows the synthesised microcapsules via polycondensation. Park et al. prepared the nano-PCMs using paraffin as a core and PU as a shell material via interfacial polycondensation. The SEM and TEM images of prepared nano-PCMs are shown in Figure 18. Pan et al. adopted the in situ emulsion interfacial polycondensation method and prepared a novel micro-encapsulated PCM using palmitic acid (PA) and AlOOH as core and shell materials, respectively.

#### 3.4.2 Suspension-like polymerisation

The suspension-like polymerisation accomplishes on the system phases, (a) the discontinuous or dispersed phase, which contains the reagents of core material and monomers including initiator which prompt the chemical reaction; (b) the continuous phase, which includes the reactants of shell materials and solvent. The process of suspension-like polymerisation consists of the following steps: (a) the dissolution of polymer monomers into core materials under stirring to obtain homogeneous oil solution; (b) this homogeneous solution is then
added to the continuous phase at constant temperature
to produce the oil-water (O/W) emulsion; (c) further an
emulsifier is added to the O/W solution to make it more
homogenised; (d) then the prepared stable emulsion is
stirred at constant high temperature for a period to give
the proper polymerisation reaction; (e) finally, the pre-
pared encapsulated PCMs capsules are filtered, washed
and dried. The schematic flow process of suspension-like
polymerisation is shown in Figure 19.148

3.4.3 | Emulsion polymerisation

The emulsion polymerisation method takes the mixing of
the polymer in the presence of emulsifier in an oiled sys-
tem. During the process, a number of thermal, chemical,
and physical processes occur to make the micro-PCM or
nano-PCM. Unlike the suspension-like polymerisation, in
the emulsion process, the initiator is solved in the aqueous
phase, and the monomer is emulsified in the polymerisa-
tion medium with the aid of a surfactant. Commonly, there
are three steps on which the emulsion polymerisation
completes its process. Firstly, (a) the insoluble monomer
with emulsifier is dispersed in solvent reaction medium
adding the surfactant and the mechanical stirring. Further,
(b) the initiator is added, which initiates the polymerisa-
tion reactions and generates the polymer membrane on
the surface of the core material. Finally, (c) the washing
and removing of the oil to form the micro-/nano-PCMs.
Figure 20 shows the schematic of common emulsion poly-
erisation method.148 In emulsion polymerisation
method, commonly used materials for shell are PS or
PMMA, and alkane is used as a core material. Additionally,
polymer polymerisation is often carried by emulsion poly-
erisation which used the liquid PCM as a core material
to prepare the micro-/nano-PCM. The properties of var-
ious studies adopting emulsion polymerisation are listed
in Table 8.

3.4.4 | Miniemulsion polymerisation

The miniemulsion polymerisation method is the most
commonly used method to prepare the nano-PCM because
the smaller encapsulated capsules can be formed as
compared with the emulsion polymerisation method.
Compared with emulsion polymerisation, miniemulsion
polymerisation occurs within the small droplet, which
requires less input energy. Thus, this technique is
employed under ambient reaction conditions which are
necessary for the production of stable nanocapsules. In
this method, the ultrasonication process is carried out
to produce laboratory scale formation, and high-pressure
homogenizer is used for large-scale processes to obtain
the homogenisation. The scheme of miniemulsion poly-
erisation is presented in Figure 21.149 The first step
of miniemulsion process, small nanometre tiny droplets
are formed in a size range of 30 to 500 nm under high
sheering effect which are stable and contain the emulsi-
fier, water, monomer, surfactant, initiator, the dispersed,
and continuous phase. The second step is comprising on
polymerisation reaction in which these droplets are poly-
merized without changing their chemical composition.
and latex properties.\textsuperscript{150} In miniemulsion polymerisation, the monomers determine the morphological characteristics of prepared nanocapsules.\textsuperscript{151,152} The miniemulsion polymerisation technique is further categorised into three classes: direct emulsion (oil in water, O/W), indirect emulsion (water in oil, W/O), and Pickering inverse emulsion. Classical emulsifiers, eg, amphiphilic oligo (methacrylic acid 41-b-methyl methacrylate 8), sodium lauryl sulfate, Tween-80, Span-20, and Span-85 are usually utilised in direct and indirect emulsions. Contrarily, in Pickering inverse emulsion, solid particles are employed as an emulsifier.\textsuperscript{47,48,153}

Cortazar and Rodriguez\textsuperscript{49} employed the miniemulsion polymerisation technique to encapsulate paraffin wax with methyl methacrylate and investigated the kinetic, phase change properties and thermal stability. The maximum amount of encapsulated paraffin wax achieved was 60 wt.% with latent heat capacity of 140.3 J/g and obtained a capsule size of 439.4. Furthermore, the authors reported that nanocapsules having a higher weight percentage of paraffin wax undergo the phase separation phenomenon. Chen et al\textsuperscript{154} adopted the miniemulsion polymerisation technique to encapsulate the n-dodecanol as a core and PMMA as a shell material using DNS-86 as a polymerizable emulsifier and hexadecane (HD) as a co-emulsifier. The nanocapsules fabricated by this method are 100 to 200 nm in diameter and present a latent heat and encapsulation efficiency up to 98.8 J/g and 82.2\%, respectively. The authors also explored the effect of the amount of emulsifier and co-emulsifier on latent heat, diameter, size distribution, and encapsulation efficiency. Zhang et al\textsuperscript{155} encapsulated n-octadecane PCM with PEMA and PMMA with an average shell thickness of 50 nm, and a core/shell weight ratio of 80/20 and obtained an average particle size of nanocapsules 140 nm and 119 nm, respectively. The authors found the encapsulation ratio and efficiency of 89.5\% and 89.5\%, respectively. Further, they reduced the degree of supercooling significantly and found that the PEMA shell has relatively better thermal performance. Wang et al\textsuperscript{156} designed a two-step Pickering emulsification technique to prepare the nanocapsules of nonadecane as a PCM with polystyrene as a shell material by using surface-modified amphiphilic zirconium phosphate platelets (ZrP) as an emulsifier for scale-up and mass production level. Further, this method is preferable to encapsulate the organic or alkane PCMs as a core material and PS, PU, styrene-butyl acrylate, and PMMA as shell materials. In conclusion, miniemulsion is the most adopted polymerisation technique in nanocapsules coating technology.
### TABLE 7 Advantages and disadvantages of chemical methods

| Techniques               | Advantages                                                                 | Disadvantages                                      |
|--------------------------|----------------------------------------------------------------------------|----------------------------------------------------|
| Interfacial polymerisation | Controllable to produce Homogeneous in size                              | High wall permeability                              |
|                          | Good mechanical resistance                                                | Difficulty in control                               |
|                          | Good thermal and chemical stability                                        |                                                    |
| Suspension polymerisation | Controllable to produce                                                  | Fewer monomers are water soluble                    |
|                          | Efficient control of heat during reaction                                 | High-cost equipment                                 |
|                          | Low-cost production                                                        |                                                    |
| Emulsion polymerisation  | Low-cost production                                                        | Limited for liquid PCMs                             |
|                          | Rapid production                                                           | Polymer is purified from the surfactant             |
|                          | Uniform morphological capsules                                              | Used only in oiled system                           |
|                          |                                                                        | Multiphases of solution                             |
| Miniemulsion polymerisation | Nanoscale production                                                     | High-cost equipment                                 |
|                          | Good thermal and chemical stability                                        | High skill is needed for preparation                |
|                          | Uniform morphological capsules                                              |                                                    |
| In situ polymerisation    | Most effective for nanoscale production                                   | High-cost equipment                                 |
|                          | Uniform coating                                                            | High skill is needed for preparation                |
|                          | Uniform morphological capsules                                              |                                                    |
|                          | Good thermal and chemical stability                                        |                                                    |

### 3.4.5 In situ polymerisation

The in situ polymerisation method involves chemical reaction in a continuous phase of two immiscible liquids (water soluble phase and oil soluble phase) rather two phase as in interfacial polymerisation. In preparation of microcapsule/nanocapsule through in situ polymerisation, the monomers are dissolved in the continuous phase; however, the polymers are not soluble in continuous phase whereby the polymerisation reaction occurs on the surface of the core materials. Commonly, there are four steps that complete the in situ polymerisation: (a) formation of the oil-water (O/W) emulsion; (b) preparation of the prepolymer mixture liquid; (c) mixing the O/W emulsion and prepolymer liquid to encapsulate the core materials; (d) washing and drying of microcapsule/nanocapsule. Figure 22 presents the example of in situ polymerisation method. Fang and his co-authors employed the ultrasonic-assistant miniemulsion in situ polymerisation technique for coating of \( n \)-octadecane as a core with polystyrene as a shell material. The authors obtained the spherical shape nanocapsules of size ranging from 100 to 123 nm in diameter. In another study, these authors coated the \( n \)-tetradecane with PS for cold energy storage of average diameter of 132 nm and achieved the melting and freezing points and latent heats values of 4.04°C and -3.43°C, 98.71 J/g and 91.27 J/g, respectively. With the same core material \( n \)-tetradecane, Fang et al. used the urea and formaldehyde as shell materials adopting in situ polymerisation technique by adding 1% to 3% NaCl to improve the thermal stability of the prepared nanocapsules. To investigate the effect of various shell materials on thermophysical properties, Konuklu et al. used the UF, MF, and UMF resins to prepare the nanocapsules of caprylic acid. The authors found the UF resin as a best resin for shell material among others in term of stability of nanocapsules. So far now, generally, the OPCMs as core materials and UF, MF, CMC, PMMA, PMF, and PAMA are used as a shell materials.

### 4 CHARACTERISTICS EVALUATION TECHNIQUES OF EPCMS

A characterisation of EPCMs depends on the desired thermal, physical, and chemical properties. The manufacturing of micro and nano level encapsulated capsules are only valuable and successful when they fulfill the industrial and end-user requirements to meet clean energy demands. The characteristics of EPCMs are analysed using various quantitative and qualitative techniques per the evaluation of the property. Table 9 presents the list of various characterisation techniques conducted by researchers.

### 4.1 Chemical analysis

#### 4.1.1 X-ray diffraction (XRD)

The X-ray diffraction (XRD) or X-ray power diffraction (XPRD) technique is adopted to measure the crystallloid phase, material structure, crystallite atomic arrangement and size, crystal orientation, or texture and can measure the various parameters such as crystallinity and stain and distinguishes the amorphous and crystalline material. The physics of the diffraction of the X-ray is similar to the diffraction of the electrons or neutrons except the only difference is the scattering mechanism.
This technique ensures the crystalline structure of microcapsule/nanocapsule preferably suitable for inorganic shell materials. For instance, Zhang et al.\textsuperscript{280} presented the XRD results of Ag/SiO\textsubscript{2} double-layered micro-PCM with \textit{n}-eicosane as a core material to investigate the crystalline structure at different reaction time. The good crystallinity was retrained of silica layer on microcapsules surface and only an amorphous silica shell was fabricated onto the \textit{n}-eicosane core. Zhao et al.\textsuperscript{244} presented the XRD patterns of Ag-paraffin@Halloysite microspheres and obtained a consistent crystalline structure of Ag nanoparticles onto surface of paraffin@Halloysite. Additionally, the crystalline structure of paraffin was not affected in Ag-paraffin@Halloysite during the encapsulation process.

\subsection{Fourier transformed infrared spectroscopy (FT-IR)}

The Fourier transformed infrared spectroscopy (FT-IR) technique evaluates the chemical composition or the functional groups of organic and inorganic compounds and microcapsule/nanocapsule of EPCMs. The FT-IR is an effective analytical technique to identify the “chemical family” of the encapsulated core and shell materials. Further, FT-IR also confirms identifying the specific impurities in a pure compound in collection of the unique absorption bands. The FT-IR is the preferred method of infrared spectroscopy passing the IR radiation through the sample. Some IR radiation is absorbed by the sample and some transmit through the sample. At the detector, a
FIGURE 18 The SEM and TEM images of nano-PCMs A, with and B, without Fe$_3$O$_4$ nanoparticles.$^{145}$ Reused with permission from Elsevier license number 4385870250913

FIGURE 19 Scheme of the suspension-like polymerisation process.$^{148}$ Reused with permission from Elsevier license number 4385870668358 [Colour figure can be viewed at wileyonlinelibrary.com]

FIGURE 20 Scheme of the emulsion polymerisation method.$^{148}$ Reused with permission from Elsevier license number 4385870668358 [Colour figure can be viewed at wileyonlinelibrary.com]

spectra arise due the singles that represents a molecular fingerprint of the sample. In IR spectroscopy, the different spectral fingerprints arise due to the chemical structure (atoms and molecules) of different materials. In FT-IR method, the infrared spectra is obtained firstly by collecting an interferogram of a sample using an interferometer. Further, Fourier transform (FT) is applied on the interferogram from which the resulting spectrum is obtained. The FT-IR spectrometer collects and digitizes the interferogram performing the FT function and then displays the spectrum. Various researchers presented the FT-IR peaks to represent the chemical composition of micro-/nano-PCMs. Presented FT-IR results by Zhang et al.$^{264}$ showed the excellent chemical composition of encapsulated KNO$_3$@SiO$_2$ microcapsules. Kahraman et al.$^{293}$ synthesised microcapsules using PS as a shell material and various $n$-alkanes
eutectics (C17-C18, C20-C17, C20-C19, and C20-C24) and obtained the excellent functional group and chemical composition of EPCMs.

### 4.1.3 Energy-dispersive X-ray spectroscopy (EDS)

The energy-dispersive X-ray spectroscopy (EDS or EDX) is an analytical technique, which is used to investigate the surface elemental analysis, chemical characterisation, or elemental composition of a sample. The EDS technique detects the X-rays emitted from the sample during the bombardment of a high-energy beam of charged particles such as electrons or a beam of X-rays focused into the sample. Normally, the EDS technique is carried out in conjunction with scanning electron microscopy (SEM). Zhang et al.\(^{280}\) performed the EDS analysis to investigate the surface elemental distribution of Ag/SiO\(_2\) double-layered microcapsules with \(n\)-eicosane as a core material along with atomic percentage. Ma et al.\(^{245}\) determined the chemical elements and purity of paraffin@TiO\(_2\) microcapsules and confirmed the formation of TiO\(_2\) shell onto the surface of paraffin wax. Geng et al.\(^{277}\) presented the EDS results with SEM of silver-coated microcapsules found the equal proportion of Ag, which was in accordance with feed ratio.

### 4.1.4 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS), which is also known as electron spectroscopy for chemical analysis (ESCA), is a surface analysis technique to study the surface chemistry or characterisation of a sample material. XPS can measure the elemental composition, empirical formula, and chemical and electronic states from the surface or within the sample. Additionally, XPS can investigate the uniformity of elemental composition of the surface as well as with other materials that contaminate a surface. The surface elemental composition analysis carried out by Zhang et al.\(^{280}\) through XPS technique and observed the elemental characteristic peaks of Ag/SiO\(_2\) double-layered microcapsules. Geng et al.\(^{277}\) presented the XPS peak spectrum of silver-coated microcapsules and observed the existence of face-centred cubic metallic silver. Advincula et al.\(^{230}\) confirmed the functional groups and binding energy of RGO-SA microcapsules with XPS technique.

### 4.2 Thermal analysis

#### 4.2.1 Thermal conductivity analysers

Thermal conductivity is the major and fundamental property for the evaluation of EPCMs for efficient TES in various thermal systems. So far, various instruments have been utilised for the measurement of thermal conductivity of microcapsule/nanocapsule such as laser flash apparatus (LINSEIS LFA1000),\(^{132}\) TC3020 thermal conductivity meter,\(^{286}\) TC3000 thermal conductivity meter,\(^{287}\) Sweden Hot Disk thermal conductivity meter,\(^{263,275}\) and EKO HC-110 thermal conductivity meter.\(^{262}\) The encapsulated capsules are pressed in a tablet form to measure the thermal conductivity of microcapsule/nanocapsule. The thermal conductivity of a single capsule can be predicted theoretically based on composite sphere approach as follows\(^{256,294-296}\):

\[
\frac{1}{k_p d_p} = \frac{1}{k_c d_c} + \frac{d_p - d_c}{k_s d_p d_c}.
\]

Here, \(k_p\), \(k_c\), and \(k_s\) are the thermal conductivities of microcapsule/nanocapsule, core material, and shell material, respectively. Additionally, \(d_p\) and \(d_c\) are the diameter of microcapsule/nanocapsule and core material, respectively. Most of the PCMs, especially OPCMs, exhibit low thermal conductivity, which reduces heat transfer performance. The sole purpose to encapsulate the PCM is to enhance their thermophysical properties to utilise them for effective and efficient heat transfer applications. The enhancement in thermal conductivity of EPCMs solely depends on the shell material. Using organic polymeric shell materials exhibit the lower thermal conductivity, which reduce the rate of heat transfer during thermal energy storage and release. However, coating of inorganic nanomaterials such as Fe\(_2\)O\(_3\),\(^{123,145}\) TiO\(_2\),\(^{125,126,132}\) SiO\(_2\),\(^{123,147,168,169}\) GNPs,\(^{286}\) Al\(_2\)O\(_3\),\(^{263}\) CaCO\(_3\),\(^{262}\) Cu\(_2\)O,\(^{158}\) and MWCNTs\(^{448}\) increases the heat transfer rate during operation. Although the higher thermal conductivity has been achieved, however, the decrease in latent heat of phase change enthalpy observed. Therefore, there should be compromised on the optimum values of thermal conductivity and latent heat of phase change enthalpy.

#### 4.2.2 Differential scanning calorimeter (DSC)

The differential scanning calorimeter (DSC) is one of the most widely adopted technique to measure the thermo-analytical properties such as melting onset and peak temperatures, cooling onset and peak temperatures, heat capacity, latent heat of melting and cooling, and degree of supercooling (defined as the difference of peak melting and cooling temperatures).\(^{277}\) During DSC analysis, the amount of energy absorbed or released upon heating or cooling is measured providing qualitative and quantitative data during endothermic (heat absorption) and exothermic (heat rejection) phase transitions. In DSC analysis, the change of heat flux is recorded with respect to
| Reference          | Method                                                       | Core                  | Shell        | Particle Size, μm | EE, % | T<sub>m</sub> | Latent Heat, J/g |
|--------------------|--------------------------------------------------------------|-----------------------|--------------|------------------|-------|--------------|-----------------|
| Zhang and Wang 146 | Interfacial polycondensation                                | n-Octadecane          | PU           | 11-20            | 87.4  | 27.04        | 188.9           |
| Hirechi 159        | Interfacial polymerisation                                  | Insecticide           | PU           | 30-40            | 90    | –            | –               |
| Salaün et al 160   | Interfacial polymerisation                                  | Xylitol               | PUR          | 11.2-21.6        | –     | –            | 196.3           |
| Park et al 145     | Interfacial polycondensation                                | Insecticide           | PU           | 400-600 nm       | –     | 56.54        | 101.1           |
| Liang et al 161    | Interfacial polycondensation                                | n-Hexadecane          | TDI, EDA     | 20-35            | –     | 29           | 80              |
| Zou et al 162      | Interfacial polycondensation                                | Insecticide           | TDI, EDA     | –                | –     | –            | –               |
| Cho et al 163      | Interfacial polymerisation                                  | n-Octadecane          | TDI, DETA    | 1                | –     | 30.8         | 112             |
| Siddhan et al 164  | Interfacial polymerisation                                  | n-Octadecane          | TDI, DETA    | 7.3              | 92    | –            | –               |
| Su et al 165       | Interfacial polymerisation                                  | n-Octadecane          | TDI, DETA    | 5-10             | 94.7  | –            | 117.5           |
| Tseng et al 166    | Interfacial polycondensation                                | n-Pentadecane, n-Eicosane, Paraffin wax | UF | 47, 79, 150 | –     | –            | 109, 148, 127  |
| Zhang et al 167    | Interfacial polycondensation                                | n-Octadecane          | SiO<sub>2</sub> | 4-30              | –     | –            | –               |
| Pan et al 146      | In situ emulsion interfacial polycondensation               | Palmitic acid         | AIOOH        | 100 nm           | 69    | 16           | 27.8            |
| Li et al 168       | In situ emulsion interfacial hydrolysis and polycondensation| Paraffin wax          | SiO<sub>2</sub> | 200-500 nm       | 31.7  | 56.5         | 45.5            |
| Liang et al 169    | In situ emulsion interfacial hydrolysis and polycondensation| n-Octadecane          | SiO<sub>2</sub> | 169-563 nm       | 49.3  | 27.35        | 109.5           |
| Yadav et al 170    | Interfacial polymerisation                                  | Butachlor             | PU           | 1-20             | –     | –            | –               |
| Yadav 171          | Interfacial polycondensation                                | Cyclohexane           | PU           | 1.6              | –     | –            | –               |
| Hong and Park 172  | Interfacial polymerisation                                  | Migrin oil            | PU           | 7.6-12.4         | –     | –            | –               |
| Hong and Park 173  | Interfacial polymerisation                                  | Ovalbumin             | PU           | 50 nm-8 μm       | –     | –            | –               |
| Kim and Cho 174    | Interfacial polycondensation                                | Octadecane            | PU           | 1-2              | 31.9  | 54.8         | –               |
| Su et al 175       | Interfacial polymerisation                                  | n-Octadecane          | PU           | 5-10             | 93.4-94.9 | 29.8-31.0 | 115.0-117.5 |
| Guanglong et al 176| Interfacial polymerisation                                  | n-Hexadecane          | PU           | 2-4              | 50.1  | 15.52        | 66.09           |
| Lan et al 177      | Interfacial polymerisation                                  | n-Eicosane            | PU           | –                | 74.6-77.6 | 35.7-36.5 | 29.34-63.55 |
| Wei et al 178      | Interfacial polymerisation                                  | Paraffin wax          | Poly-amide   | 6.4              | 99    | 29-44        | 121.7           |
| Huang et al 179    | Suspension-like polymerisation                              | Na<sub>2</sub>HPQ<sub>7</sub>H<sub>2</sub>O | PMMA | –                | 6.8               | 51    | 150         |
| Qiu et al 180      | Suspension-like polymerisation                              | n-Octadecane          | BMA          | 1-46             | –     | 20.9-21.6   | 116.4-144.3     |
| Reference               | Method                        | Core                  | Shell                | Particle Size, μm | EE, % | $T_m$ | Latent Heat, J/g |
|------------------------|-------------------------------|-----------------------|----------------------|-------------------|-------|-------|------------------|
| Tang et al\(^1\)\(^81\) | Suspension-like polymerisation | n-Octadecane          | ODMA-MAA             | 0.5-4             | –     | 21.1 | 93               |
| Sánchez-Silva et al\(^1\)\(^82\) | Suspension-like polymerisation | Paraffin wax         | PS, MMA              | 380               | –     | 40.66-41.81 | 83.70-96.47     |
| Sánchez et al\(^1\)\(^83\) | Suspension-like polymerisation | Paraffin wax, Tetradecane | PS                 | 38.01, 11.24, 0.07, 0.07, | –     | –     | 41.65, 48.92, 0. |
|                         |                               |                       |                      |                   |       |       |                  |
|                         | PEG 800, PEG 1000, RT27, RT20, Nonadecane |                     |                      | 27.85, 64.87, 10.64 | –     | 0, 58.83, 12.01, 119.80 |                  |
| Sánchez et al\(^1\)\(^84\) | Suspension-like polymerisation | Paraffin wax         | PS                  | ~200              | 75.6  | 98-113 | 21.2-41.7        |
| Borreguero et al\(^1\)\(^85\) | Suspension-like polymerisation | RT27                 | PS                  | 500               | –     | –     | –                |
| You et al\(^1\)\(^86\)  | Suspension-like polymerisation | n-Octadecane         | PS-DVB              | 80                | –     | 29    | 126              |
| You et al\(^1\)\(^87\)  | Suspension-like polymerisation | n-Octadecane         | PS-DVB              | 71-207            | –     | 29    | 125              |
| Li et al\(^1\)\(^88\)   | Suspension-like polymerisation | n-Octadecane         | PS, PSB, PSD, PSDB, PDVB | ~50              | –     | 24.34-30.84 | 22.0-156.9      |
| Chaiyasat et al\(^1\)\(^89\) | Microsuspension polymerisation | n-Octadecane         | PDVB                | ~1.5              | –     | 22.6  | 192              |
| Qiu et al\(^1\)\(^90\) | Suspension-like polymerisation | n-Octadecane         | BDHA, DVB, TMPTA, PETRA | 0.72-0.75             | –     | 29.3-35.2 | 83.7-156.4      |
| Cheng et al\(^1\)\(^91\) | Suspension-like polymerisation | n-Octadecane         | TPGDA               | 300-600 nm        | 100   | –     | 104              |
| Ma et al\(^1\)\(^92\) | Suspension-like polymerisation | Paraffin wax, Butyl stearate | Acrylate-based polymer | 10-80             | 46-68 | 29.08-32.12 | 63.98-93.97    |
| Sanchez et al\(^1\)\(^93\) | Suspension-like polymerisation | Paraffin wax         | PS                  | 4.80              | –     | –     | 102.42           |
| Sanchez-Silva et al\(^1\)\(^94\) | Suspension-like polymerisation | RT31                 | PS                  | 4.0-53.2          | 49.0-67.9 | 31.56 | 75.7-135.3      |
| Borreguero et al\(^1\)\(^95\) | Suspension-like polymerisation | Paraffin wax         | PS                  | 3.83, 3.97        | 43.6, 35.1 | – | 58.6, 79.0      |
| Qiu et al\(^1\)         | Suspension-like polymerisation | n-Octadecane         | PBMA, PBA           | 2.75              | 47.7-55.6 | 29.1-31.6 | 96-112           |
| Ma et al\(^1\)\(^96\) | Emulsion polymerisation       | Paraffin wax          | PMMA                | 0.25              | –     | 24-33 | 101              |
| Giro-Paloma et al\(^1\)\(^97\) | Emulsion polymerisation       | Paraffin wax, Palmitic acid | PSCeEA          | 0.166, 0.265      | –     | 36.71, 59.12 | 49.03, 97.93    |
| Sarı et al\(^1\)\(^98\) | Emulsion polymerisation       | n-Octacosane          | PMMA                | 0.25              | –     | 50.6  | 86.4             |
| Sarı et al\(^1\)\(^99\) | Emulsion polymerisation       | n-Heptadecane         | PMMA                | 0.14-0.40         | –     | 18.2  | 81.5             |
| Alkan et al\(^1\)\(^100\) | Emulsion polymerisation       | Docosane              | PMMA                | 0.16              | –     | 41.0  | 54.6             |
| Alkan et al\(^1\)\(^101\) | Emulsion polymerisation       | n-Eicosane            | PMMA                | 0.70              | –     | 35.2  | 84.2             |
| Alay et al\(^1\)\(^102\) | Emulsion polymerisation       | n-Hexadecane          | PMMA                | 0.22, 1.05        | –     | 15.69, 17.34 | 68.89, 145.61   |
| Alay et al\(^1\)\(^103\) | Emulsion polymerisation       | n-Hexadecane          | PMMA                | 140-466 nm        | –     | 17.23 | 148.05           |
| Baek et al\(^1\)\(^104\) | Emulsion polymerisation       | n-Octadecane          | PS                  | 80 nm             | 14.6-56.8 | – | 6.48-49.76      |
| Sarı et al\(^1\)\(^105\) | Emulsion polymerisation       | n-Heptadecane         | PS                  | 1-20              | 63.3  | 21.48 | 136.89           |

(Continues)
| Reference | Method                         | Core                               | Shell                      | Particle Size, μm | EE, %   | $T_m$      | Latent Heat, J/g |
|-----------|-------------------------------|-----------------------------------|----------------------------|-------------------|---------|-----------|-----------------|
| Sar et al 153 | Emulsion polymerisation       | $n$-Nonadecane                    | PMMA                       | 0.1-35            | 60.3    | 31.23     | 139.20          |
| Sar et al 205 | Emulsion polymerisation       | $n$-Heptadecane, $n$-octadecane, $n$-nonadecane, $n$-eicosane, $n$-tetraicosane | PMMA                       | 0.01-100          | 50.2-65.4 | 19.24-35.80 | 171.14-265.60   |
| Sar et al 206 | Emulsion polymerisation       | $n$-Tetracosane/$n$-Octadecane PS |                            | 0.01-115          | 64.4    | 25.96     | 156.39          |
| Sar et al 207 | Emulsion polymerisation       | Capric/stearic acid               | PMMA                       | 1.3              | –       | 21.37     | 116.25          |
| Luo and Zhou 208 | Miniemulsion polymerisation | Paraffin wax                      | PS                         | <100 nm           | –       | –         | –               |
| Chen et al 154 | Miniemulsion polymerisation   | $n$-Dodecanol                     | PMMA                       | 150 nm            | 82.2    | 18.2      | 98.8            |
| Chen et al 209 | Miniemulsion polymerisation   | $n$-Dodecanol                     | SBA                        | 100 nm            | 98.4    | 27        | 109.2           |
| Li et al 210   | Miniemulsion polymerisation   | $n$-Hexadecane                    | UF                         | 270 nm            | –       | 16.15-16.36 | 114.6-143.7     |
| Fuensanta et al 211 | Miniemulsion polymerisation | RT80                             | SBA                        | 52-112 nm         | 78-80   | 77.7-84.1 | 4.9-23.9        |
| Fang et al 154 | Miniemulsion polymerisation   | $n$-Tetradecane                   | PS                         | 132 nm            | 89      | 4.04      | 98.71           |
| Fang et al 213 | Miniemulsion in situ polymerisation | $n$-Octadecane              | PS                         | 100-123 nm        | –       | 30-35    | 124.4           |
| Fang et al 212 | Miniemulsion in situ polymerisation | $n$-Octadecane               | PS                         | 108-126 nm        | –       | –         | 88.35-124.4     |
| Fang et al 211 | Miniemulsion polymerisation   | $n$-Dotriacontane                | PS                         | 168.2 nm          | 61.23   | 70.9      | 174.8           |
| Tumirah et al 214 | Miniemulsion in situ polymerisation | $n$-Octadecane                   | PS-MMA                      | 102 nm            | –       | 29.5      | 107.9           |
| Wu et al 215   | Miniemulsion polymerisation   | Paraffin wax                      | PS                         | 100 nm            | 47.7-55.6 | 29.1-31.6 | 96-112          |
| Zhang et al 155 | Direct miniemulsion polymerisation | $n$-Octadecane               | PEMA, PMMA                  | 140 nm, 119 nm    | 89.5    | 32.2, 31.9 | 198.5, 208.7    |
| Hu et al 216   | In situ polymerisation        | Paraffin wax                      | CMC-MF                      | 50 nm             | 63.1    | 24.4      | 83.46           |
| Nan et al 217  | In situ polymerisation        | $n$-Octadecane                   | P(MMA-co-AMA)              | 577-693 nm        | 64.0-71.6 | 24.7-27.4 | 129-151         |
| Fang et al 213 | In situ polymerisation        | $n$-Tetradecane                   | UF                         | 100 nm            | 60      | 5.57-9.01 | 66.01-134.16    |
| Choi et al 218 | In situ polymerisation        | $n$-Tetradecane                   | PVA, PS, PMMA, PEMA        | 23.15, 16.89, 18.59 | –       | 2.06, 5.97, 5.68 | ~0, 66.26, 80.62 |
| Jin et al 219  | In situ polymerisation        | Paraffin wax                      | UF                         | 20                | –       | 53.3-5.44 | ~98.5 to ~200.4 |
| Zhang et al 220 | In situ polymerisation        | $n$-Octadecane                   | MF                          | 0.9-9.2           | –       | 30.4-30.5 | 169-172         |
| Li et al 221   | In situ polymerisation        | $n$-Octadecane                   | MF                          | 2.2               | 59      | 40.6      | 144             |
| Hong and Park 222 | In situ polymerisation        | Migrin oil                       | MF                          | <10               | –       | –         | –               |
| Salaün et al 223 | In situ polymerisation        | $n$-Hexadecane, $n$-Eicosane     | MF                          | ~10               | 70      | –         | 163-170         |
| Zhang and Wang 224 | In situ polymerisation        | $n$-Octadecane                   | MF                          | 20 nm             | 92      | 26.91     | 146.25          |
| Zhang et al 225 | In situ polymerisation        | $n$-Octadecane                   | UMF                         | 0.2-5.6           | 65.78   | 32.77-34.88 | 91.10-241.68    |
| Zhang et al 226 | In situ polymerisation        | $n$-Octadecane                   | MF                          | 0.2-1.8           | –       | 24.4-36.2 | 44-166          |
| Fan et al 227  | In situ polymerisation        | $n$-Octadecane                   | MF                          | 1-2               | –       | –         | 102-166         |

(Continued)
| Reference       | Method               | Core                     | Shell                | Particle Size, μm | EE, % | $T_m$ | Latent Heat, J/g |
|-----------------|----------------------|--------------------------|----------------------|-------------------|-------|-------|----------------|
| Guo et al \(^{228}\) | In situ polymerisation | Dodecanol                | PEG modified MF      | 0.83 ± 0.23-14.4 ± 5.56 | –     | 25.8  | 118.9          |
| Konuklu et al \(^{229}\) | In situ polymerisation | Decanoic acid            | PMUF                 | 0.28              | –     | 33    | 88            |
| Krupa et al \(^{230}\) | In situ polymerisation | Paraffin wax             | MF                   | 15 ± 3            | –     | 129.4 | 157           |
| Yuan et al \(^{231}\) | In situ polymerisation | Paraffin wax             | SiO\(_2\), GO       | ~10               | 49.6  | 49.7  | 87.1           |
| Fan et al \(^{232}\)  | In situ polymerisation | n-Octadecane             | MF                   | ~1                | 20    | –     | 160           |
| Zhang et al \(^{233}\) | In situ polymerisation | n-Octadecane, n-nonadecane, n-eicosane | MF | 0.3-6.4 | 70 | 36.5, 219.3, 45.3 | 167, 161, 172 |
| Shin et al \(^{234}\)  | In situ polymerisation | n-Eicosane               | MF                   | 0.1-10            | 53    | 36.9  | 134.4          |
| Shin et al \(^{234}\)  | In situ polymerisation | n-Eicosane               | MF                   | 1.89              | –     | 36.9  | 134.3          |
| Boh et al \(^{235}\)  | In situ polymerisation | P1-S, RT25, RT40        | Amino-aldehyde       | 5.91, 2.78        | –     | –     | –              |
| Sarier and Onder \(^{12}\)| In situ polymerisation | n-Octadecane, n-eicosane, n-hexadecane | MF | 1-500 | – | 17.7 | 44.6 |
| Rao et al \(^{236}\) | In situ polymerisation | n-Docosane               | MF                   | 10                | –     | –     | 150            |
| Salaün and Vroman \(^{237}\) | In situ polymerisation | n-Docosane               | MF                   | 5-20              | 68-135.4 | 55.69-56.72 | 17.74-57.81 |
| Yuan et al \(^{238}\) | In situ polymerisation | n-Dodecanol              | PMF                  | 1-10              | –     | –     | –              |
| Yu et al \(^{239}\) | In situ polymerisation | n-Dodecanol              | MF                   | 30.6              | 93.1  | 21.5  | 187.5          |
| Lee et al \(^{240}\) | In situ polymerisation | n-Octadecane, n-hexadecane | MF | 5-20 | – | – | 150-210 |
| Li et al \(^{221}\) | In situ polymerisation | n-Octadecane, n-hexadecane | MF | 2.2 | 59 | 40.6 | 144 |
| Fu et al \(^{241}\) | In situ polymerisation | n-Docosane               | MF                   | 3.6               | –     | –     | –              |
| Silakhori et al \(^{242}\) | In situ polymerisation | Paraffin wax             | Aniline (C\(_6\)H\(_7\)N) | 300-500 nm     | 49.7  | 53.4  | 65.1           |
time; however, the heating rate and sample mass is most important because the changing heat rate and sample mass will give temperature-heat flow responses.\textsuperscript{293,297}

### 4.2.3 Thermogravimetical analysis (TGA)

The thermogravimetry or thermogravimetical analysis (TGA) technique measures the amount and rate change of the material weight as a function of temperature or at isothermal condition as a function of time in a controlled atmospheric conditions upon melting and solidification.\textsuperscript{246}

The change in the mass of sample material of microcapsule/nanocapsule is examined under the various thermal modes such desorption, absorption, sublimation, vaporisation, oxidation, reduction, and decomposition.\textsuperscript{298}

### 4.3 Physical analysis

#### 4.3.1 Performance parameters

In the literature, a few mathematical relations have been used to address the physical and thermal performance of EPCMs. These relations are mainly affected by the mass of core and shell materials, mass of emulsifier, and cross-link agent, herein the synthesis encapsulation technique. The theoretical and actual loading or core content of PCM can be calculated as follows\textsuperscript{158}:

\[
C_{th} = \frac{m_{\text{core}}}{m_{\text{core}} + m_{\text{shell}}} \times 100\% \quad (2)
\]

\[
C_{act} = \frac{m_{\text{core}} - m_{\text{shell}}}{m_{\text{core}}} \times 100\% \quad (3)
\]

Major thermal performance of EPCMs are generally evaluated using encapsulation ratio (ER), encapsulation efficiency (EF), thermal energy storage capability (TESC), and thermal cycling performance (TCP) as follows\textsuperscript{244,245,299}:

\[
ER = \frac{\Delta H_{m,\text{EPCM}}}{\Delta H_{m,\text{PCM}}} \times 100\% \quad (4)
\]

\[
EF = \frac{\Delta H_{m,\text{EPCM}} + \Delta H_{s,\text{EPCM}}}{\Delta H_{m,\text{PCM}} + \Delta H_{s,\text{PCM}}} \times 100\% \quad (5)
\]

\[
\text{TESC} = \frac{\Delta H_{m,\text{PCM}}(\Delta H_{m,\text{EPCM}} + \Delta H_{s,\text{EPCM}})}{\Delta H_{m,\text{EPCM}}(\Delta H_{m,\text{PCM}} + \Delta H_{s,PCM})} \times 100\% \quad (6)
\]

\[
\text{TCP} = \frac{\Delta H_{m,\text{EPCM}}'}{\Delta H_{m,\text{PCM}}} \times 100\% \quad (7)
\]

Here, \(\Delta H_{m,\text{EPCM}}\) and \(\Delta H_{s,\text{EPCM}}\) are the change in enthalpies of melting and solidifications, respectively, of EPCM, and \(\Delta H_{m,\text{PCM}}\) and \(\Delta H_{s,\text{PCM}}\) are the change in enthalpies of melting and solidifications, respectively, of PCM. The change in enthalpy or latent heat of fusion is measured by the DSC. During the practical utilisation of EPCMs in various applications, the shell of the encapsulated microcapsule/nanocapsule possesses a crack or porous structure resulting in the leakage of the core PCM. So the core percentage or leakage rate in microcapsule/nanocapsule at various times is usually used to define the leakage-performance.\textsuperscript{249,280} The leakage rate (\(L_r\)) between the initial mass (\(m_0\)) of capsules and after heating periodically at certain melting temperature, indicated as \(m_t\), is defined as follows:

\[
L_r = \frac{m_0 - m_t}{m_0} \times 100\% \quad (8)
\]

Herein, it can been noticed that increasing the thickness although deceases the percentage of leakage rate of the capsules. However, as a result of this, ER will decrease simultaneously.
### TABLE 9  Characterisation techniques used by the various researchers for characteristics evaluation of EPCMs

| Characterisation Technique | References |
|---------------------------|------------|
| X-Ray diffraction (XRD)   | 55,56,72,75,87,102,110,125,126,128,130,133,155,168,173,219,232,233,241,243-245 |
|                           | 38,43,91,98,106,109,123,124,132,147,158,169,213,214,216,231,246,252 |
| Fourier transformed infrared spectroscopy (FT-IR) | 87,96,118,129,163,165,166,172,173,175,177,203,219-221,225,226,233,237,238,239,254 |
|                           | 45,69,70,74,130,131,133,144,160,161,182,187,196,199,202,224,239,255,256 |
|                           | 4,54,56,102,127,128,134,146,154,155,167,168,190,191,209,211,245,257,258 |
|                           | 43,94,99,121,123,125,126,145,153,178,192,213,216,229,230,242,259,260 |
|                           | 44,83,91,98,109,124,132,140,169,181,197,204-207,214,231,247,261-263 |
|                           | 37,147,158,228,245,248-250,264-267 |
| Scanning electron microscopy (SEM) | 73,79,86,96,111,129,166,172,173,175,183,203,218,220,221,225-227,232-234,236,245,268 |
|                           | 12,45,70,72,87,135,144,157,164,186,199,202,219,224,237-239,254,255,269-271 |
|                           | 69,75,78,102,120,130,131,133,134,137,146,154,167,182,187,188,190,194,196,198,200,201,241,256 |
|                           | 4,14,49,54,56,87,135,144,157,164,186,199,202,219,224,237-239,254,255,269-271 |
|                           | 38,43,81,94,95,99,121,123,125,126,145,153,180,181,192,204,205,216,229,230,246,259-261 |
|                           | 85,90,91,98,106,109,124,132,134,156,169,197,206,207,228,231,247,262,263,274,275 |
|                           | 37,147,158,248-252,265-267,276-278 |
| Transmission electron microscopy (TEM) | 54,56,70,72,75,87,100,102,132,134,155,168,191,203,208,209,211,255,270,273,279 |
|                           | 98,106,109,110,123,132,145,146,156,158,169,213,214,245,247,248,277 |
| Energy-dispersive X-ray spectroscopy (EDS) | 56,102,106,109,123,147,158,245,262,265,269,274,277,280-283 |
| X-ray photoelectron spectroscopy (XPS) | 123,126,132,138,160,243,230,251,257,274,277,280 |
| Optical microscopy (OM) | 43,99,123,138,140,142,156,249,262,284,285 |
| Thermal conductivity analysers | 132,147,225,262,263,275,276,286,287 |
| Differential scanning calorimeter (DSC) | 12,73,113,117,129,165,166,173,175,177,183,203,218,220,221,225,232,236,268,279,288,289 |
|                           | 45,69,70,72,74,87,120,130,131,134,144,157,161,182,186,196,199-202,219,224,237,254 |
|                           | 14,54,78,102,127,128,134,146,154,155,160,167,187-191,194,209,241,243,256,257,272 |
|                           | 4,38,43,56,94,99,100,110,123,125,126,138,153,168,176,213,229,230,242,290 |
|                           | 44,132,153,180,181,192,197,204,205,214,214,260-262 |
|                           | 37,85,91,98,106,109,124,140,156,158,169,206,207,228,231,247,262,263,264,275 |
|                           | 238,239,246-248,252,265-267,276,277 |
| Thermogravimetric analysis (TGA) | 45,72,135,157,173,175,177,186,199,219,221,225,227,237-239,269,270 |
|                           | 14,69,75,120,130,131,144,146,154,160,167,182,187,188,190,196,198,200,256 |
|                           | 4,43,54,56,118,128,134,155,155,168,178,189,191,211,231,242,243,257,290 |
|                           | 38,99,123,132,138,145,153,180,192,204,205,214,216,229,230,246,259,260,262 |
|                           | 37,91,98,106,109,124,147,158,169,197,206,207,228,231,247,251,263,265,266,275,277,291 |
| Atomic force microscopy (AFM) | 85,197,228,248,249,257,259,292 |
| Brunauer, Emmett, and Teller (BET) | 257 |
| Raman Spectroscopy | 231,238 |
| Small angle X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS) | 99,131,144,167,224,262 |

#### 4.3.2  Optical microscopy (OM)

To evaluate the particle size, morphology, transparency, colour, and fixation, a few researchers have presented images of EPCMs using optical microscopy (OM) technique.99,138,285 Wang et al285 presented the images of SiC-/PMF-coated n-octadecane microcapsules and revealed that nano-SiC solid particles could be absorbed at oil-water interface. Additionally, it showed the 10 μm size of microcapsules using OM technique.

#### 4.3.3 Scanning electron microscopy (SEM)

The SEM technique, based on scattered electrons, is used to determine the particle size and shape using electron microscope of the microcapsule/nanocapsule. SEM uses a higher energy beam of electron on the surface of the sample, which generates various signals showing the image of the sample surface. These variety of signals reveal the various characteristics information of the sample including
topography (the surface features or texture), morphology (the shape and size), composition (elements and compounds) and crystallography (atoms arrangement). Various research has presented SEM images to represent chemical composition, morphology, and crystallography of EPCMs, as mentioned in Table 9.

4.3.4 Transmission electron microscopy (TEM)

TEM, based on the transmitted electrons, is used to measure at higher resolution than SEM, such as nano level closer to the atomic structure. So the morphology and PSD of microcapsule/nanocapsule can also be determined by TEM at a smaller level (eg, nanometres), which is beyond the limit of SEM. In TEM, the electron passes through the sample, whereas in SEM, the electron beam just scans over the surface of the sample material. Geng et al presented TEM images of Ag-MMF–coated microcapsules of 1-tetradecacanol with diameter of 100 nm.

4.3.5 Atomic force microscopy (AFM)

The atomic force microscopy (AFM) is a surface topography measuring technique, which measures the surface images near nanometre resolution as well as the local properties such height, friction, and magnetism with a scanning probe. Further, AFM can also evaluate the mechanical properties of the microcapsule/nanocapsule. Zheng et al evaluated the highest elastic modulus of CNTs coated n-eicosane microcapsules. Huang et al evaluated the surface profile of CNTs coated n-octadecane microcapsules and obtained the average roughness and root mean square roughness with CNTs, which were 17.12 nm and 21.09 nm, respectively, approximately three times that of microcapsules without A-CNTs/PSS multilayers.

4.3.6 Brunauer, Emmett, and Teller (BET)

The BET technique is used to measure the specific surface area of the solid including pore size distribution by adsorption/desorption of nitrogen gas on the surface and then calculating the amount of the adsorbate gas into the surface corresponding to a monomolecular layer of the surface. The BET equation can be used to determine the surface area of the wide variety of gases or vapours. The most commonly used BET equation is described below, in Equation 9.

\[
\frac{x}{V(1-x)} = \frac{1}{V_m \cdot c_{BET}} + \frac{x(1-c_{BET})}{V_m \cdot c_{BET}}
\]

where \( V \) and \( V_m \) are the volumes of absorbed molecules and monolayer volume, respectively, \( c_{BET} \) is the BET constant, and \( x \) is the relative pressure \( (x = P/P_o) \).

4.3.7 Small angle X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS)

The small angle X-ray scattering (SAXS) is used to determine the crystalline structure of polymers coated microcapsule/nanocapsule at a range of 0.02° to 10°. The wide angle X-ray scattering (WAXS) or wide angle X-ray diffraction (WAXD) is used to measure the crystalline structure of inorganic- and organic polymeric–encapsulated materials at wider angles at 2\( \theta > 1^\circ \). The Bragg peaks (diffraction peaks) are analysed by function of scattering angles, which arise by scattering from the sub nanometre size crystal structures. A few researchers have utilised SAXS and WAXS techniques for EPCMs.

5 STABILITY OF EPCMS

The stability of ECPMs is the real challenge for the current industrial revolution. Stability of EPCMs is mainly concerned with thermal and chemical stability to ensure the long-term usage of micro-/nano-encapsulated PCMs. Generally, a number of repeated thermal cyclic tests are performed to validate the thermal reliability by measuring the thermophysical properties. The quality of the encapsulated PCMs is evaluated by assuring that there is no geometrical variation, leakage of microcapsule/nanocapsule, sedimentation, aggregation, and crystallisation of interlayer materials. A thermodynamically and chemically encapsulated PCMs ensures the long-term performance as TES materials for industrial and research applications. Further, thermal and chemical stability of the EPCMs enhances the economic feasibility maintaining their latent heat of fusion and melting for employing under repeated melting/freezing cycles with time.

5.1 Chemical stability

The chemical stability of the encapsulated capsules is generally determined by adopting the anti-osmosis test in which sealing performance of encapsulated capsules of PCMs is determined. The anti-osmosis test determines the weight loss of the extracted microcapsule/nanocapsule, and it can be used to evaluate the durability of the encapsulated capsules. Zhang et al conducted the anti-osmosis to evaluate the leaf performance of SiO\(_2\) (shell material) and n-octadecane (core material) under different conditions. The authors reported that microcapsules of 50/50 weight ratio had the best anti-osmosis
performance as compared with others weight ratios. Further, they evidenced that the release rates of microcapsules depend on the thickness of the silica shell. The greater the thickness of the shell, the lesser the release rate of the encapsulated capsules. A similar method to determine the leaking performance or durability of micro-encapsulated n-octadecane was developed by Zhang and Wang. The authors used SMA, SDS, and PVA as emulsifiers, and results showed that by using SMA and SDS, as shown in Figure 23, the release rate of the microcapsules increased with increasing weight percentage of the core materials. Further, the authors reported that release rate of microcapsules prepared by using SDS was much higher than that of microcapsules using SMA at the same weight ratio. Su et al. also adopted the same method and SMA was used as a surfactant with percentage of 1.0, 2.0, 3.0, and 4.0% under the presences of ethyl alcohol as an extraction solvent. They found that the 4.0% of SMA showed the lower release rate of PU shell, as shown in Figure 24. Further, they suggested that this releasing phenomena might be attributed to the emulsion effect and shell polymerisation.

5.2 Thermal stability
The thermal stability of the encapsulated microcapsule/nanocapsule of PCMs has the greater potential and significance in TES systems. Several studies have been conducted to ensure the consistency in latent heat of fusion and melting temperature of EPCMs. Thermal cycles or thermal cycling tests can be conducted using TGA and DSC. Silakhori et al. conducted the thermal cycles tests using TGA and DSC methods up to 1000 cycles for paraffin wax/polyaniline nanocapsules and found the chemical and thermal structures of the capsules remained unchanged. Similarly, Hawlader et al. claimed that encapsulated capsules of paraffin wax maintained their original geometrical profile and energy storage capacity even after 1000 thermal cycles. Fortuniak et al. used DSC for 50 cycles of fusion and crystallisation and reported the proof of thermal stability of microcapsules of n-eicosane coated with polysiloxane. Sarı et al. performed the FT-IR, TGA, and DSC analysis of PMMA/n-octadecane microcapsules for 5000 thermal cycles, shown in Figure 25. They reported that melting temperature changed from 51.1°C to 52.3°C, freezing temperature was changed from 53.7°C to 55.2°C, and the latent heats of melting and freezing were measured as 79.9 J/g and 81.7 J/g, respectively, after 5000 thermal cycling. The authors concluded that there was good thermal and chemical stability of PMMA/n-octadecane microcapsules in terms of changing of its thermal properties. Alkan et al. carried out the FT-IR, DSC, and TGA tests for thermal and chemical stability of PMMA/docosane after 1000, 3000, and 5000 thermal cycles. The authors found the melting point of PMMA/docosane changed from 40.1 to 41.4°C and crystallising point changed from 41.6 to 41.7°C; moreover, the latent heat of melting and crystallisation was found of 75.2 J/g and 67.7 J/g, respectively, after 1000, 3000, and 5000 thermal cycles. The authors evidenced that there was no significant changed in phase change thermal properties as well as in chemical structure of the microcapsules after thermal cycling tests, shown in Figure 26. Sharma et al. carried out the 1500 repeated melt/freeze cycles to study the thermal stability of commercial grade acetamide, stearic acid, and paraffin wax. The DSC curves of three PCMs concluded that acetamide and paraffin wax showed
convection heats during phase transformation define the employability of EPCMs for a specific application. In this section, we reviewed some potential applications, which have been greatly accelerated incorporating micro and nano EPCMs.

6.1 Solar-to-thermal energy storage

An unlimited, economic, and sustainable energy source has always been a potential requirement in the sight of researchers and industrialist. One such energy source is the sun. Here, the question is how to utilise solar energy in an efficient and longer time period to meet the energy requirement for both in day and especially in night time as more heat and electricity are required because of the absence of sun. To address this challenge, novel smart energy storage materials are needed to be developed, which can efficiently store this renewable solar energy source along with reducing global warming and climate changes issues. Therefore, EPCMs have been gaining the promising attention in recent years to absorb solar thermal energy in the form of latent heat and release it later on to meet the energy demands. The utilisation of micro- and nano-PCMs has been under investigation for photo-thermal conversion, solar cells, direct absorb solar collector, photo catalyst, storage tank or container, heat exchanger, and minichannel to harvest and convert solar energy directly and indirectly. Zeng et al. synthesised the core-shell nanoparticles using Sn/SiO2/Ag, where Sn was used as the core material to store the thermal energy, SiO2 was used as a shell material to provide containment, and Ag shell was used to enhance the light absorption intensity. They found good optical absorption and TES capabilities of Sn/SiO2/Ag composite nanoparticles, which improved the volumetric absorption efficiency of DASC from medium- to high-temperature range. Zheng et al. investigated the geometry-dependent heating efficiency and stability of hollow structure micro-PCMs (h-micro-PCMs) and solid PCM core particles (s-micro-PCMs) to enhance the thermal diffusivity and reliability of micro-PCMs for solar-thermal energy conversion and storage systems. The results revealed more stability and higher heat diffusivity within and above the phase transition range in case of h-micro-PCMs than s-micro-PCMs. Pethurajan et al. synthesised the SiO2/D-mannitol micro-PCMs using sol-gel technique for solar energy harvesting and storage systems. Fundamental thermophysical properties were studied and found enhancement in thermal conductivity of 1.77 W/m.K. Additionally, they found excellent thermal stability that after 100 cycles, latent heat of melting was 250.75 J/g, and encapsulation ratio and efficiency were reported of 88.925% and 85.024%,
Thermal management is highly emerging and keen requirement for the efficient performance of thermal systems. The effective thermal management requires a highly power, which encourages researchers to develop practical devices or systems of higher energy conversion efficiency. From the last three decades, researchers have been putting efforts on solar-to-thermal energy harvesting and conversion using PCM, which stores the heat through absorption only during hours of sunshine. Contrarily, there is a huge challenge for countries located at the upper reaches of the Northern hemisphere, which lack sunlight throughout the winter season. To overcome this challenge, studies are available that developed the electrical conductive micro-/nano-PCMs to convert and store energy from electrical-to-thermal. The conductive EPCMs convert the electrical energy into heat on applying the small input voltage and store that heat in form of latent heat while melting of the PCMs within the microcapsule and nanocapsule. Zheng et al. synthesized a joule heating system to reduce the convective heat transfer from electrothermal system to the surrounding by inserting the highly conductive and stable microcapsules of docosane and GO-CNT as core and shell material, respectively. The results shown in Figure 28A-E illustrate that with loading of 5% of micro-PCMs, the working temperature can be improved by 30% even at lower voltage and ambient temperature, which ensures a potential usage in daily household heat storage applications.

Figure 28C further presents that heat storage and release time-temperature curves are similar to solar-to-thermal energy conversion and storage. The conversion and storage efficiency from electrical-to-thermal energy can be calculated by using Equation 11:

$$\eta = \frac{m \Delta H}{VIt}$$

Here, \( m \) and \( \Delta H \) are the mass and phase transition enthalpy of EPCMs, respectively, and \( V \), \( T \) and \( t \) are the voltage, current, and time duration while phase transformation, respectively. To achieve the higher efficiency, EPCMs should have high TES capacity and high electrical conductivity so that it can be driven by low voltage. Recently, Hussain et al. synthesized the bifunctional nano-PCMs consisting oleic acid (OA)-PEG core and SiO\textsubscript{2}/SnO\textsubscript{2} shell materials to store the thermal and electrical energies. The authors reported the thermal and electrical conductivities of 0.7053 W/mK and 1.08 \times 10^{-7} S/cm, respectively. Additionally, it was suggested that OA-PEG/SiO\textsubscript{2}/SnO\textsubscript{2} nano-PCMs can be used as electrode material for electrochemical energy storage.

6.2 Electrical-to-thermal energy storage

The energy harvesting and conversion from electrical to thermal is an emerging area to store heat for beneficial usage. The fundamental evaluation parameter is the enhanced or reduced temperature at a certain input energy harvest and conversion characteristics. They found that micro-PCMs eutectics consisting of paraffin@Cu-Cu\textsubscript{2}O by a hydrothermal method for solar energy storage and photo-thermal conversion and found the encapsulation efficiency of 62.79%. Further, micro-PCMs capsules are suspended in DI water studied the photo-thermal conversion characteristics. They summarised that paraffin@Cu-Cu\textsubscript{2}O slurry had the better light absorbing properties, thermal conductivity, and photo-thermal conversion performance, which can be potentially used for DASC systems. Chen et al.\textsuperscript{306} found the melting temperature and latent heat of 59.28°C and 91.94 J/g, respectively, of SA/MWCNTs prepared by vacuum absorption method. Further, they estimated the photo-thermal conversion efficiency by suspending the SA/MWCNTs into water making a stable suspension. The authors predicted the excellent photo-thermal conversion performance with temperature increased from 30°C to 80°C and found the 85% receiver efficiency, which shows its potential to store solar energy for practical applications. Zhao et al.\textsuperscript{344} developed innovative hybrid micro-PCMs consisting of Ag-Paraffin@Halloysite to store solar energy and studied the catalytic reactions by self-assembly method. Figure 27 shows the catalytic activity of Ag-Paraffin@Halloysite used as a catalysis and revealed the better conversion activity of 95.3% in 6 min compared with one without heat storage with conversion of 71.1% in 6 min for catalytic reduction of 4-nitophenol. The efficiency (\( \eta \)) of solar-to-thermal energy conversion and storage systems confined with EPCMs can be determined from Equation 10:

$$\eta = \frac{m \Delta H}{\Delta t}$$

Here, in Equation 10, \( m \) is the mass of confined EPCMs, \( \Delta H \) is the latent heat enthalpy during phase transformation, \( \Delta t \) is the effective surface area of solar system, \( \Delta t \) is the intensity of solar irradiation, and \( \Delta t \) is phase transformation completion duration. To achieve the higher efficiency, EPCMs should have high TES capacity and high electrical conductivity so that it can be driven by low voltage. Recently, Hussain et al.\textsuperscript{299} synthesised the bifunctional nano-PCMs consisting oleic acid (OA)-PEG core and SiO\textsubscript{2}/SnO\textsubscript{2} shell materials to store the thermal and electrical energies. The authors reported the thermal and electrical conductivities of 0.7053 W/mK and 1.08 \times 10^{-7} S/cm, respectively. Additionally, it was suggested that OA-PEG/SiO\textsubscript{2}/SnO\textsubscript{2} nano-PCMs can be used as electrode material for electrochemical energy storage.
conductive media to transfer the heat flux from hot source towards the sink. PCMs, with their dual favourable thermal properties of isothermal phase transition temperature and high latent of fusion, have increased the demand for thermal cooling of electronics devices, Li-ion batteries, photovoltaic modules, high power lasers, thermoelectric and thermochemical systems, photo-thermal conversion systems, solar thermal energy storage systems, exothermic chemical reactions, and energy harvesting industrial power plants.\textsuperscript{109,310} For cooling of each system, it requires a confine amount of PCM and range of operating temperature. Overall, cooling techniques are classified as active cooling and passive cooling. Here, we summarise the active cooling technique based on single-phase and multiphase fluids based on EPCMs. For cooling of high heat generating microprocessing units, microchannel cooling technique has been introduced, which uses the heat transfer fluid (HTF) to transfer the heat energy from hot source to cold source. The HTF is selected based on its viscosity and heat transfer capacity. The heat transfer capacity of single-phase fluid (eg, water) is very low to ensure the efficient thermal performance maintaining the device temperature at a comfortable level. In order to enhance the heat transfer capacity of HTF, the microcapsule/nanocapsule are dispersed into the base fluid. The prepared fluid after adding the microcapsule/nanocapsule is called slurry, which has the capability to enhance the high heat transfer and high heat storage capacities by combining the latent heat of microcapsule/nanocapsule and sensible heats both base fluid and microcapsule/nanocapsule. This, EPCMs slurry (consisting of solid/liquid mixture), also called multiphase fluid, has multifunctional characteristics to serve as both heat HTFs and energy storage fluids (ESFs).\textsuperscript{311} The emulsion of macro- and micro-PCMs in base fluids under high pressure causes the fracture of capsules, thus increases the viscosity of slurry, reducing the heat transfer capacity, and requiring a higher input power for pumping the slurry. Therefore, to address these issues, nano-PCMs have been dispersed into the base fluid. The effective specific heat ($C_{\text{eff}}$) of EPCMs slurry as a function of volume fraction ($\phi$) of encapsulated capsules can be defined by Equation 12 as:

$$C_{\text{eff}} = C_0 + \phi H_{\text{EPCM}} / \Delta T$$  \hspace{1cm} (12)
Here, \( C_o \) is the specific heat of base fluid, \( H_{EPCM} \) is the latent heat of dispersed EPCM per unit volume, and \( \Delta T \) is the temperature difference between the transfer surface and bulk fluid or the difference between the encapsulated capsules melting (\( T_m \)) and freezing (\( T_f \)) temperatures. Hong et al.\(^{133} \) synthesised the SiO\(_2\)-encapsulated In nanoparticles and polymer-encapsulated paraffin wax nanoparticles using colloid method, and then the slurry was prepared by dispersing into poly-\( \alpha \)-olefin (PAO) and water for potential high and low temperature applications, respectively. The heat transfer coefficients of PAO containing 30\% In nanoparticles by mass and water containing 10\% paraffin wax nanocapsules by mass are 1.6 and 1.75 times, respectively, higher than that of the base fluids. The comparison of adding nano-PCMs consisting of polymer/paraffin wax of 28 vol.\% added with water was carried out by Wu et al.\(^{215} \) The enhancement in heat transfer coefficient was found by 50\% and 70\% for jet impingement and spray cooling, respectively, compared with base fluid. The authors prepared without and with SiO\(_2\)-encapsulated In nano-PCMs using colloid method and dispersed into PAO and conducted the experiments in a microchannel heat exchanger to study heat transfer characteristics.\(^{105} \) The authors found the heat transfer coefficient of 47 000 W/m\(^2\).K without SiO\(_2\) coating of 30\% In into PAO, which was two times improvement over the single-phase PAO. Further, they suggested after thermal cycling test involving 5000 cycles that In nanoparticles can be used without encapsulation.

In practical applications of micro- and nano-PCMs, slurries at component level, the heat transfer, and fluid flow characteristics inducts, tubes, channels and thermal storage characteristics in a tank have been investigated. The design of advance microchannel is shown in Figure 29, which has the significant potential to overcome the internal heat generated inside the miniature and highly integrated electronics components or systems. The hybrid water-based suspensions consisting of Al\(_2\)O\(_3\) nanoparticles (nanofluid) and micro-PCMs particles (slurry) were
prepared, and then heat transfer characteristics were studied flowing through a circular tube\[^{312}\] and minichannel heat sink.\[^{313}\] The highest heat transfer enhancement of 57% was achieved at the highest flow rate in case of nanofluid, whereas the heat transfer enhancement was 51% at lowest flow rate in case of slurry. Seyf et al\[^{314}\] investigated effect of mass concentration and melting range of nano-PCMs dispersed in PAO as well as Re number on thermal and hydrodynamics characteristics of a microtube heat sink. They found that nano-PCM slurry as a coolant enhanced the thermal performance by decreasing the generated total entropy, thermal resistance, increasing the Nu number, and maintaining the temperature uniformity. However, an increase in the pressure drop was observed with the increase of mass concentration, which requires more pumping power. Liu et al\[^{287}\] prepared the micro-PCM slurry composed of water/ethanol as a base fluid and paraffin/melamine resin micro-PCM as additive and studied the heat transfer performance in a horizontal circular tube. The results revealed that convective heat transfer coefficients of micro-PCM slurry were about 2 times and 3 times at 5% and 10% mass fractions, respectively, higher than to the base fluid. The drastic increase of pressure drop is due to the higher viscosity of slurry, which increases by higher loading of capsules and Re number. Moreover, the higher heat transfer rate can also be achieved by reducing the thickness of the thermal boundary layer.\[^{315}\]

### 6.4 Building

Micro- and nano-PCMs are currently employed in building in various forms such as concrete mixes, cement mortar, wall boards, gypsum plaster, sandwich panels, and slabs to meet the energy consumption of buildings for heating, cooling, air conditioning and ventilation, water heating, and lighting.\[^{316}\] The embedment of EPCMs has significant potential to increase the thermal inertia at constant mass in buildings especially mixing with concrete, which influence its thermophysical and mechanical properties.\[^{317}\] Additionally, the embedment of micro- and nano-PCMs in concrete increases the thermal and acoustic insulation of walls. Giro-Paloma et al\[^{318}\] reported the mechanical properties of micro-PCMs synthesising of RT-21 with acrylic shell. The nano-indentation technique was used to determine the mechanical properties such as modulus of elasticity, load at maximum displacement, and displacement at maximum load. The results showed the significant mechanical resistance and stiffness of RT-21 microcapsules, and also better stability was achieved with less short emission of volatile organic compounds. Aguayo et al\[^{319}\] proposed
the infrastructural concrete mixing with two paraffin wax–based micro-PCMs for mitigating early age cracking and freeze-and-thaw–induced damages. The evaluations of micro-PCMs on cement hydration and pore structure were carried out, and it was ascertained that mechanical properties such as comprehensive strength of cement mortars was strongly dependent on the mechanical properties of micro-PCMs. Cao et al320 fabricated the concretes of high TES by mixing the micro-PCMs of RT-27 coated with the LDPE-EVA copolymer shell into portland cement concrete (PCC) and geopolymer concrete (GPC). Figure 30 shows the SEM images of PPC and GPC cements incorporating of micro-PCMs capsules. The results found higher heat storage capacity and lower thermal conductivity, simultaneously. The significant loss in compressive strength was observed by adding micro-PCMs capsules. However, the compressive strength fulfils the mechanical European regulation for concrete applications.

Wei et al321 reported the durability of cementitious composite containing commercially available micro-PCMs. The results revealed that micro-PCMs reduced the rate and extent of water sorption and did not affect the dry shrinkage of cementitious composites. However, in specific cases, micro-PCMs improved the durability of cementitious composites. Apart from the investigation on mechanical properties, the effect of thermal deformation was examined by Young et al.322 The effective thermal deformation coefficient was predicted and found similar to the shell materials. Finally, a design rule was proposed to design the EPCM-mortar composites, which found useful in the built environment and high performance composites. The other possibilities of using EPCMs are with building structures through wall boards,323 gypsum plaster,324,325 sandwich panels,326 and slabs,327 which could lead to reduce the energy demand in both residential and commercial building sectors.

6.5 Textiles

Various schemes have been investigated of EPCMs incorporating with textiles such to protect or give a durable finish on cotton or woollen, durable fragrances, and skin softeners. Meanwhile, micro-PCMs have been utilised for waste yeast cells, coating on the surface of fabric or embedded within fibre Nelson.328 Sarier and his co-authors32,119 firstly reported the thermal regulation or thermal comfort of four different

**FIGURE 30** SEM images of A, PCC without micro-PCMs, B, PCC containing 3.2 wt.% micro-PCMs, C, GPC without micro-PCMs, and D, GPC containing 2.7 wt.% micro-PCMs.320 Reused with the permission from Elsevier license number 4444700728610
Foam capsules of containing n-octadecane, n-octadecane/PE600, n-eicosane/n-hexadecane, and PEG/Na₂CO₃·10H₂O/n-hexadecane as a core materials coated with PUF. The energy absorption capacities were enhanced from 2.5 to 4.5 times relative to the reference fabric at a particular temperature. Later on, authors found the higher thermal conductivities of microcapsules, which can be employed for thermal cooling of clothing fabrics, medical and automobile textiles, and building materials. Additionally, the phase change enthalpies of 137 and 168 J/g for n-hexadecane and n-octadecane, respectively, were achieved using silver nanoparticles. Alay et al. synthesized the micro-PCMs of n-hexadecane/PBE and n-hexadecane/PMMA with the aim to increase the physical interaction between the microcapsules and fibre surface for heat storage and thermoregulation in fabrics. The pad-cure method was adopted to add the micro-PCMs on woven fabrics. The results showed that the cotton, cotton/polyester, and microfibre polyester fabrics were capable to absorb heat of 6.56 and 25.98 J/g with n-hexadecane/PBE, 4.95, 10.02, and 8.38 J/g, respectively, with n-hexadecane/PMMA. Moghaddam and his co-authors prepared the microcapsules of non-oxadecane as a core and sodium alginate as a shell materials for application of thermal comfort of textile fabric. The authors found the high energy storing density more than 137.83 J/g for phase transition temperature of 30 to 31°C, which was the suitable for thermal regulation in textile. Aksoy and his co-authors synthesized the micro-PCM of n-octadecane/PE600, n-eicosane/sodium alginate, and n-eicosane/PMMA-co-AA to enhance the textile thermal comfort, thermal stability, and flame-retardant properties incorporated with cotton fabrics by pad-dry-cure method. The optical images proved the presence of microcapsules incorporated fabric homogeneously onto the surface which are mainly located between the fibres and fibre spaces, as shown in Figure 31. The heat storage enthalpy of 97 to 114 J/g was achieved, which showed the significant potential for textile applications and thermal regulating properties of micro-PCM incorporated with fabrics. Further, the authors reported durability of microcapsules onto the fabric surface after washing and rubbing tests, and inconsistencies of micro-PCMs with fabrics are due the chemical compatibility of the fabric material and shell material of microcapsules.

Recently, Sun and Iqbal synthesized nano-PCMs containing n-octadecane and n-eicosane as core materials and applied on the cotton fabric through a pad-dry-cure process and compared with commercial available micro-PCM of n-octadecane. The results revealed that nano-PCM had 28% more capacity to absorb latent heat than commercial micro-PCM and nano-PCM treated cotton fabric showed the better durability due to its better adhesion with fibrous material of cotton while washing.

### 6.6 Foam

Foam is potentially used in structures to enhance the thermal performance, especially to reduce the rate of heat transfer or to increase the thermal resistance, acting as an insulating material. Mostly, PS and PU are applied with micro- and nano-PCMs in building structures such as wall, windows roofs and floors, automotive and aerospace interiors, and biomedical applications. You et al. synthesized the n-octadecane/PU micro-PCMs and inserted it inside the foam. They reported that latent of fusion of micro-PCMs depends on the weight ratios of added microcapsules, ie, increasing the content of micro-PCMs increases the enthalpy and vice versa. The maximum value of 12 J/g at 12.59 wt.% of micro-PCMs was achieved. Borreguero and his co-authors synthesized the rigid PU foams of varying weight concentrations of RT-27-based micro-PCMs for the purpose of building insulations and TES. The authors reported that increasing the micro-PCMs contents decreased the thickness of foam but increased the density and TES capacity. The PU foams with 18 wt.% of microcapsules enhanced the TES capacity meanwhile along with sustaining the mechanical properties without addition of fillers. Whereas at higher content of 21 wt.% of microcapsules caused the reduction in mechanical properties. However, the 11 wt.% containing foams maintained the advantages of improving TES capacity and exhibited higher compressive strength and elastic modulus. Later, the authors fabricated the rigid PU incorporating 18 wt.% microcapsules of two difference shell materials consisting PS and PMMA, named as mSP-(PS-TR27) and Micronal DS 5001X. Figure 32A,B exhibits the SEM of PU foams containing 18 wt.% of mSP-(PS-TR27) and Micronal DS 5001X, respectively. The results revealed that micro-PCMs of both shell materials improved the TES capacity of PU foams. Additionally, larger size of PS and agglomeration of PMMA microcapsules caused the strut rupture and damaging the mechanical properties.

Recently, Serrano et al. developed the rigid PU of varying the weight percentage from 0% to 50% of microcapsules of named mSD-(LDPE.EVA-RT27) and found the 40 wt.% optimum weight percentage of microcapsules to produce thermal regulating foams having latent heat of 34.4 J/g, which was higher than those rigid PU of similar materials reported in the literature. Further, the authors suggested that if this rigid PU will be employed in building, the amount of CO₂ leaving to the atmosphere can be reduced.
resulting in save the energy. Qiu et al.339-342 prepared the PS foam with microcapsules containing paraffin wax and DEEP as core and PMAA-co-EMA as a shell materials and found that micro-PCM had good thermal regulation potential and TES capacity treated with foam. Later, they synthesised the micro-PCM of hybrid shell materials of PMMA and UF coated on n-tetradecane and found the higher enthalpy of 175.5 J/g. Additionally, the authors reported that the foam treated with micro-PCMs has the better thermal regulating properties than raw foam.342
6.7 | Medical industry

The antibacterial effectiveness of EPCMs is a significant and emerging area for the development of hybrid functionality materials. Silver-based nanomaterials are significantly used as a shell materials with EPCMs because of their inherent antimicrobial properties in medical application. Tobaldi et al.\(^{343}\) developed the silver-modified titania nanoparticles through green aqueous sol-gel method to study the antibacterial and photocatalytic properties under both the UV and visible-light exposures. Under UV-light source, silver nanoparticles showed the significant antibacterial activity against *Escherichia coli* (Gram-negative bacteria) than methicillin-resistant *Staphylococcus aureus* (Gram-positive bacteria). Zhang et al.\(^{280}\) synthesised the multifunctional micro-PCMs of *n*-eicosane as core and silver/silica of double-layered as shell material and found the high antibacterial especially against *E. coli*, *S aureus*, and *Bacillus subtilis*. The antibacterial effectiveness, shown in Figure 33, revealed that bacterial activities for *E. coli*, *S aureus*, and *B. subtilis* were inhibited up to 64.6%, 99.1%, and 95.9%, respectively, when contacting the microcapsules for 2 hours.

7 | FUTURE RESEARCH ON EPCMS

Micro- and nano-EPCMs have the potential features in future applications. So far, many OPCMs have been used as a core material for encapsulation, also most studies focused to develop micro-PCMs. A few studies have been reported to encapsulate the nano-PCMs. Although many researchers are currently working on the preparation and characterisation of nano-PCMs, however, there is the still need for further improvement in engineering applications. Followings are suggestions for future works:

- **Long-term stability:** The stability of micro-/nano-PCMs is the major need for the applications in every aspects of the life, especially when it is under usage of heat transfer and flow conditions.
- **Efficiency enhancement:** The encapsulation efficiency of the production of micro-/nano-PCMs is still quite low, which is still facing the lack of to meet the requirements of industrial applications.
- **Encapsulation of IPCMs:** Since the inorganic PCMs (salt hydrates and molten salts) have high latent of fusion during phase transformation, they have more potential in TES applications, eg, active and passive heating and cooling through solar energy. However, they can degrade in moisture environment. Untill now, research has focused on use of OPCMs as core materials. Therefore, there is the need of micro-/nano-encapsulation of molten salts and salt hydrates to use a core materials.
- **Subcooling or supercooling:** The supercooling of micro-/nano-PCMs is the major obstacle in industrial applications. Further investigations of micro-/nano-PCMs are needed to overcome this issue to enhance the thermal stability and efficiency of thermal systems.
- **Leakage performance:** More studies are needed to adopt a standard mechanical test to study the durability or leakage of EPCMs, especially the nano-PCMs to enhance its chemical stability.
- **Application of EPCMs:** Up to now, little investigations have been reported using EPCMs especially nano-PCMs in solar energy, battery and electronic thermal management, solar energy storage, solar panels thermal cooling control, smart building, waste heat recovery, etc. Therefore, new technologies using nano-PCMs should be developed with potential feature to overcome the deficiency of conventional technologies.
- **Enhancement of thermal properties:** In the encapsulation of PCMs, it has been reported that the melting temperature latent heat of fusion are reduced as compared with pure PCMs. The purpose of PCMs is to use as energy storage materials in TES systems without loss of heat transfer and fluid flow performance. Hence, this is real challenge of EPCMs to increase or maintain the latent heat of fusion with different melting and freezing temperatures. Therefore, new studies are needed to focus in this direction of encapsulation of PCMs. Additionally, the lower thermal conductivity is also a real challenge of PCMs. Some novel encapsulation techniques are needed to enhance the thermal conductivity
of PCMs at the cost of not affecting the latent heat of fusion of PCMs.

8 | CONCLUDING REMARKS

This review paper comprehensively covers research progress on the development of macro-, micro-, and nano-EPCMs conducted from the last few decades. Initially, the ideal characteristics of EPCMs are elaborated for the selection of a specific criteria and application. Further, various encapsulation technologies based on different methods such as physical-mechanical, physical-chemical, chemical-mechanical, and chemical methods have been thoroughly explained to synthesis the macrometre-, micrometre-, and nanometre-encapsulated capsules. Additionally, thermophysical properties such as thermal conductivity, latent heat of enthalpy, encapsulation ratio, and encapsulation efficiency are summarised respective to each method. In a similar way, detailed characteristics evaluation techniques of chemical, thermal, and physical properties have been discussed. Stability of EPCMs based on chemical and thermal properties are also discussed. Finally, potential applications of EPCMs have been explained in detail. The following conclusions are summarised from this review:

• The encapsulation of OPCMs coating with a polymer shell material is simple and does not require any complication and can be achieved adopting simple polymerisation techniques.
• The encapsulation of IPCMs is difficult and expensive because of the hydrophilic nature of salt hydrates, which have the characteristics to alter their water content, thus limited to used only inverse emulsion and addition of polymerisation reactions.
• Efficiency and stability of capsules during encapsulation can be restrained by monitoring the molecular weight of the polymers in shell formation process.
• Lower molecular weight shell materials, although increase the encapsulation efficiency but contrarily reduce the mechanical strength and mobility of smaller molecules. Hence, there should be precise selection of encapsulation technique and reactants to obtain the required thermophysical properties.
• The selection of each core-shell confinement technology is based on morphological parameters of capsules such as size, distribution, degree of dispersion, environment of use and selection of shell material. A specific shell material has its own merits and disadvantages regarding thermophysical properties point of view.
• IPCMs as shell materials are found favourable for encapsulation because they have high thermal conductivity; however, they possess low encapsulation efficiency, longer cross-linking, and are less stable.
• Overall, it is concluded that after encapsulation of PCMs, the leaking, subcooling, and segregation issues had been overcome to some extent; however, the melting temperature and latent heat of fusion were decreased, which limits the EPCMs for thermal management solutions.
• Considering all the encapsulation techniques, the in situ polymerisation technique is found to be one of the better ones, offering more encapsulation efficiency and thermophysical stability.
• This review reveals the good thermal and chemical stability of EPCMs, which are strongly influenced by the morphology of encapsulated capsules.
• EPCMs are the most suitable for thermal management and TES applications in conjunction with various subsystems such as heat sinks, micro-minichannels, heat pipes, heat exchangers, wall-boards, panels, and slabs.

CONFLICT OF INTEREST

The authors declare no conflict of interest regarding this review article.

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