Review Article

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Phase change materials for building construction: An overview of nano-/micro-encapsulation

Abstract: Buildings contribute to 40% of total global energy consumption, which is responsible to 38% of greenhouse gas emissions. It is critical to enhance the energy efficiency of buildings to mitigate global warming. In the last decade, advances in thermal energy storage (TES) techniques using phase change material (PCM) have gained much attention among researchers, mainly to reduce energy consumption and to promote the use of renewable energy sources such as solar energy. PCM technology is one of the most promising technologies available for the development of high performance and energy-efficient buildings and, therefore, considered as one of the most effective and ongoing fields of research. The main limitation of PCM is its leakage problem which limits its potential use in building construction and other applications such as TES and textiles, which can be overcome by employing nano-/micro-encapsulation technologies. This paper comprehensively overviews the nano-/micro-encapsulation technologies, which are mainly classified into three categories including physical, physiochemical and chemical methods, and the properties of microcapsules prepared. Among all encapsulation technologies available, the chemical method is commonly used since it offers the best technological approach in terms of encapsulation efficiency and better structural integrity of core material. There is a need to develop a method for the synthesis of nano-encapsulated PCMs to achieve enhanced structural stability and better fracture resistance and, thus, longer service life. The accumulated database of properties/performance of PCMs and synthesised nano-/micro-capsules from various techniques presented in the paper should serve as the most useful information for the production of nano-/micro-capsules with desirable characteristics for building construction application and further innovation of PCM technology.

Keywords: phase change materials, encapsulation, properties

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1 Introduction

Phase change materials (PCMs) are a group of functional materials that support the same purpose as a function of temperature with intrinsic capability of absorbing, storing and releasing thermal energy in form of latent heat known as enthalpy of fusion [1–3], during phase transition cycles at their operating temperatures under isothermal conditions. In general, PCMs are distinguished according to the phase change they undergo at a particular temperature level and are classified based on their physical transformation of absorbing/storing or releasing thermal energy capabilities, as result of undergoing a particular phase transformation from one state to another (e.g. solid to liquid or liquid to gas) at

their operating temperatures [4]. It is evident from the critical examination that PCMs can enhance the performance as well as the safety, with respect to their premium energy storage. Due to the numerous unique advantages they possess including high energy density, abundance in nature, wide temperature range and low cost, they are often concerned for building materials, electronic devices, lithium-ion-battery, and in solar energy systems to improve the heat storage of the water tanks to enhance the solar energy utilisation efficiency [5,6]. Overall, PCM application because of their aforementioned intrinsic characteristics ranges from the hand warmer to green buildings; however, for most applications, PCMs with a narrow phase change temperature range with a corresponding high latent heat value, along with robust chemical stability, are preferred because they can store and release higher amounts of energy cycles. Availability of PCMs in a wide range of melting points [7] is the main reason why they are extensively utilised in several different real-world applications including the following: (1) developing smart thermal microgrids; (2) portable thermal batteries; (3) indoor thermal management systems; (4) thermoregulating textiles, (5) warm supplies thermal protection; (6) in solar-driven cookers, (7) in solar heating systems; (8) water heaters; (9) refrigerators; (10) air-conditioning; (11) for cooling; (12) for the enhancement of thermal comfort in buildings; (13) thermal performance of building materials; (14) for the fabrication of energy-saving equipment, (15) in healthcare; and (16) food preservation [8–10]. Overall, they are highly beneficial in any application that relies on controlled and efficient thermal energy storage (TES) and releases, commonly achieved by exploiting their melting and crystallisation behaviour. It is critical that PCM selected for a designated practical purpose has a phase change temperature (e.g. operating/working temperature) within the temperature range of the given application; otherwise, they will behave like conventional sensible heat storage materials [11]. The suitable working temperature ranges of textile and building applications are 18–35°C and 19–26°C [12].

PCMs are considered to play a vital role since a few decades in efficient latent heat storage applications, as advanced latent heat thermal energy storage (LHTES) materials [13], for their incorporation in TES systems enable adequate control over the operating parameters of the system through the utilisation of the exothermic and endothermic phase transitions, which allows thermal energy to be stored more effectively [14]. Theoretically, they can store 5–14 times more thermal energy per unit volume than conventional sensible heat storage materials such as rock, masonry, and water [15], and their high storage density enables the attainment of a compact energy storage system, operating under isothermal conditions [16]. Recently, the principle of PCM is being exploited and developed in building energy conservation systems and in solar heating, mainly to enhance their energy efficiency [17,18], since it is considered as the most practical solution available to reduce the volume of fossil fuel consumed. Primarily, because the building sector is one of the largest energy-consuming sectors; so, it is critical to advance the building energy performance; the increased demand of fossil fuel is posing critical environmental problems such as rapid climate change, along with threatening global economy due to the increasing costs of fossil materials and finite resources. Employing PCM technology in buildings will lower the heating and cooling loads by reducing the heat transferred through the building envelope, so that the indoor temperature will be maintained within the thermal comfort range of occupants by reducing temperature swings, and consequently, the total energy consumption of building will be reduced significantly by load reduction or shifting [2]. The thermal performance of PCMs integrated in buildings depends entirely upon the melting temperature, thermal conductivity and TES density. PCMs with rapid melting and crystallisation/solidification points are considered as suitable candidates for TES applications [19]. Designing a heat storage system is a complex task since it is not restricted to the thermal performance of the system only, but also involves taking into consideration the cost, safety and sustainability of materials used and processes employed [20].

In the past, various PCM integration methods have been reported such as direct incorporation, immersion, shape-stabilization and encapsulation, e.g. nano-, micro- and macro-encapsulation [21]; however, latter approach has not proven to be practical in the past [22]. Direct incorporation of PCM can be done by the means of the imbibing technique (e.g. direct incorporation), in which construction materials like gypsum boards [23], concrete blocks, or bricks [24] get immerged into PCM baths, which results in PCM being adsorbed onto the pores of the construction materials; despite being practical, final PCM-filled materials obtained has faced serious phase segregation problems due to PCM leakage, in addition to difficulty in moisture transfer across the enclosure [25]. Also, PCM direct integration into building material requires special latent heat devices or heat exchange surfaces, which leads to increased associated

costs and increased thermal resistance between the PCM and the environment; therefore, not many building materials will be able to incorporate PCMs directly.

Like any other technologies, PCMs are also facing challenges. First, an ideal PCM is expected to meet a number of criteria with respect to the thermophysical properties including high enthalpy per unit volume, suitable phase change temperature, no supercooling, long-term chemical stability and high thermal conductivity. Unfortunately, aforementioned merits are rarely possessed fully by most PCMs, which means these shortcomings may result in degrading the performance of the system used for TES and thereby hinder their final applications [26]. Also, construction materials capable of incorporating PCMs are relatively limited, since PCMs have poor compatibility with most buildings materials. Well-known drawbacks of PCMs includes the following: (1) leakage problem that occurs during the phase transition process and (2) their inherently low thermal conductivity (e.g. poor working efficiency). Leakage problem can cause serious damages, such as contamination or device failure if PCM is used in packaging or electronic devices [1,10], and low thermal conductivity means rate at which PCM absorbs/stores and releases energy will be extremely slow making them unsuitable for most applications. The leakage problem is most serious one since it undesirably suppresses the potential practical application of PCMs in buildings and other applications significantly; however, this can be overcome by employing either the nano/micro-encapsulation or shape stabilization technology. Nano-/micro-encapsulation technology involves encapsulating PCM with a continuous polymeric material, whereas in the shape-stabilization technology, the chosen PCM gets embedded into a supporting material. However, latter technology is considered as the most effective strategy to overcome the aforementioned issues, and it also encourages industrial scale production of powder or granulates of PCMs composites, which surely widens the potential scope of PCMs, especially organic PCMs in real applications [10]. Although shape-stabilisation technology is a highly feasible method, in terms of economy and practicality, it is impossible to substitute nano-/micro-encapsulation technology with it completely in certain applications, e.g. for thermal regulation in buildings and textiles, the use of PCM microcapsules is required, while PCM composite resulting from shape-stabilisation technology is undesirable. Nano-/micro-encapsulation technology usually encapsulates organic PCMs including fatty acids, paraffin within polymers because they exhibit numerous benefits such as appropriate calorific value, non-

corrosion and non-supercooling properties [27]; however, they display major drawbacks such as low thermal conductivity and flammability, which tends to limit their real-world applications. On the other hand, inorganic PCMs do have number of benefits such as high energy density, relatively high thermal conductivity and low cost, but their applications are hindered significantly due to the following two serious drawbacks they exhibit: (1) phase separation/segregation and (2) sub-cooling/supercooling behaviours [28].

2 Classification of PCMs

PCMs used for LHTES systems can be classified into four states according to the phase change mechanism they are subjected to and the phase transition temperature: (1) solid–solid (S–S), (2) solid–liquid (S–L), (3) solid–gas (S–G) and (4) liquid–gas (L–G) (Figure 1). However, for practical purposes, solid–liquid PCMs are commonly used because other varieties such as solid–gas and liquid–gas are not compatible with building materials [29] due to some technical limitations including the following: (1) large volume changes during the phase transition process and (2) existence of high pressure of the gas phase in the system [30,31]; therefore, it will not be discussed further. Despite the fact that a wide variety of PCMs with different melting point ranges are available on the market, the most commonly used type of solid–liquid PCMs are categorised into three types: (1) organic, (2) inorganic and (3) eutectic mixtures. Literature reports that solid–solid PCMs have one major advantage over solid–liquid PCMs [32], i.e. they require no encapsulation since no fluid (i.e. gas or liquid) gets generated during the phase transition process; so, the overall cost will be reduced because nano-/micro-encapsulation technology will not be required. Furthermore, it allows direct incorporation of PCM in building materials and/or building components. Also, solid–solid PCMs are believed to have good compatibility with building materials; however, till date no study has investigated the compatibility between the synthesised solid–solid PCMs and building materials. In general, a PCM undergoes phase change as a result of getting activated by a stimulus such as heat, light or pressure/strain. PCMs have different with some of them having multiple of the mentioned stimuli for their activation, and their phase change occurs within their specific boundary conditions such as changes in temperature, light, concentration of solvents and pH [33].
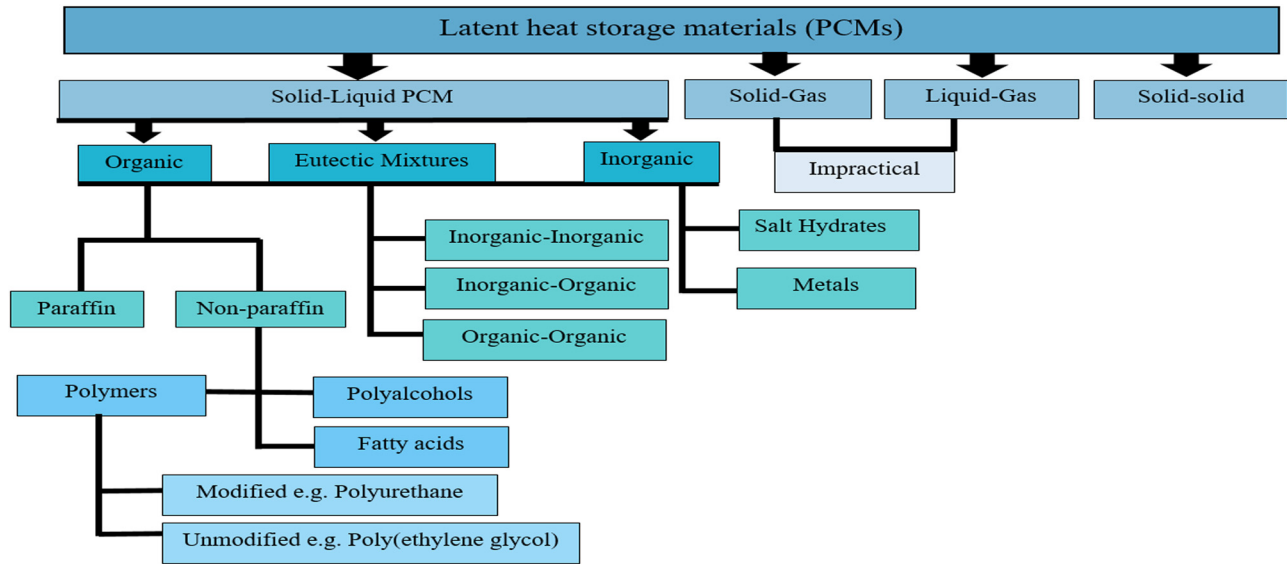
Figure 1: Classification of PCMs.

Several factors tend to influence their effectiveness and applications such as good thermal properties depend entirely upon suitable phase transition temperature, high latent heat of transitions per unit weight, high thermal conductivity and large specific heat capacity. In addition, PCMs are also expected to possess other characteristics such as a favourable phase equilibrium and high density. Critical kinetic properties that PCMs should exhibit are little or no sub-cooling effect during freezing, possess sufficient crystallization rate and solidification and melting should occur at the same temperature without phase segregation. Overall, PCMs should have the following desirable characteristics: (1) good chemical properties to ensure completion of reversible freezing/melting cycle, (2) long-term chemical stability, (3) good compatibility with other materials, (4) undergo no degradation after being subjected to long-term thermal cycles, (5) non-corrosive, (6) non-toxic, and (7) no fire hazard and should contain non-explosive compounds only [34]. Till date, literature has majorly reported microencapsulation of commercially available organic PCMs such as paraffin due to their non-corrosive and hydrophobic nature, which are main desirable characteristics that PCMs are expected to have, to avoid deterioration of thermal and structural strength of encapsulated PCM after being subjected to large number of thermal cycles. Hydrophilic nature of PCM will result in adsorption of water molecule, and this will influence the properties of PCM greatly and thus its performance. Therefore, encapsulation of organic PCMs is preferred over other PCMs such

as salt hydrates [35]. Solid–liquid PCMs are commonly utilised as efficient storage materials currently since they are capable of absorbing, storing or releasing large amounts of heat energy, almost isothermally by undergoing phase change, while having relatively high heat capacity and storage, and they experience relatively smaller volume changes during the phase transition process when compared with the liquid–gas PCMs [1], and they have higher latent heat storage capacities than the solid–solid PCMs. The PCM to be used for an application in various fields, such as construction, refrigerators, air-conditioning, textiles, food preparation, astronautics and waste heat recovery, is determined based on the temperature at which phase change occurs, better known as its operating temperature [36]. Vast number of solid–liquid PCMs have been prepared in the past to deduce a solution that provides a highly effective storage system at low costs. However, this has not been possible yet, since solid–liquid PCMs have poor shape-stability, making it difficult for them to retain their original solid state during the phase transition process, so to encourage its potential application, the encapsulation technology must be employed, which results in increasing the overall costs greatly. In addition, solid–liquid PCMs face other operational problems such as supercooling and corrosion [37]. Nevertheless, PCMs have their superior properties for one over the others as summarised in Table 1. These advantages and disadvantages of different PCMs lead to various processing, formulations and end-user requirements.

Table 1: Typical advantages and disadvantages of organic, inorganic and eutectic mixtures PCMs

PCM type	Advantages	Disadvantages	Ref.
Organic	• No supercooling • No phase segregation during the crystallisation process • High latent heat of energy storage • High resistance to corrosion • No toxicity • Smaller volume change • High compatibility with construction materials • Can be incorporated directly • Can be impregnated into materials • Good chemical stability and inert i.e. unreactive • High TES • High range of melting temperatures • Low vapor pressure during phase change • Good thermal performance even after subjection to prolonged thermal cycling, i.e. good thermal behaviour • Excellent freezing and melting properties • Good thermal stability • Adjustable transition zone • Good nucleation rate • Recyclable • Self-nucleation • Congruent-melting	• Low thermal conductivity (e.g. typically around 0.2 W/m K for paraffins) • Large volume change (especially paraffins) • Expensive, i.e. non-paraffins are around three times more expensive than paraffins • High flammability • Low phase change enthalpy • Low volumetric storage density and melting point • High volatility	[11,31,38,39]
Inorganic	• High TES density • High thermal conductivity • Less expensive when compared with organic PCMs. • Non-flammable • High phase change enthalpy and sharp phase change • Small volume change • High latent heat of fusion • Recyclable	• Prone to corrosion, i.e. corrosive to most metals • Some degree of toxicity • Requires container and support • Supercooling • Phase segregation • Low thermal performance after subjection to prolonged thermal cycling, i.e. poor thermal behaviour • Cannot be incorporated directly • Decomposition • Moderately compatible with construction materials, i.e. not compatible with all building materials • Incongruent melting and dehydration during thermal cycling • Poor nucleating properties – nucleating and thickening agents are required to their applications • Low-temperature range	[11,31,38]
Eutectic mixtures	• Sharp melting points • High volumetric storage density • No phase segregation • No congruent phase change	• Some of them suffer from super-cooling • Low total latent heat capacity • Strong odours • Limited data are available in the literature on their thermophysical properties • High cost	[11,31,38]

3 Nano-/micro-encapsulation of PCM

3.1 Encapsulation technologies

Encapsulation technology was first introduced and developed in 1940s and 1950s by Barett K. Green [35,40], when it was called microencapsulation, and since then it has been developed further, researched and applied in various sectors including chemistry, biology and medicine due to the remarkable advantages it exhibits [1,41]. Overall, it is possible to develop value-added products using this microencapsulation technique, and it can be defined as the process by which one or more compounds in form of individual solid particle or liquid droplets (e.g. the core) get surrounded by a protective layer, by the means of a continuous polymeric film, composed of one or more materials (e.g. the shell), to produce a core–shell structure; or by which the internal core material gets dispersed throughout the protective material matrix, mainly to isolate, and thereby protect the core substance (PCM) from the surrounding, which is composed of various external environmental factors such as light, high oxygen concentration, heat, moisture and also to prevent volatile compounds from evaporating, to mask unpleasant odours and tastes or to release the internal material at controllable speeds [1,42]. Microencapsulation of core material ensures significant reduction in the reactivity of the core material, promotes controlled release of the core materials and, in addition, eases the handling, application and storage of the core material. However, its function depends highly upon its intended final application. The morphology of microcapsule is influenced by the core material as well as the processing technique applied [43]. Figure 2 shows the appearance of a typical microcapsule. In general, there are three main requirements that have to be established for successful encapsulation of PCMs: (1) the formation of shell surrounding the PCM core completely, (2) formed shell must prevent the leakage of melted PCM and (3) no incorporation of impurities in the core/shell system. Therefore, nano-/micro-capsule synthesised needs to be capable of withstanding the applied mechanical and thermal stresses. Capsules resulting from microencapsulation technique is termed according to their size and are namely nanocapsules, microcapsules or macrocapsules. The main difference between nano-, micro- and macro-capsules lies in the size and shape of capsules produced,
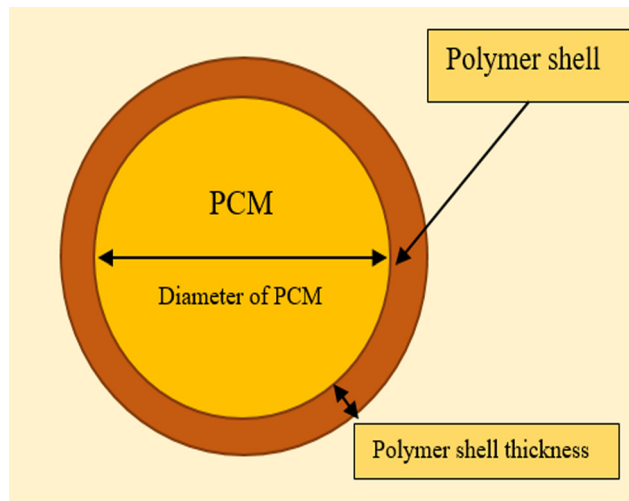

Figure 2: Appearance of a typical microcapsule containing a PCM core.

which are influenced greatly by the synthesis approach applied and the type of shell material used. If capsules are composed of a diameter in the range 0 to 1,000 nm (e.g. in the colloidal range), they are classified as nanoparticles, better known as nanocapsules, nanoparticles or nanospheres [44–46]. If capsule contains a diameter less than 1 mm or 1 cm, they are called microcapsules, where capsules of diameters greater than 1 mm or 1 cm are classified as a macrocapsules [28]. Figure 3 illustrates how capsules are classified according to their size. In general, microencapsulation and nanoencapsulation processing techniques tend to be more complicated, when compared with the macroencapsulation processing, since the capsule size is much smaller (e.g. less than 1 mm); however, reducing the capsule size is more advantageous since such particles have higher structural stability and better fracture resistance [47]. Macroencapsulation is usually conducted by filling the prepared shells with liquid PCMs, and the resulting macrocapsules are produced by encapsulating PCM in pouches, shells, tubes, thin plates and spheres [28]. Mentioned encapsulation techniques are reported to be advantageous because they allow for more flexible choices of PCM and shell material selection, according to the practical requirement. But to achieve optimum performance, correct selection of PCM and shell materials needs to be made, usually accomplished by following a standard selection procedure. The major drawback of microencapsulated PCMs is their inherently low thermal conductivity because the shell material (e.g. polymer) is of relatively low thermal conductivity [9].
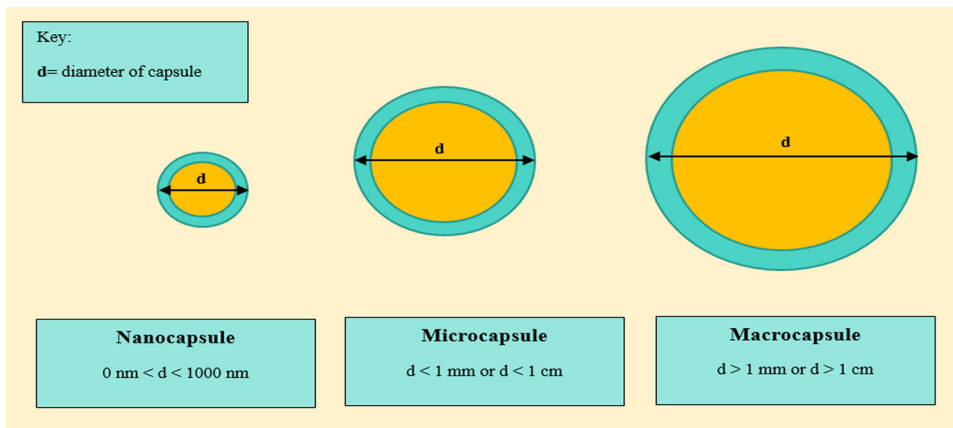
Figure 3: Classification of capsules according to their size.

3.2 Encapsulation methodologies

There are numerous types of physical and chemical methods developed in the past for the synthesis of microcapsules; however, chemical and physical methods were commonly used for the microencapsulation of PCMs. The latter technique can be subdivided into two types, i.e. physio-chemical and physio-mechanical [48]. The commonly used physical methods are pan-coating, air-suspension coating, spray drying, centrifugal extrusion and vibrational nozzle, while commonly used chemical methods are *in situ* polymerisation, interfacial polymerisation, suspension polymerisation and emulsion polymerisation [49]. The type of microencapsulation technique to be used is deduced by various factors such as (1) the type of shell material used (e.g. chemical composition of material), (2) the nature of the core material to be encapsulated (e.g. hydrophobic or hydrophilic) and (3) the release mechanisms to be encountered for the intended application. Overall, it depends entirely upon the physical and chemical properties of the materials used [8,49]. Selection of encapsulation technique, shell material and core material is made based on the final application of the product. Therefore, factors such as physical and chemical stability, concentration, required particle size and manufacturing cost should be considered because they dictate the final performance of the synthesised capsules [48]. Also, each microcapsule to be produced has to meet particular demands concerning the properties of the capsule, i.e. particle size/particle size distribution, thickness of shell and mechanical characteristics [50]. The employed technique should be controlled to prevent fracture of synthesised capsules caused by collision, and the strength of shell formed should be adequate to resist stress conditions, such as volumetric changes generated during the phase transition process [35]. Figure 4 shows different microencapsulation approaches available. It is impossible to produce microcapsules of average diameter less than 100 μm by employing the physical method [51], and
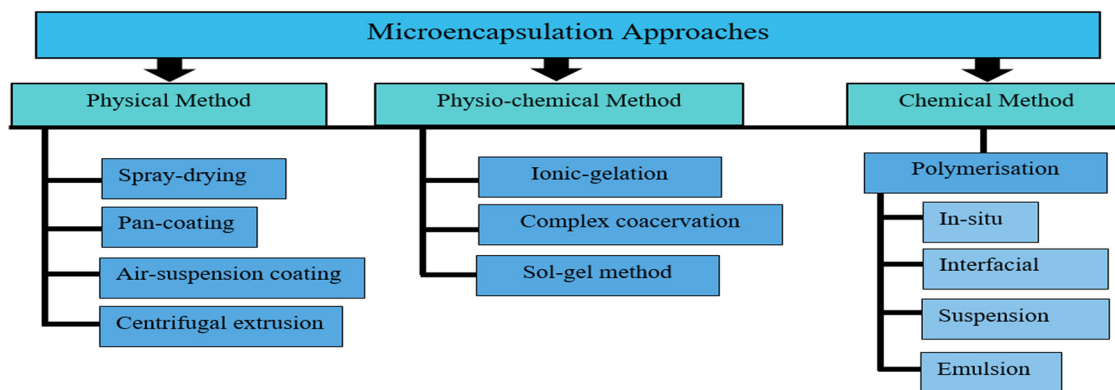

Figure 4: Different microencapsulation technologies.

therefore, for the synthesis of nanocapsules, chemical methods should be employed [29].

3.2.1 Shell materials

Characteristics and performance of microcapsules synthesised by the employment of various approaches are influenced greatly by the chemical and physical properties of the shell material used, and therefore, the selection of shell material is very important. There are in total three different types of shell materials such as organic, inorganic and organic–inorganic hybrid shell.

3.2.1.1 Organic shell material

Examples of organic shells reported in the past are mainly melamine-formaldehyde (MF) resin, urea-formaldehyde (UF) resin, poly(urea-urethane), polyurea (PU) and acrylic resins, and these types of shell materials are known to offer structural stability to the microcapsules, since they have excellent durability during the repetitive phase change process; however, they exhibit poor chemical and thermal stabilities. Out of all organic shell materials available, acrylic resins that are copolymers of methacrylate are commonly used for the microencapsulation of PCMs because they consist of several advantages such as non-toxicity, easy handling, high mechanical strength and chemical resistance, along with good optimal clarity. Resulting microcapsules can be used in thermal management and conservation applications in the solar energy technology because poly(methyl methacrylate) (PMMA) shell material exhibits exceptional sunlight stability [10].

3.2.1.2 Inorganic shell material

Commonly used inorganic shell materials are silica, titania, calcium carbonate, polystyrene (PS) and zinc oxide. Literature reports that utilisation of inorganic shell material is better than the organic ones because they exhibit numerous desirable characteristics such as excellent thermal stability, relatively high thermal conductivity, better mechanical durability, chemical inertness, and non-toxicity. Therefore, synthesised microcapsules can be used for thermal management of buildings and in automotive applications. Silica (SiO_2) is one of the extensively studied inorganic material for the microencapsulation of organic PCMs such as paraffin [10] because it is susceptible to surface modification with different functional groups [52].

Compared with organic shell materials that possess drawbacks including toxicity, flammability, poor heat transfer performance and poor thermal stability, inorganic shell materials are more advantageous and, therefore, have gained more attention in the recent times [53]. Encapsulating flammable organic PCM like paraffin wax within an inorganic shell material tends to reduce its flammability [35].

3.2.1.3 Organic–inorganic hybrid shell material

They exhibit outstanding characteristics when compared with both organic and inorganic shell materials such as superior thermal conductivity, chemical stability, and mechanical robustness, and hence, aforementioned properties are achieved by incorporating inorganic additives such as silver nanoparticles, iron nanoparticles or silicon nitride in the organic shell. One of the common drawbacks of employing this approach is the superficial attachment of inorganic additives on the microcapsules, and in addition, they are observed to detach from the surface during the repetitive phase transition process. However, it is possible to enhance this approach by employing chemical hybridisation of organic and inorganic shell materials, which usually results in improving the mechanical strength of shell material significantly, and its thermal performance [10].

3.2.2 Physical encapsulation

3.2.2.1 Spray drying process

Spray drying process is a simple, convenient, reproducible and scalable drying technology with significant encapsulation efficiency, first developed in the 1930s, and since then it has attracted many due to the advantages it exhibits such as comparatively low production cost, uses less energy, and it is ideal for temperature sensitive materials (e.g. food and biological items) [54,55]. It is one of the oldest encapsulation methods commonly used due to the feasible processing steps it consists of [56]. The simple processing steps of this method includes the following: (1) heating the drying gas, (2) generation of droplets, (3) drying of droplets formed and (4) collection of isolated particles produced (see Figure 5), and they are comparable to the "one stage drying operation." It allows various liquids to be converted into solid particles with adjustable size, distribution, shape, porosity, density, and chemical composition [55], and with this process, it possible to produce a wide range of microcapsules at good yield, and the synthesised microcapsules are
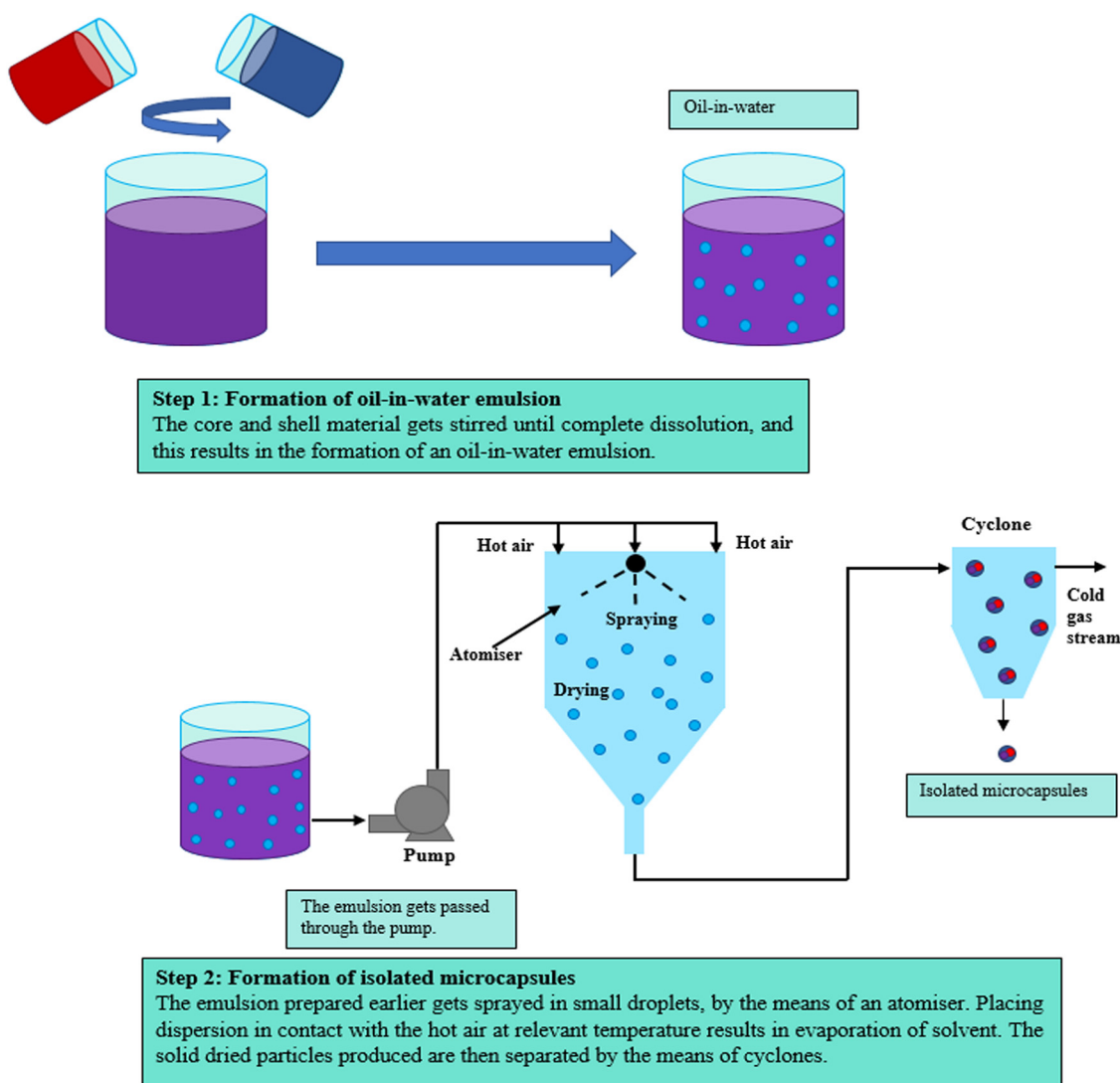
Step 1: Formation of oil-in-water emulsion
The core and shell material gets stirred until complete dissolution, and this results in the formation of an oil-in-water emulsion.

Oil-in-water

Cyclone

Hot air   Hot air

Spraying

Atomiser

Drying

Cold gas stream

Isolated microcapsules

Pump

The emulsion gets passed through the pump.

Step 2: Formation of isolated microcapsules
The emulsion prepared earlier gets sprayed in small droplets, by the means of an atomiser. Placing dispersion in contact with the hot air at relevant temperature results in evaporation of solvent. The solid dried particles produced are then separated by the means of cyclones.

Figure 5: Schematic representation of the spray drying method employed for the synthesis of isolated microcapsules.

reported to have good encapsulation efficiency. Furthermore, it covers a range of feedstock and product applications such as core material used can be in solution, suspension, slurry or molten form. This method is well established in the food industry [57], pharmaceutical industry [55,58] and lately to microencapsulate PCMs [41]. However, it does have drawbacks such as the spray drying equipment is very expensive and bulky. Moreover, it produces microcapsules in powder form, which requires further processing (e.g. agglomeration), and the resulting product has very low overall thermal efficiency, mainly because a large volume of heated air gets passed at high velocity through the chamber without contacting the particles and, therefore, makes no direct contribution to drying. Conversely, this technique is limited by the number of shell materials existing, i.e. shell material should be soluble in water (e.g. hydrophilic) [48]. Hawlader et al. [41] fabricated microcapsules containing paraffin-wax as a core material with gelatine/acacia as shell materials by this spray drying method. The microencapsulation efficiency was observed to decrease with increasing core/shell ratio due to the presence of insufficient amount of shell material for complete encapsulation. Addition of cross-linking agent provided the amount that does not exceed the range of 6–8 mL, resulted in enhancing the microencapsulation efficiency greatly. The presence of crosslinking agent in excess (i.e. greater than 8 mL) caused alteration of the mechanism and inability to integrate into the network. Borreguero et al. [59] microencapsulated paraffin Rubitherm ®RT27 with

and without carbon nanofibers (CNFs) within a low density polyethylene ethyl-vinyl-acetate shell. Results demonstrated that the particle size and shape of microcapsules collected from the collection vessel were better than the ones collected from the inside of the drying vessel. Hence, the microcapsules obtained from the inside of the drying chamber was bound together due to the melting of the polymer (e.g. they had agglomerated), whereas the ones collected from the collection vessel exhibited a more homogeneous and spherical shape with an average diameter of 3.9 μm and a paraffin content of 49%. The stiffness of resulting microcapsules was observed to have increased after incorporating CNFs, and thus, observations showed that CNFs were mainly found inside the microcapsules or had formed bridges between the microcapsules which led to the modification of the final particle size. Adding CNFs influenced the morphology of the microcapsules, and thereby, it promoted agglomeration. Thermal stability studies conducted on over 3,000 cycles indicated that the wax present between the synthesised microcapsules was melted and solidified in a reversible manner during the 30 years of continuous operation time, and the results indicated that these microcapsules exhibited greater thermal stability when compared with ones formed with PS. Fei et al. [60] microencapsulated *n*-octadecane (C18) within a titania shell via a rapid aerosol process with a hydrothermal post-treatment. Results showed that microcapsules with 80% C18 content were obtained with diameters in the range of 0.1–5.0 μm with two structures of dense or hollow structures, and the microcapsules exhibited an enthalpy in the range of 92–97 J/g.

3.2.2.2 Pan-coating

In this pan-coating method, widely used in the pharmaceutical industry, small-coated capsules are formed by mixing dried coating material with the solid particles, followed by melting of the coating material to ensure that solid capsules get surrounded with the coating material, and finally, cooling to enable solidification. In an alternative approach, the coating material gets sprayed gradually on the core material, by the means of tumbling in a vessel, unlike the conventional pan-coating method, which involves mixing coating material at the very start of the encapsulation process; however, this alternative approach is considered to be better, since it has shorter processing time and reduced costs [8].

3.2.2.3 Air suspension coating

This technique provides enhanced controls and flexibility when compared with the pan coating technique because it operates by altering the times at which the core particles pass the coating zone. During this process, the solid particles get coated and dried while remaining in their suspended position, by the means of an air stream moving in the upwards direction. This technique is reported to be unsuitable for the encapsulation of PCMs; however, they are commonly applied in the pharmaceutical industry, food industry and the production of cosmetics [8].

3.2.2.4 Centrifugal extrusion

It is a process developed by Southwest Research Institute. In this process, the core material, in liquid form, passes through the inner tube and the coating material, which is usually immiscible with the core material, passes through an annular tube around it. Vibration of the head results in emerging the core and coating material from the orifice at the ends of the tube, then they get broken down into spherically shaped drops, caused by the tensile forces present on the surface. No previous studies have used this method to encapsulate PCM. These drops will get solidified in a bath by the means of heating or suitable chemical reactions [8].

3.2.3 Physic-chemical encapsulation

3.2.3.1 Ionic-gelation

This is a simple and easy method commonly used in the pharmaceutical industry, mainly in drug delivery systems and food industry for the synthesis of nanoparticles. In this method, a hydrophobic drug such as curcumin gets dissolved completely in the chosen solvent, followed by the addition of the polymer solution, under constant stirring condition. The encapsulation efficiency is influenced greatly by the degree of crosslinking that has occurred along the polymer [61]. Also, it is based on the ability of polyelectrolytes to crosslink by the application of either extrusion or emulsification/gelation, in the presence of multivalent counter ions such as Ca^{2+}, Ba^{2+}, and Al^{3+} to produce the hydrogels. For instance, the ionic gelation of alginate and calcium ion results in the formation of calcium alginate (CaAlg) microcapsules [8]. This method has not yet been employed for the encapsulation of PCMs.

3.2.3.2 Complex coacervation

This is a term commonly used in colloidal chemistry to indicate the associative phase separation process that gets induced as a result of modifying the environment of the media such as pH, ionic strength, temperature or solubility under controlled conditions (see Figure 6) and can be defined as a colloidal phenomenon that involves liquid–liquid phase separation of a single or a mixture of two polymers of opposite charges in aqueous solution, resulting from triggering caused by electrostatic interactions, hydrogen bonding, hydrophobic interactions and/or polarisation-induced attractive interactions. Chemical or enzymatic crosslinking agents commonly used includes glutaraldehyde or transglutaminase. The degree of interaction present between the biopolymers depend highly upon factors such as biopolymer type, e.g. molar mass, flexibility and charge, pH, ionic strength, concentration and ratio of biopolymers [62]. In this process, the phase rich in colloidal is called the coacervate phase, while the phase containing minor amounts of colloidal is called the equilibrium phase [63]. There are two types of coacervation processes: (1) simple and (2) complex; however, both processes will have the same microcapsule formation mechanism, with only exceptions being the polymer system involved in the reaction, and the mechanism of phase separation (e.g. phase separation process varies in both processes). In the simple coacervation method, a desolvation agent gets added during the phase separation process, whereas the complex coacervation method is more about the complexation taking place between the oppositely charged polymers and usually results in the synthesis of stable and small-sized particles. Hence, complex coacervation process initiates through the interaction between the oppositely charged polymers or macromolecules such as proteins or polyelectrolytes [64]. The initial step involves the preparation of the emulsion by dispersing the core material (oil) into an aqueous polymer solution. Addition of second polymer solution followed by the addition of salt or by altering the pH temperature or by dilution of the medium results in the deposition of the shell material onto the core particles. The microcapsules obtained are then stabilised by crosslinking, desolvation or thermal treatment, and nano-/microparticles are usually collected by centrifugation. This technique is inexpensive and makes use of environmentally friendly solvents only; however, major shortcoming is that it requires the use of large amount of solvents [61]. Figure 6 illustrates the processes involved in the complex coacervation method.

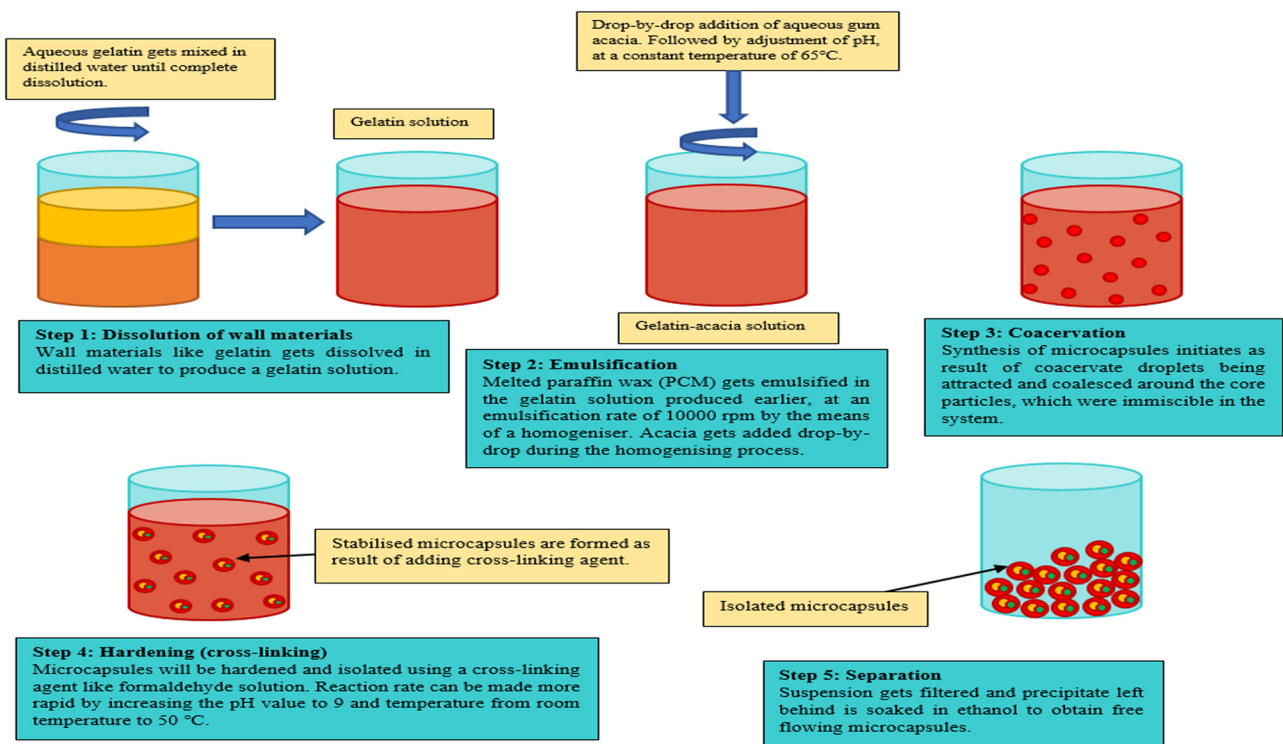Hawlader et al. [65] microencapsulated paraffin wax within a gelatin/gum acacia shell by the complex

Figure 6: Schematic representation of the fundamental steps involved in a complex coacervation process.

coacervation method. Optimising processing conditions was determined based on the response surface method. Results indicated that increasing the paraffin wax/shell material ratio will improve the paraffin encapsulation ratio, and thereby, increases the content of paraffin wax encapsulated. At higher encapsulation ratio of paraffin wax, microcapsules exhibiting lower hydrophilicity were obtained. Hawlader et al. [41] used the same method to fabricate microcapsules containing paraffin-wax as a core material with gelatine/acacia as shell materials. Onder et al. [66] microencapsulated different paraffin waxes, namely *n*-hexadecane, *n*-octadecane and *n*-nonadecane with natural and biodegradable polymers, namely gum Arabic–gelatin mixture. Deveci and Basal [67] microencapsulated *n*-eicosane within a chitosan (CHI)/silk fibroin (SF) shell. Results demonstrated successful production of spherical particles by the coacervation process, and it confirmed the possibility of using SF/CHI wall materials to encapsulate PCM. Jun-xia et al. [68] microencapsulated sweet orange oil within a soybean protein (SPI)/gum Arabic (GA) shell. Results showed that pH 4 was determined as the electrical equivalence point, and the optimum SPI/GA ratio was 1.0. Observations showed that high ionic strength was non-beneficial for this process; however, adding sucrose resulted in enhancing the microencapsulation efficiency and product yield significantly. Bayés-García et al. [69] microencapsulated Rubitherm®R27 with two different shell material compositions namely sterilised gelatine/arabic gum (AG) and agar–agar (AA)/AG by the complex coacervation method and reported encapsulation ratios of 49 and 48%, respectively. In general, caprylic acid is considered as the most promising fatty acid to be used in various fields such as building, textile, agriculture, food and transportation, since they possess several desirable characteristics such as high latent heat storage capacity (~158 J/g) and suitable melting points (e.g. in the range 15–17°C). Application of caprylic acid is challenging since it is a liquid at room temperature. Konuklu et al. [70] microencapsulated caprylic acid with various shell materials including UF, MF and urea–melamine–formaldehyde (UMF) by both simple and complex coacervation methods but results demonstrated that caprylic acid could not be microencapsulated via the complex coacervation method. In addition, observation showed that shell of poor quality was produced in the absence of formaldehyde crosslinking agent. They reported that the fabricated microcapsules of this study can be used in TES applications, since they exhibited adequate latent heat storage capacities. Malekipirbazari et al. [71] microencapsulated paraffin wax within a gelatin/acacia shell by the complex coacervation method and reported that the fabricated microcapsules have good prospects in TES applications, since they possessed high latent storage capacity.

3.2.3.3 Sol–gel method

The term sol–gel is the abbreviation of solution-gelation, and it refers to the sol as a stable dispersion of colloidal particles present in the solvent, and gel as the three-dimensional network linked by covalent bonds, and intermolecular forces (e.g. van der Waals forces and hydrogen bonds) composed of the aggregates of the sol particles [14,72]. Sol–gel process is utilised to synthesise various nano-inorganic materials or composite materials by the organic or inorganic materials of metal solution–gelation ("sol–gel") polymerisation process at low temperatures [73,74] and is considered as a highly flexible method for the synthesis of diverse range of materials, e.g. wide range of nano-/micro-structures [75–77], and only requires mild conditions. In this method, a solution (e.g. sol) is initially formed as result of mixing chosen precursor such as a particular metal alkoxide with a solvent, catalyst, and complexing agent. This results in the formation of a stable dispersion of polymers or colloidal particles in chosen solvent as a result of hydrolysis reaction undergone by the precursors. Resulting solution is then added into the PCM oil-in-water emulsion, which results in producing a gel containing discrete microcapsules with PCM droplets entrapped inside them. Inorganic shell materials such as silica and titanium oxide are the most commonly used shell materials. Hydrolysis of precursor compounds such as tetraethoxysilane, sodium silicate or methyl triethoxysilane leads to the formation of the sol solution. During this process, the pH value is maintained very low, usually in the range 2–3, to ensure sol–solution undergoes hydrolysis reaction. Decreasing the pH will promote hydrolysis by protonating the leaving group [75]. Silicate solution gets added into the PCM oil-in-water emulsion drop-by-drop, while continuously stirring the emulsion, to avoid the formation of any continuous gel, instead to encourage the formation of discrete silica gel walls around the PCM droplets. Condensation polymerisation reaction of silica solid particles occurs, and as result, the PCM droplets get surrounded by the silica shells. Figure 7 illustrates the fundamental processing steps involved in the sol–gel method.
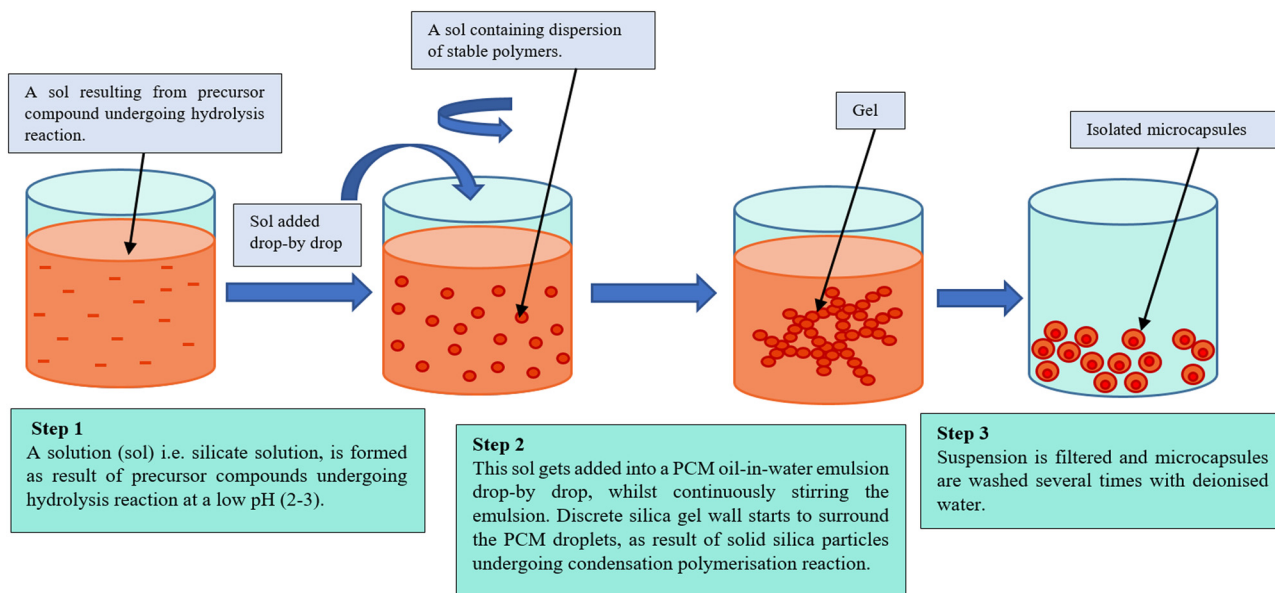
Figure 7: Schematic representation of a sol–gel process.

3.2.4 Chemical encapsulation

3.2.4.1 *In situ* polymerisation

In this *in situ* method, droplets are initially formed as a result of dispersing core material (PCM) into an aqueous phase consisting of a small fraction of the emulsifier (Figure 8). This is followed by the addition of adequate monomers or pre-polymers of urea with formaldehyde or melamine with formaldehyde. The pH of the system will then get reduced, which initiates the polycondensation reaction. As result, it yields cross-linked UF or MF resins. Once the resin reaches a high molecular weight, it will become insoluble in the aqueous phase and thus, a precipitate will be formed which is normally observed to deposit at the oil–water interface of the droplet. The resin will eventually harden, and thereby shell of the microcapsule gets formed. Table 2 summarises the properties of microcapsules produced by this method.

In general, high reactivity leads to shorter reaction time [83], and this depends greatly upon the type of resin used. Reaction proceeds much faster with MF resins and slower with UF resins. In addition, MF microcapsules have enhanced thermal stability. Park et al. [84] microencapsulated fragrant oil within a UF shell, while Lee et al. [85] microencapsulated floral oil with MF shell material. From latter study, results indicated that the morphology of fabricated microcapsules are influenced mainly by the formaldehyde/melamine molar ratio and the pH of the reaction mixture. Su, Ren and Wang [86] used MF to prepare several types of microcapsules and evaluated their mechanical strengths. Strength of the MF shell reduced as the mass ratio of core/shell increased, and at a core/shell mass ratio of 3:1, the yield point was deduced to be 1.1×10^5 Pa. Salaün et al. [83] microencapsulated *n*-hexadecane within a MF shell. Results indicated that as the melamine/formaldehyde (MF) molar ratio increased, the surface of the microcapsules became rougher which was attributed by a higher degree of cross-linking of the MF resin, while decreasing the MF molar ratio resulted in producing microcapsules of reduced sizes i.e. a narrow particle distribution was obtained. The poor strength of MF shell can be overcome using amino-aldehyde crosslinking agent, and in addition, its thermal performance will also be improved. The brittleness, and rigidity (e.g. toughness) of this shell can further be enhanced by adding resorcinol as an impact modifier. Zhang and Wang [78] microencapsulated *n*-octadecane within a resorcinol-modified MF shell. Microcapsules with compact surface was obtained at the core/shell weight ratio of 75/25, and the results showed that these microcapsules exhibited better anti-osmosis property when compared with others. Fang et al. [87] prepared nanocapsules by encapsulating *n*-tetradecane within an UF shell. They used sodium dodecyl sulphate and resorcin ($C_6H_6O_2$) as the emulsifier and the system modifier, respectively.

Previous studies had investigated the influence of stirring rate, emulsifier content, cyclohexane on diameter, surface morphology, phase change properties and thermal stabilities of microcapsules produced by this
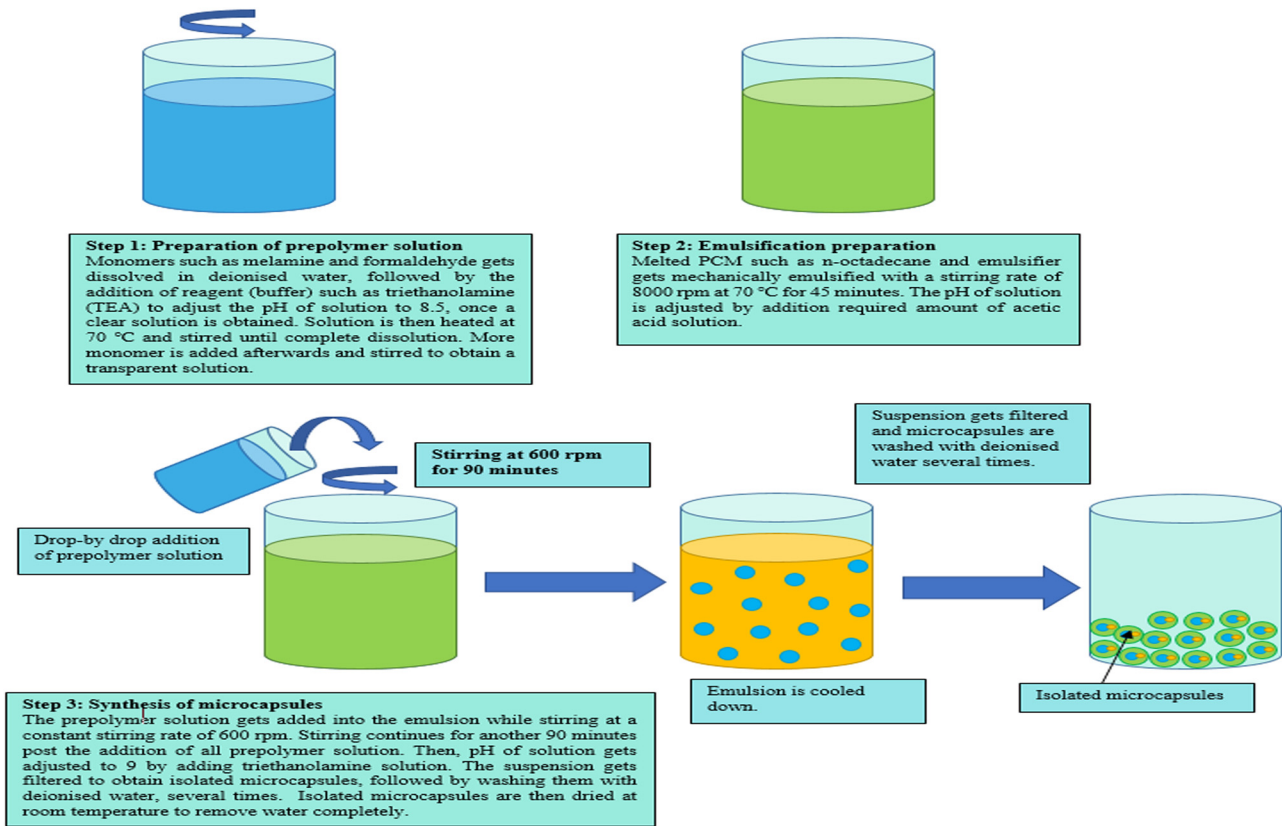
Figure 8: Schematic representation of the interfacial polymerisation method employed for the synthesis of microcapsules.

method [80,81,88,89]. Zhang et al. [88] microencapsulated n-octadecane within an UMF copolymer shell. They observed by mixing 30–40% of cyclohexane in the oil phase with heat-treatment under adequate conditions enhanced the thermal stability of synthesised

microcapsules significantly by inducing a free space with 5–28% of volume expansion ratio inside the microcapsules [89]. Zhang and Wang [78] reported that microencapsulation efficiency reduced when the amount of styrene–maleic anhydride (SMA) copolymer used

Table 2: Properties of microcapsules prepared by *in situ* polymerisation method collected from previous literature

PCM/core material	Shell material	Properties of microcapsules	Ref.
Styrene	MF resin	• Particle size was in the range 20–71 μm ▪ Core material content was ~60%	[78]
n-Octadecane	MF	• Average diameter of 2.2 μm • Average content of 59 wt% • Latent heat of 144 J/g	[79]
n-Octadecane	MF	• Average diameter of 9.2 μm at stirring rate of 4,000 rpm • Average content of 70 wt% • Latent heat of melting 169 J/g	[80]
n-Octadecane	Urea–melamine–formaldehyde	• Average PCM content of 72 wt% • Latent heat of ~164 J/g • Average diameter of 0.8 μm	[81]
n-Nonadecane	Urea–melamine–formaldehyde	• Average PCM content of 69 wt% • Latent heat of ~233 J/g	[82]
n-Eicosane	Urea–melamine–formaldehyde	• Average PCM content of 71 wt% • Latent heat of ~172 J/g	[82]

increased at a core/shell weight ratio of 80/20 because the shell became too thin, so that it resulted in inducing leakage of *n*-octadecane. Microcapsules containing 80% of *n*-octadecane content were successfully produced at a core/shell weight ratio of 75/25, and the optimum microencapsulation efficiency was 92%. Fang et al. [87] reported that using resorcin as crosslinking agent improved the encapsulation efficiency by allowing a high mass content of core material to be encapsulated within the shell. Hence, as the resorcin concentration increased from 0.25 to 5%, the mass ratio of *n*-tetradecane increased from 30.4 to 61.8%. However, if resorcin concentration was too high, the stickiness of nanocapsules formed increased, and made it more difficult to produce regular nanospheres. Su et al. [90] microencapsulated *n*-octadecane with methyl methacrylate (MMA) and methacrylic acid (MAA) as shell monomers (e.g. methacrylate-co-methacrylic acid) (PMMA-MAA) and concluded that best microcapsules were produced at shell monomer weight ratio of 80% MMA: 20% MAA. They reported that the microencapsulation efficiency was in the range of 70.4–79.8%, which was due to the high weight percentage of shell that reduced the evaporation of shell monomers significantly. Chen et al. [91] prepared a novel type of octadecylamine-grafted graphene oxide (GO-ODA) – modified microencapsulated PCMs by encapsulating *n*-octadecane within a MF (MF) shell and reported the encapsulation efficiency to be 88%.

3.2.4.2 Interfacial polymerisation/polycondensation

During this process, the microcapsule wall of the polymer gets formed at the interface present between the two phases provided that each phase contains a suitable reaction monomer. In the beginning, a multifunctional monomer gets dissolved in the organic core material, and the resulting mixture formed in the aqueous phase containing a mixture of emulsifiers and protective colloid stabilisers. Finally, a combination of monomers will be added to the aqueous phase to generate the polymer shell. Figure 9 shows the schematic representation of the processes involved in the interfacial polymerisation method for the encapsulation of PCMs.

In this technique, the wall of the capsule is formed by the means of rapid polymerisation of the hydrophilic and lipophilic monomers, which occurs at the interface of the oil-in-water emulsion. The solution containing a particular lipophilic reactant gets emulsified in the aqueous phase, containing an emulsifier. Then, a

particular hydrophilic reactant will be added, in aqueous phase, which results in initiating the interfacial polymerisation, and thereby, a shell will be formed [8]. Once the reaction gets initiated, the wall formed will be turned into a barrier to diffusion, and finally, the rate of interfacial polymerisation reaction gets limited, which results in affecting the morphology and unity of the shell of capsule formed. Interfacial polycondensation, in an emulsion system, is one of the most commonly used chemical methods for the microencapsulation PCMs, due to the advantages such as high reaction speed, mild reaction courses and low permeability. Selection of shell material is very crucial to facilitate the microencapsulated PCMs in various applications because their shell structure determines their chemical and thermal stabilities, release properties, and compatibility. Normally, the structure of the shell material is governed by the monomers, and processing techniques are used. In the past, various shell materials have been investigated, such as melamine formaldehyde (MF) resin, PS, PMMA and UF resin; however, such materials only possess limited applications due to their serious drawback: high chances of emitting toxic gases [92]. In the past, interfacial polymerisation has been used to microencapsulate PCMs with PU shell, due to its formaldehyde-free properties, and it is usually formed by reacting aromatic diisocyanate and aliphatic primary diamines. Unfortunately, this reaction is stated to exhibit serious problems, including production of linear structures, and fast rate of reaction which leads to the generation of microcapsules with poor thermal stability, and compactness [93,94]. Table 3 shows summarises the properties of microcapsules fabricated by this method.

Cho et al. [97] microencapsulated octadecane using toluene-2,4-diisocyanate (TDI), and diethylenetriamine (DETA) as reactive monomers in the disperse phase and aqueous phase, respectively. Multiple reactions resulted in the formation of the PU shell. Polyurea microcapsules had formed as result of the reaction taking place between TDI and DETA, and by the hydrolysis of TDI at the interface, which occurred as result of TDI reacting with amines, in the presence of excess TDI with hydroxyl (OH) group of the non-ionic surfactant (NP-10). Resulting PU microcapsules had an average diameter ranging from 0.1 to 1 µm which is considered as the desirable particle size range for most applications [97]. Su et al. [98] used the same method, and materials along with SMA solid as the dispersant to microencapsulate *n*-octadecane, and resulting microcapsules exhibited particle size in the range of 1–20 µm. Wei et al. [99] microencapsulated paraffin within a new type of
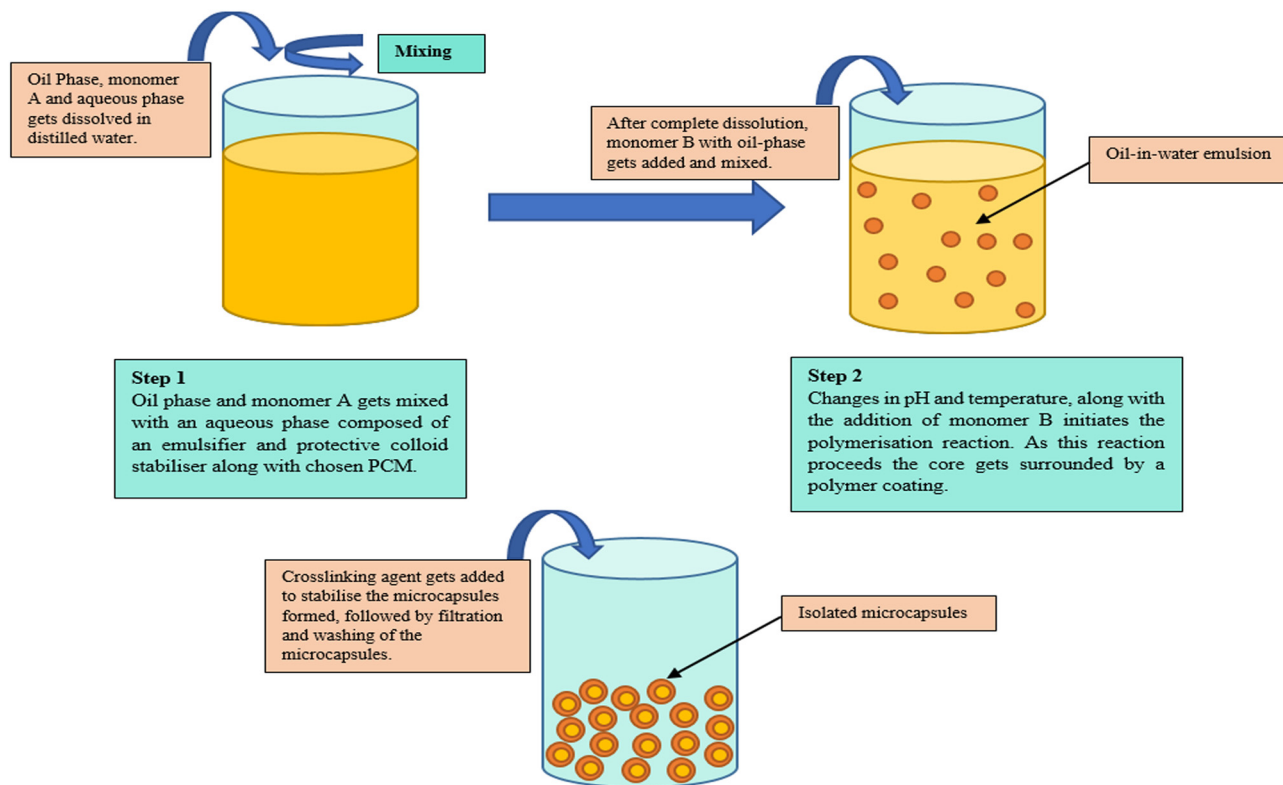
Figure 9: Schematic representation of the suspension polymerisation method employed for the synthesis of microcapsules.

polyamide shell, and prepared microcapsules with an average diameter of 6.4 μm. They found that the resulting microcapsules dispersed in water and organic solvents easily and exhibited good thermal and chemical stability. Zhan et al. [92] encapsulated paraffin within a new type of PU shell which was prepared using isophorone diisocyanate (IPDI) and ethylene diamine (EDA) as shell monomers. Incorporation of IPDI was observed to improve the flexibility of shell formed around the PCM core. Also, the type of emulsifier used influenced the morphology of the microcapsules produced. Hence, microcapsules produced with nonyl phenyl ether (OP-10) as emulsifier exhibited a spherical shape, whereas the ones produced with sodium dodecylbenzenesulfonate as emulsifier had non-spherical structures and adhered to each other. Furthermore, they concluded that the adequate amount of emulsifier required to produce microcapsules of enhanced thermal properties was 1.20 g.

Tamami and Koohmareh [100] prepared new series of PUs derived from 4-aryl-2,6-bis(4-isocyanatophenyl) pyridines by the polycondensation process between 4-aryl-2,6-bis(4-isocyanatophenyl)pyridines with several types of aromatic diamines. They demonstrated successful production of molecule-designed PUs exhibiting

good thermal stability; however, the synthesised shell material was observed to possess brittle nature. Zhang and Wang [93] prepared microcapsules by encapsulating *n*-octadecane within modified-PU shells. They prepared the shells using 2,4-tolyene diisocyanate (TDI) as the oil-soluble monomer, along with three different types of aliphatic amines consisting of various soft segments in the molecular chain, namely EDA, DETA and amine-terminated polyoxypropylene (Jeffamine T403). SEM analysis results showed that microcapsules produced using Jeffamine as the amine monomer exhibited a smoother and compact surface than the ones produced using EDA and DETA. Furthermore, these Jeffamine-based microcapsules were observed to have the largest mean diameter, higher encapsulation efficiency, and better anti-osmosis property. Liang et al. [95] micro-encapsulated butyl stearate (PCM) by an emulsion system with TDI and EDA monomers and deduced the suitable ratio of weight of core/shell to be 70/30, since encountering higher weight ratios reduced the thermal stability of the microcapsules. Zhan et al. [92] deduced that microcapsules exhibiting a compact structure, good anti-permeability and high stability can be produced at a core/shell ratio of 75/25. Ben Abdelkader et al. [101] microencapsulated neroline fragrance with polyurethane

Table 3: Properties of microcapsules prepared by interfacial polymerisation collected from previous literature

PCM/core material	Shell material	Properties of microcapsules	Ref.
Butyl stearate	Polyurea	• Heat of fusion ~80 J/g • Melting point ~28.7°C • Particle diameter ~20–35 µm • Good property of thermal periodicity • Good thermal stability after subjection to 400 repetitive heating and cooling cycling	[95]
n-octadecane	Silica	• Particle size 17.0 µm • Good thermal stability • Enhanced thermal conductivity due to the presence of silica • Optimum thermal conductivity (at core/shell weight ratio of 50/50) ~0.6547 W m^{-1} K^{-1}	[96]
Octadecane	Polyurea	• Particle size 0.1–1 µm • Melting point 28–30°C • Latent heat of fusion ~62.6–112 J/g • Heat of crystallization 20.9–22.7°C	[97]
Paraffin RT21	Polyurea (IPDI and EDA as wall monomer)	• Mean particle diameter was 2.40 µm • Latent heat was 92.5 J/g • Good anti-osmosis property • Good anti-permeability and high stability	[92]
n-Octadecane	Polyurea	• Mean particle size 5–20 µm • Jeffamine-based microcapsules exhibited better phase change properties, anti-osmosis property but poorer thermal stabilities	[93]
Butyl stearate	Cross-linked network polyurethane with pentaerythritol used as a crosslinking agent	• Diameter of a microcapsule in the range 10–35 µm • Enthalpy was in the range 77–81 J/g. Thus, microcapsules have good latent heat storage performance • Enhanced thermal stability due to the presence of network polyurethane shell	[94]

shell using isosorbide and hexane diisocyanate monomers.

Polyurea is considered as one of the most suitable shell materials since polymerisation reaction occurs more rapidly, resulting in producing relatively small and uniform particles. Moreover, PUs are insoluble in water, and they have the potential to incorporate both hydrophilic and hydrophobic core materials. However, they exhibit low stiffness, which is likely to limit the practical applications of the PU microcapsules [102]. Xing et al. [103] endeavoured to enhance the strength of the polymer shell by preparing a series of paraffin double-shell microcapsules exhibiting a relatively low shell permeability. Results showed that reaction between polypropylene glycols and TDI led to the formation of the inner shell, while the outer shell was formed as result of TDI reacting with amines in aqueous phase. Lu et al. [104] used the same method and materials along with SMA solid as the dispersant while butyl stearate was used as the PCM to fabricate microcapsules containing double shell. The stability of these double-shell

microcapsules against water-wash and ethanol-wash and thermal resistance was reported to be better than the one of the single-shell microcapsules fabricated by Liang et al. [95]. You et al. [105] observed by adding DVB crosslinking agent, the elastic modulus of shell increased, and the appearance of microcapsules was enhanced when compared with the ones produced in the absence of DVB. Li et al. [106] prepared novel PCM microcapsules with styrene–divinylbenzene copolymer as the inner shell and polyurethane as the outer shell. Both styrene and divinylbenzene was used as co-solvent and shell-forming monomers; however, the microcapsules produced exhibited poor mechanical strength, thus majority of microcapsules obtained was broken.

3.2.4.3 Suspension polymerisation

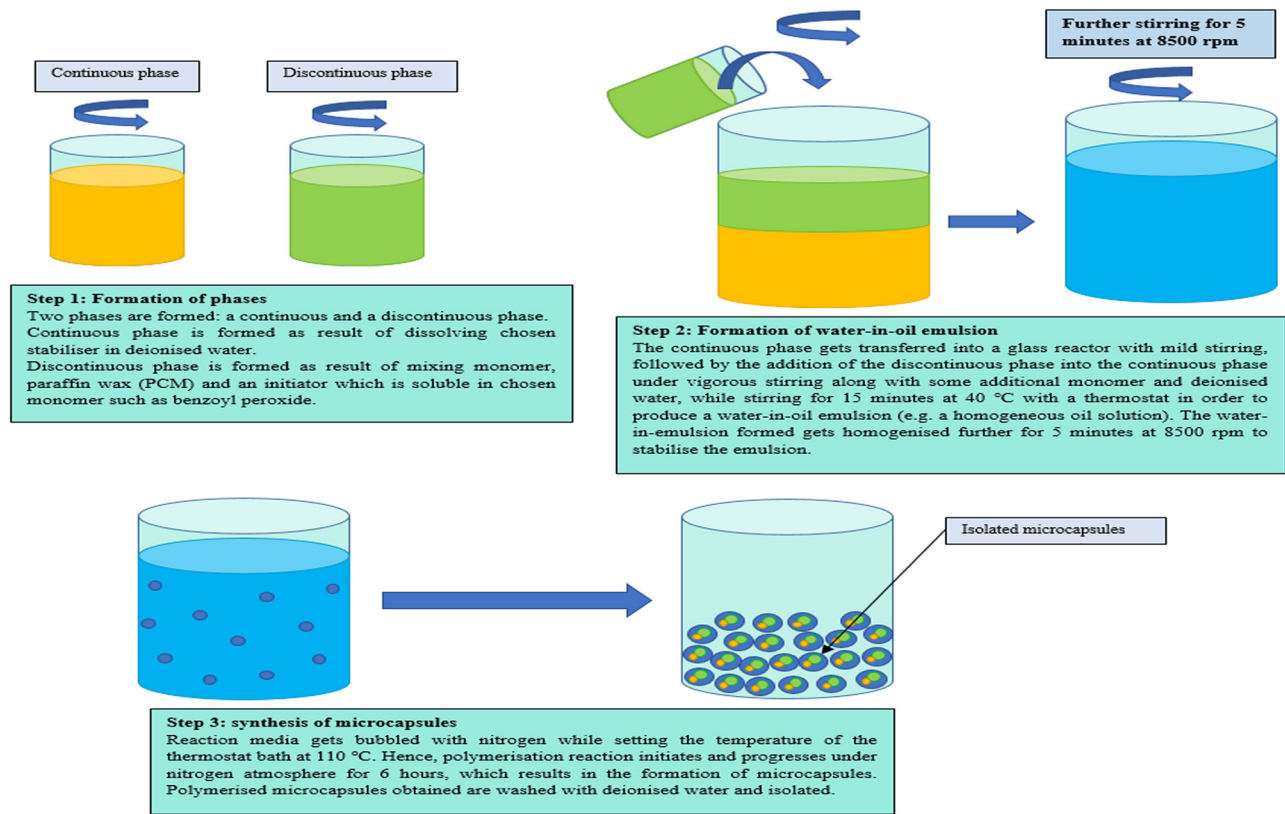It is one of the most extensively employed chemical method by researchers for the encapsulation of PCM (see

Continuous phase

Discontinuous phase

Further stirring for 5 minutes at 8500 rpm

Step 1: Formation of phases
Two phases are formed: a continuous and a discontinuous phase.
Continuous phase is formed as result of dissolving chosen stabiliser in deionised water.
Discontinuous phase is formed as result of mixing monomer, paraffin wax (PCM) and an initiator which is soluble in chosen monomer such as benzoyl peroxide.

Step 2: Formation of water-in-oil emulsion
The continuous phase gets transferred into a glass reactor with mild stirring, followed by the addition of the discontinuous phase into the continuous phase under vigorous stirring along with some additional monomer and deionised water, while stirring for 15 minutes at 40 °C with a thermostat in order to produce a water-in-oil emulsion (e.g. a homogeneous oil solution). The water-in-emulsion formed gets homogenised further for 5 minutes at 8500 rpm to stabilise the emulsion.

Isolated microcapsules

Step 3: synthesis of microcapsules
Reaction media gets bubbled with nitrogen while setting the temperature of the thermostat bath at 110 °C. Hence, polymerisation reaction initiates and progresses under nitrogen atmosphere for 6 hours, which results in the formation of microcapsules. Polymerised microcapsules obtained are washed with deionised water and isolated.

Figure 10: Schematic representation of the emulsion polymerisation method employed for the synthesis of microcapsules.

Table 4: Outlines the properties of microcapsules obtained by employing a suspension-like polymerisation method

PCM/core material	Shell material	Properties of microcapsules	Ref.
PRS® Paraffin wax	PSt	• Particle diameter ~30 µm	[109]
Paraffin wax	St and MMA	• Energy storage capacity of 41.65 J/g	[110]
		• Latent heat per mass (at MMA/St proportion of 4) ~84.04 J/g	
		• Enhanced thermal conductivity and mechanical strength	
PRS® Paraffin wax	St	• Latent heat ~41.65 J/g (lower than pure paraffin)	[107]
Tetradecane		• Optimum melting heat (nonadecane) was 119.80 J/g	
Rubitherm® R27		• Mean diameter of Rubitherm® R20 was the smallest	
Rubitherm® R20			
Nonadecane			
Paraffin	MMA and TEVS	• Enhanced thermal stability, thermal conductivity, and heat transfer rate, i.e. thermal conductivity was reported to reach an increment of 116%	[9]
		• Electrical resistance of PCM greater than 10^{10} Ω/sq	
n-Octadecane	St-DVB	• Thermal decomposition temperature ~230°C	[105]
		• n-Octadecane content (at monomers/n-octadecane mass ratio 1:1) ~56.8%	
		• Optimum enthalpy of 57 J/g (at monomers/n-octadecane mass ratio of 5:2)	
		• Average particle size ~71 µm (at stirring rate of 1,200 rpm)	
Paraffin wax	Polystyrene	• Average particle size was 4.53 µm	[111]
		• Average storage capacity (latent heat) was 104.7 J/g	

Figure 10) due to its advantages such as its simple, cheap, robust, and environmentally friendly. The basic procedures followed for the microencapsulation of PCMs includes: (1) the polymer monomer gets dissolved into the organic phase (core material), (2) the oil/water emulsion gets formed and (3) the monomer molecules

from the core materials get separated and precipitated, and thereby, the solid shell gets formed. This technique is governed by multiple simultaneous mechanisms namely: (1) particle coalescence followed by break-up, (2) secondary nucleation and (3) diffusion of monomer towards the interface. The combined effect of the mentioned mechanisms will determine the size, structure, and surface properties of fabricated microcapsules. In this technique, the degree of encapsulation achieved and the properties of final microcapsules depends mainly upon the complex interaction taking place between the polymer system (e.g. initiator, monomers and polymers) and the continuous phase (e.g. water and suspension agent) present on the surface of the droplets [107]. The morphology of fabricated microcapsules is influenced by the following factors: (1) the mobility present between the components, (2) compatibility between the monomers and polymers, (3) hydrophobicity and (4) the reactivity ratios between the monomers [108]. In general, some suspension polymerisation processes require special precautions to be taken. For example, when using PS, styrene-methyl-poly(divinyl-benzene) (PDVB), methacrylate and polyurethane as shell materials nitrogen gas protection facility should be available during the fabrication process, which could take around 5–24 h [90]. Table 4 summarises the final properties of microcapsules resulting from the suspension polymerisation method. Selecting a proper shell material is crucial, in order to microencapsulate PCMs successfully. Intensive work on microencapsulation of PCMs with various shell materials such as organic and inorganic shells are found in the literature. This method only allows the encapsulation of non-polar PCMs. Sánchez et al. [107] demonstrated the possibility of preparing microcapsules with high loading capacity; thus, they successfully fabricated microcapsules with around 50% PCM content by weight (e.g. 50 wt%) but the optimum encapsulation efficiency will change if a different PCM was used. Also, results demonstrated that it is impossible to encapsulate poly(ethylene glycol) within the designated shell due to its hydrophilic nature.

You et al. [105] microencapsulated *n*-octadecane (PCM) within a styrene (St)-divinylbenzene (DVB) copolymer shell and observed that as the DVB content increased, the enthalpy of microcapsules decreased. Supatimusro et al. [112] used poly(divinylbenzene) as the shell material instead. Results indicated that shell of microcapsules was dent as the DVB content reduced, thus low DVB content encourages the formation of non-spherical microcapsules. Therefore, they concluded that DVB content influences the shape of the microcapsules

produced. Yin et al. [113] deduced that the addition of DVB improved the mechanical strength of the shell; however, incorporating high content of DVB causes serious problems such as cramming of cavities present in the microcapsules with polymeric beads, or difficulty in separating polymer onto the droplet surface during polymerisation. Taguchi et al. [114] microencapsulated *n*-pentadecane within an MMA shell. Later, Sánchez-Silva et al. [110] microencapsulated paraffin wax within a shell material based on a copolymer of MMA and styrene (St), and results demonstrated the unfeasibility of microencapsulating the PCM when the MMA/St ratio was 2.0, and the monomer/paraffin mass ratio was 3.0. Ma et al. [115] microencapsulated hexadecane (HD) within a shell material resulting from mixing N,N-dimethylaminoethyl methacrylate (DMAEMA) and styrene monomers together. Results showed that the presence of insufficient amount of DMAEMA monomers led to incomplete microencapsulation of HD, and as content of HD increased, it became more difficult for the shell material to encapsulate the PCM. Li et al. [116] microencapsulated *n*-octadecane with different types of copolymer shells including styrene-1,4-butyleneglycol diacrylate copolymer, styrene-divinylbenzene copolymer, PSDB and PDVB, and the results demonstrated that PSDB shell was unable to prevent penetration of *n*-octadecane gas through the intact shell when the microcapsule was subjected to heat processing at 200°C for 30 min. Yin et al. [113] used Pickering emulsion polymerisation to microencapsulate dodecanol (PCM) with a new polymer/SiO$_2$ hybrid shell, and the results indicated that the impregnation of SiO$_2$ in the shell led to the enhancement of the mechanical strength of the shell. Thus, the content of SiO$_2$ had to be either 5% or 10% in order to fabricate the microcapsules successfully. In the recent times, the interest of using long-chain acrylate monomers for the microencapsulation of PCMs is growing, mainly for the synthesis of a softer shell. Qiu et al. [117] microencapsulated *n*-octadecane within a poly(lauryl methacrylate) (PLMA) shell and concluded that these microcapsules had good potential to be used in TES and thermal regulation applications. They found that using pentaerythritol tetraacrylate crosslinking agent enhanced the mechanical strength of the PLMA shell sufficiently. However, increased degree of PLMA shell resulted in reducing its strength, although thermal stability was observed to improve greatly with minor enhancement of the thermal resistance temperature of the microcapsules. Previous literature has reported that the thermal conductivity and TES capacity of organic PCM can be enhanced by adding either nano-materials

or minerals. Sahan and Paksoy [118] investigated the role of nanomagnetite (Fe_3O_4) nanoparticles on the heat transfer properties on PCM (e.g. paraffin) and reported that the addition of this particular type of nanoparticles (particle size in the range of 1–100 nm) [119] is effective in enhancing the heat transfer properties of PCM significantly. Lashgari et al. [120] prepared magnetic microcapsules with *n*-hexadecane/Fe_3O_4 as the core material and PMMA as the shell material and reported successful production of microcapsules exhibiting novel dual functional features, such as superparamagnetic properties with low remanence and coercivity.

3.2.4.4 Emulsion polymerisation

Figure 11 shows the basic steps involved in the emulsion polymerisation method. In this method, an insoluble monomer contained in the solvent gets dispersed uniformly by the means of mechanical stirring in the reaction medium which contains a particular emulsifier and surfactant. As result, a polymer membrane gets formed on the surface of the core once the initiator gets added.

Thereby, the polymerisation reaction gets initiated in the aqueous phase, which results in the growth of formed polymer particles due to progression of the polymerisation reaction [121]. This method is beneficial for the polymerisation of polymers and can be used to encapsulate designated PCM within a shell; thus, for the synthesis of nanocapsules (e.g. NanoPCM). Alkanes (e.g. paraffins) were the common PCMs used extensively in previous studies, and they were encapsulated within a PS or PMMA shell [122]. Table 5 summarises the properties of microcapsules obtained from this method.

Cho et al. [128] successfully encapsulated *n*-octadecane within a PS shell to produce nanocapsules of high adhesive property. They used alkali-soluble resin, poly (styrene-*co*-acrylic acid) as a surfactant and cetyl alcohol as a co-surfactant with DVB as the crosslinking agent. Sari et al. [123] fabricated novel microcapsules by encapsulating *n*-heptadecane (PCM) within a PMMA (transparent acrylic polymer) (PMMA) shell. Fortuniak et al. [129] used the co-emulsion polymerisation method to microencapsulate *n*-eicosane within polyhydromethylsiloxane shell. Results demonstrated that microparticles containing *n*-eicosane core was embedded in
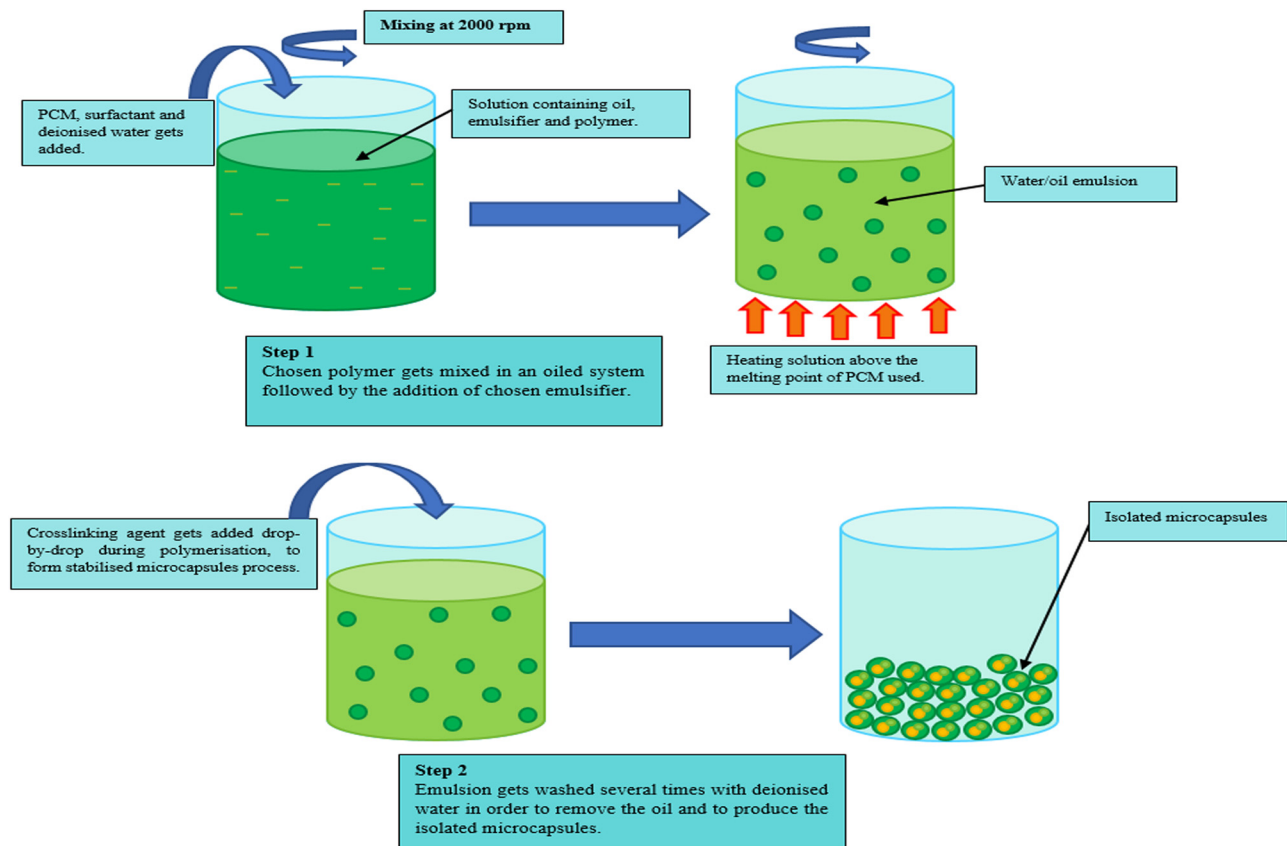

Figure 11: Schematic representation of *in situ* polymerisation method employed for the synthesis of microcapsules.

Table 5: Properties of microcapsules prepared by the emulsion polymerisation method

PCM/core material	Shell material	Properties of microcapsules	Ref.
n-Heptadecane	PMMA	• Microcapsules varied in a narrow range of 0.14–0.40 µm and the average diameter was 0.26 µm (produced at a stirring rate of 2,000 rpm) • Good thermal reliability post-exposure to 5,000 repetitive thermal cycling • Good thermal stability • Latent heats of melting and freezing were 81.5 and −84.7 J/g, respectively, reported to have satisfactory thermal properties for energy storage applications • The temperature of melting and freezing was 18.2 and 18.4°C, respectively • *N*-Heptadecane content of ~38 wt%	[123]
Docosane	PMMA	• Average diameter of 0.16 µm • Latent heats of melting and freezing were 54.6 and −48.7 J/g, respectively • Encapsulation ratio of docosane was 28 wt% • Average latent heats of melting and crystallization were 75.2 and 67.7 J/g, respectively • Good chemical stability since no chemical degradation occurred during 5,000 thermal cycling	[124]
n-Octacosane	PMMA	• Average diameter of 0.25 µm at a stirring rate of 2,000 rpm • Temperatures of melting and freezing 50.6 and 53.2°C, respectively • Latent heats of melting and freezing 86.4 and −88.5 J/g, respectively, and thus, average latent heats of melting and freezing post 5000 thermal cycling was 79.9 and 81.7 J/g, respectively • Good chemical stability • Average *n*-octacosane content of 43 wt%	[125]
n-Hexadecane	PMMA	• Mean particle size of 0.22–1.05 µm	[126]
n-Eicosane	PMMA	• Mean diameter of 0.7 µm at a stirring rate of 2,000 rpm • Latent heat of melting and freezing was 84.2 and −87.5 J/g • 35 wt% content of PCM	[127]
n-Docosane	PMMA	• Average diameter of 0.16 µm • Latent heat of 54.6 J/g • Encapsulation ratio of 28 wt%	[124]
n-Octadecane	MF	• Encapsulation ratio of ~40 wt% • Average diameter of ~1.3 µm • Latent heat of 166 J/g • Microcapsules exhibited a thermal resistant temperature of ~270°C	[80]

the polysiloxane shell. They used 1,3-divinyltetramethyl-disiloxane as the crosslinking agent to stabilise the shell and thereby promote the product yield of microcapsules formed. Formaldehyde-based polymers including MF, UF and melamine–urea–formaldehyde are conventionally used for the encapsulation of PCMs in numerous studies, despite possessing a serious drawback; they release formaldehyde residues/fumes that can cause health and environmental problems. Konuklu and Paksoy [130] microencapsulated caprylic (octanoic acid), an eutectic mixture, within a PS shell. Two types of crosslinking agents were used: ethylene glycol dimethacrylate (EGDMA) and allyl methacrylate (AMA) to optimise the strength of the shell formed around the core. PS shell has advantages over the conventionally used shell materials such as they are clear, inexpensive, non-toxic and easy to handle and process. Results demonstrated that type of cross-linking agent used had significant impact on morphology of microcapsules produced. Microcapsules exhibited a uniform geometry was produced with EGDMA, whereas non-spherical or agglomerated microcapsules was observed to be produced with AMA crosslinking agent. Also, increasing the amount of crosslinking agent resulted in decreasing the latent heat capacity of the microcapsules. Overall, both type and quantity of crosslinking agent used influenced the microencapsulation efficiency greatly. Numerous studies on the encapsulation of traditional organic PCMs such as paraffins and paraffin waxes are available since it is challenging to encapsulate fatty acids (e.g. eutectic mixtures) because they contain reactive functional groups; however, a limited number of studies have demonstrated the possibility of encapsulating fatty acids via the emulsion polymerisation method. Sari [131]

prepared micro-nanocapsules successfully by encapsulating three different types of fatty acids such as capric acid, lauric acid and myristic acid within a PS shell via the emulsion polymerisation method. The encapsulation ratios obtained were 45.4, 43.56 and 48.7 wt%, respectively. In a later study, Sari, Alkan and Özcan [132] prepared nano-/micro-capsules by encapsulating capric-stearic acid eutectic mixture (C-SEM) within a PMMA shell.

4 Conclusions

PCMs have number of benefits; however, the leakage problem limits their application greatly. This shortcoming can be overcome through the employment of the nano-/micro-encapsulation technologies. Current study has extensively reviewed the specifications of PCMs, encapsulation technology/methods, and provided a summary of properties of nano-/micro-capsules fabricated in previous studies. The encapsulation methods of PCM used to overcome the leakage problem of solid–liquid PCMs have been discussed to get a better understanding of factors likely to influence the final properties of synthesised nano-/micro-capsules. Nano-/micro-encapsulation technologies have gained considerable attention, mainly because it allows for more flexible choices of shell materials and PCM selection according to the practical requirements. Major shortcomings of this technology include high processing costs, and selecting the correct materials. Therefore, to widen the potential usage of this technology, it is necessary to reduce the overall encapsulation costs, facilitate production methods, and enhance the stabilisation of PCMs. Most studies have focused on microencapsulating PCM within synthetic petroleum-based polymers; however, it will be more beneficial to develop and apply nanoencapsulation techniques for the synthesis of nanocapsules, since they have number of desirable characteristics, including better loading capacity and encapsulation efficiency, improved structural stability and fracture resistances, when compared with microcapsules resulting from microencapsulation. To promote the sustainability of the encapsulation technology, it is necessary to utilise biopolymers such as cellulose/nanocellulose as shell materials because such polymers are environmentally friendly and are available abundantly.

Conflict of interest: The authors declare no conflict of interest regarding the publication of this paper.

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