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

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Abstract

With advancement in technology, the nanotechnology, various thermal energy storage (TES) materials have been invented and modified with promising thermal transport properties. The solid–liquid phase change materials (PCMs) have been extensively used as TES materials for various energy applications due to their highly favourable and potential thermal properties. The class of PCMs, organic phase change materials (OPCMs) have more potential and advantages over the class, inorganic phase change materials (IPCMs) having high phase change enthalpy (positive advantage). However, the OPCMs possess low thermal conductivity as well as density and suffer leakage during the melting phase. The encapsulation technologies (i.e. 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, their stability, applications and future perspective of micro/nano–PCMs as TES materials. The potential applications such as solar–to–thermal, electrical–to–thermal, 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 the mico/nano–PCMs for the researchers who are working in the area of thermal energy storage.

Keywords: Nanotechnology, Thermal energy storage, Phase change materials, Micro–encapsulated, Nano–encapsulated, Micro–PCM, Nano–PCM, Encapsulation technologies

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1. Introduction

After energy crisis of the 1970s, the world is facing worse shortage of energy resources and facing economic decline cumulatively. Researchers are looking forward towards different energy storage technologies based on renewable and sustainable resources to meet the future energy requirements [1]. The 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. The TES technology has the high heat capacity and enthalpy of fusion with capability of absorbing and releasing extensive amount of thermal energy while 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 bases of chemical composition, PCMs are classified in to major categories, organic phase change materials (OPCMs) and inorganic phase change materials (IPCMs). The positive advantage of PCMs especially, OPCMs which includes paraffins (*n-alkanes*) and non-paraffins (*n-alkenes*) materials, are more stable and high energy storage density and no segregation, non-toxic, self nucleation (super-cooling), non corrosiveness and non-reactive [2]. Contrarily, IPCMs have the high volumetric energy storage density, relatively high thermal conductivity and flame retardancy. In spite of this, IPCMs possess the sub-cooling and phase separation which reduce their instant release and utilization of thermal energy for large–scale TES applications. The OPCMs have the lower thermal conductivity [3] also they suffer the leakage problem and sub–cooling phenomenon during phase transition [4]. The lower thermal conductivity of OPCMs materials reduces the rate of heat transfer which causes increase in temperature gradient and insensitivity to temperature changes across the system boundaries. The OPCMs with potential advantage as TES materials are being under applications of air conditioning i.e. natural air cooling [5], cold thermal storage and absorption refrigeration [6, 7], waste heat recovery [8, 9], solar energy storage [10, 11], thermal regulating fabric [12, 13], passive heating of building [14, 15, 16, 17], heat pipes [18], desalination [19], thermal management of electronic devices and electric vehicle batteries [20, 21, 22, 23, 24, 25, 26, 27, 28, 29], space craft [30, 31], 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 [32, 33]. However, the leakage issue and lower thermal conductivity of OPCMs causes harm with interacting medium and losses the energy efficiency of the thermal system.

In the past, to solve the aforementioned challenges related with both types of PCMs efforts have been made. Various conventional approaches such as the adding up 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 crystallization procedure [34]. In contrary, the addition of conductive fillers and flame-retardants has reduced the disadvantages of OPCMs. On the other hand, these efforts would certainly lessen the energy storage density of PCMs due to the presence of inactive mass [35]. 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 [36, 37]. 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 [38]. 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. So, 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. Therefore, confinement is useful to reduce the drawbacks of PCMs as well as to enhance the thermophysical properties. For example, the confinement of salt hydrates inside packaging materials not only restrains the loss of water of crystallization 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 classify into *macro–confinement*, *micro–confinement* and *nano–confinement*. Different kind of physical properties like adhesion forces, Van der Waals interactions, capillary actions and surface chemistries are more effective at the nanoscale while confinement. For that reason, nano–confinement technology has proven to more valuable than macro and micro–confinement [39, 40]. Additionally, nano–confinement provide 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 into 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 exhibits the zero–dimensionality. longitudinal confinement is also similar to core–shell confinement but it has the 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 nanofibers (fibrous confinement) employing coaxial electrospinning technique. Interfacial or layer confinement technology cover 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 develop infiltration method, shown in Figure 1. In term of size, the term core–shell nano-confinement is used if the size of the capsules vary between $1 - 1000nm$ and for longitudinal confinement, the diameter of nanotubes or nanofibers should vary from $1 - 1000nm$.

Here in 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)* [42, 43, 44]. The EPCMs are tiny capsules or containers, consisting of two parts: (i)

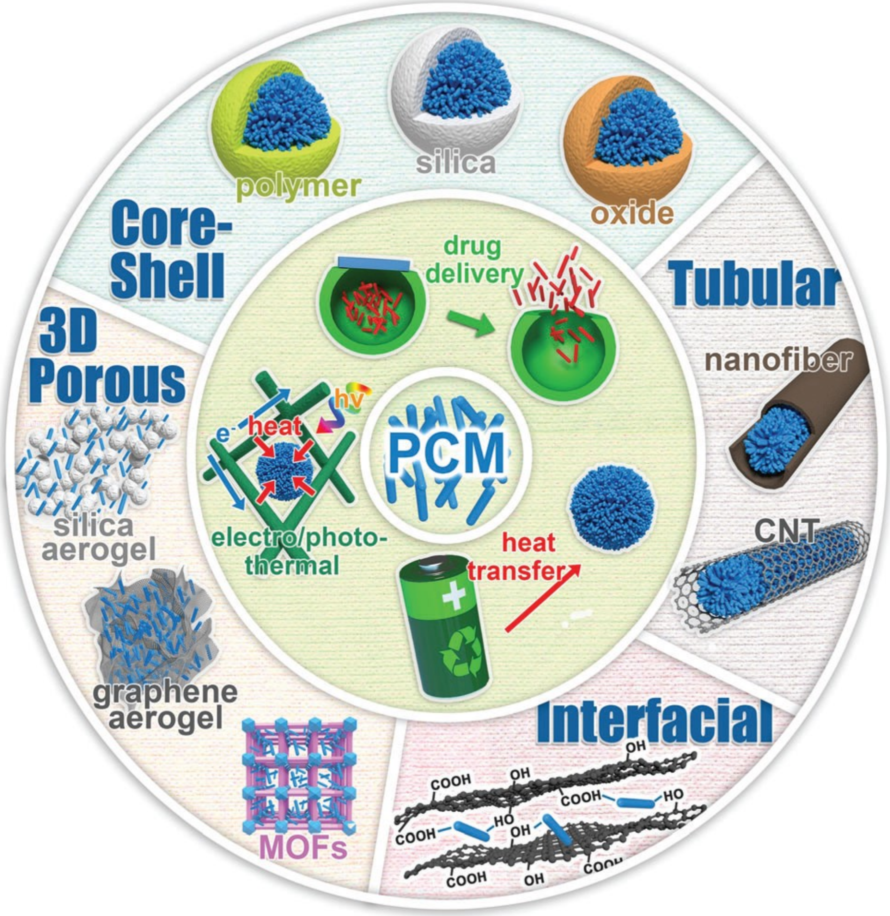


Figure 1: *Confinement strategies and potential applications of PCMs.* Reused from Ref. [41] with permission from The Royal Society of Chemistry.

core of PCMs and (ii) shell of polymer or inorganic materials which may have core–shell, multi–shell and polynuclear structure depending on the synthesis technique, as shown in 2. These capsules are both in 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 [45]. The material of coating shell has a very significant importance in terms to provide structural integrity and stability. Particularly, to gain the 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 both in non-flow and flowing system. Weight percentage of both core and shell materials are relatively depends on each other which defines the 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* [46, 47, 48]. Therefore, the mass of coating material needs to be optimized to obtain the desired thermophysical properties. Various coating materials such as organic polymers, silica, metal oxides and hydroxides have been utilized. 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 processable and compatible with PCMs [49]. In addition, as the polymers have the flexible nature which compensate the expanded volume of PCM while phase transition resulting ease the melting and keep the shape in stable of prepared NCs. Such promising physical properties of polymers prefer them to use as shell material for PCM encapsulation. Heretofore, polystyrene (PS), polyurea (PU), poly(urethene), polyacrylates, poly-amide (PA), polymethyl methacrylate (PMMA), polyethly methacrylate (PEMA) and formaldehyde resins have been utilized as shell materials to encapsulate OPCMS. So far many encapsulation technologies have been introduced as (i) micro and nano encapsulation, (ii) shape–stabilized composite, and (iii) intercalation. The encapsulation of the PCMs are classified into three major categories based on the particle size under core-shell confinement strategy:

- Macro–encapsulated PCM (Macro–PCM) ($1mm$)
- Micro–encapsulated PCM (Micro–PCM) ($1 - 1000\mu m$)
- Nano–encapsulated PCM (Nano–PCM) ($1 - 1000nm$)

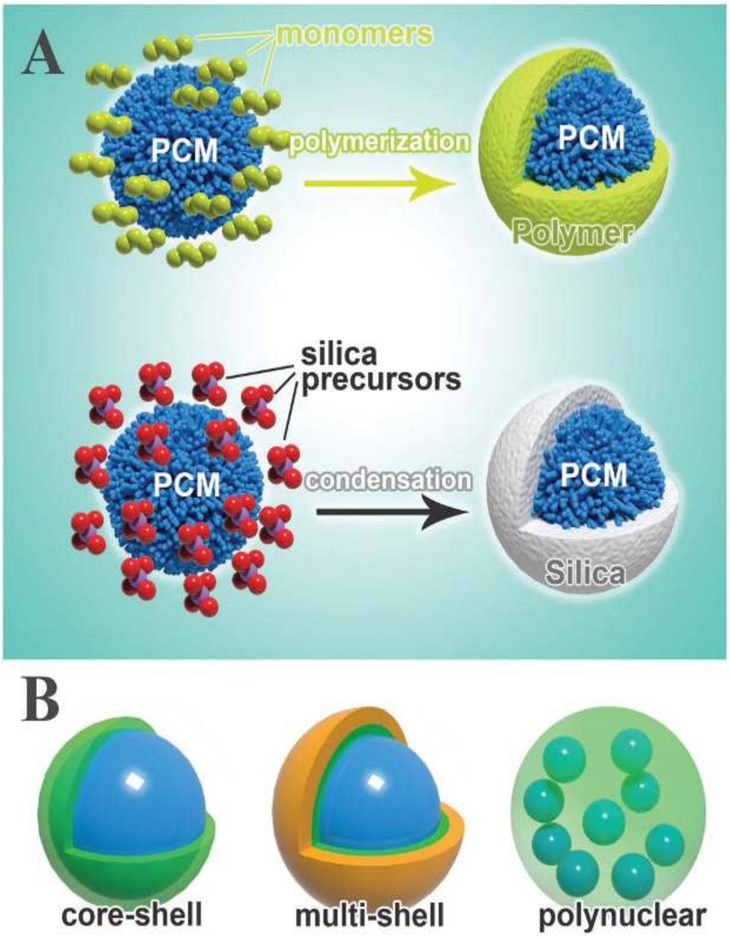


Figure 2: *(A)-Synthetic illustration of phase change EPCMs (B) and various structures.* Reused from Ref. [41] with permission from The Royal Society of Chemistry.

The OPCMs with temperature range of −10 to 80°C are mostly under development with various encapsulation techniques into micro and nano capsules [50]. The encapsulation techniques depend on the physical and chemical properties of shell and core materials as well the method of encapsulation [50, 51, 52]. From the 50 years developments in nanotechnology, the macro and micro encapsulation technologies of PCMs have gained a lot of improvement increasing the thermal performance and stability of encapsulated PCMs. As the stability of the EPCMs capsules relies on the size of particles, micro-PCMs can increase the viscosity of the fluid [53, 54, 55] also they can fractured in the fluid flow resulting the 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 taken the attention as new TES materials for energy storage applications [56]. Additionally, the nano-PCMs have volume and surface effect, easily dispersed in fluid and steadily flow in slurry make them favourable in thermal energy storage and thermal management applications [57, 58].

Up to now, a few studies have summarised the progress on preparation of micro–PCMs [59, 60] and nano–PCMs [40]. However, this review critically summarises the 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 the thermal storage and heat transfer performance. Further, the detailed discussion on preparation technologies to encapsulate PCM into macro–, micro–, and nano–sized of capsule are discussed using physical–mechanical, physical–chemical, chemical–mechanical and chemical encapsulation methods. Thermophysical properties of these novel EPCMs are summarized representing their enhancement in thermal conductivity, latent heat of fusion and encapsulation efficiency. Additionally, the detail discussion on characterisation techniques are explained to evaluate the chemical, thermal, physical, morphological, thermal reliability and thermal cyclic properties of EPCMs. The stability which is a real challenge of the PCMs capsules is discussed with respect to chemical and thermal properties point of view to explore the functionality and thermodynamic nature as an energy storage materials. The potential applications such as solar–to–thermal, electrical–to–thermal, thermal management, building, textile, foam, and medical industry of micro and nano PCMs are reviewed critically. Finally, this review paper highlights the emerging future research directions of EPCMs for the scientist and researchers to explore the unhidden characteristics in area of TES.

2. Ideal characteristics of EPCM

An ideal characteristics of EPCM significant influence the thermal systems while performing as a TES material especially at varying operating conditions. Thus, for an ideal EPCM it is necessary to meet the specific criteria and environment conditions for a longer duration. Figure 3 presents the ideal characteristics of EPCM which are necessary for utilization of thermal applications. Since, these ideal characteristics of EPCMs depend on their fundamental chemical, physical, thermal and economics properties which are as follows [61]:

- Sufficient phase–transition temperature: The suitable phase change temperature of EPCM is very essential and must match the operating conditions of specific application at melting and solidification temperature points.
- High latent heat of fusion: The latent heat of fusion, also called enthalpy of fusion, of the EPCM

is the most desirable thermal property to absorb large amount of heat with less amount of volume especially to reduce the size of the TES system which makes it light weight. EPCMs based on the organic PCMs as core materials and polymeric materials as a shell, have the tendency to absorb higher latent heat.

- High thermal conductivity: The higher thermal conductivity provides the additional capability to store thermal energy while sensible heating phase resulting lower the charging and discharging phases. The inorganic materials coated EPCM have the more potential to increase the thermal conductivity resulting in transmit the heat at higher rate. However, the increase in thermal conductivity of EPCMs causes the less absorption of latent heat fusion.
- Durability: The EPCM must has to withstand from damage, friction, wear and tear. The strength of coated shell of EPCM has to sustain its mechanical properties while flowing through system.
- High density and small volume change at phase transition: The high density of the EPCM helps to reduce size of encapsulated container at smaller level. The small volume change while phase transformation help to minimize the complexity of the EPCM storage container.
- Congruent melting: The congruent melting of the EPCMs helps to prevent the irreversible segregation resulting reduces the loss of storage capacity while recycling.
- Favourable phase equilibrium: The favourable or suitable phase equilibrium temperature ensure the heat storage and extraction at constant temperature in TES system.
- Long–term chemical stability: The continuous charging and discharging of EPCMs, water loss, decomposition or chemical interaction with storage container can undergo the degradation in EPCMs. So, it is highly preferred that EPCMs should maintained its long–term chemical stability and corrosion resistance interacting with other materials.
- Non–hazardous: For safety measures, the EPCMs should be non-toxic, non-flammable and non-explosive.
- High nucleation rate: An ideal EPCM should have high nucleation rate and good crystallization rate.
- Low super–cooling or sub–cooling: The low sub-cooling, also called super-cooling, ensures the melting and cooling at the same temperature which is due to metastable condition of the EPCM while solidification which means that during cooling the EPCM is not in thermodynamics equilibrium state. The super–cooling particularity occurs in salt-hydrates which prevents the extraction of thermal energy.
- Low vapour pressure and adequate crystallization rate: The low pressure and rapid crystallization of EPCM help to reduce the design complexity of EPCM storage system.

- Low cost and availability: The cost and availability of EPCM have the 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 the cost of ECMs.

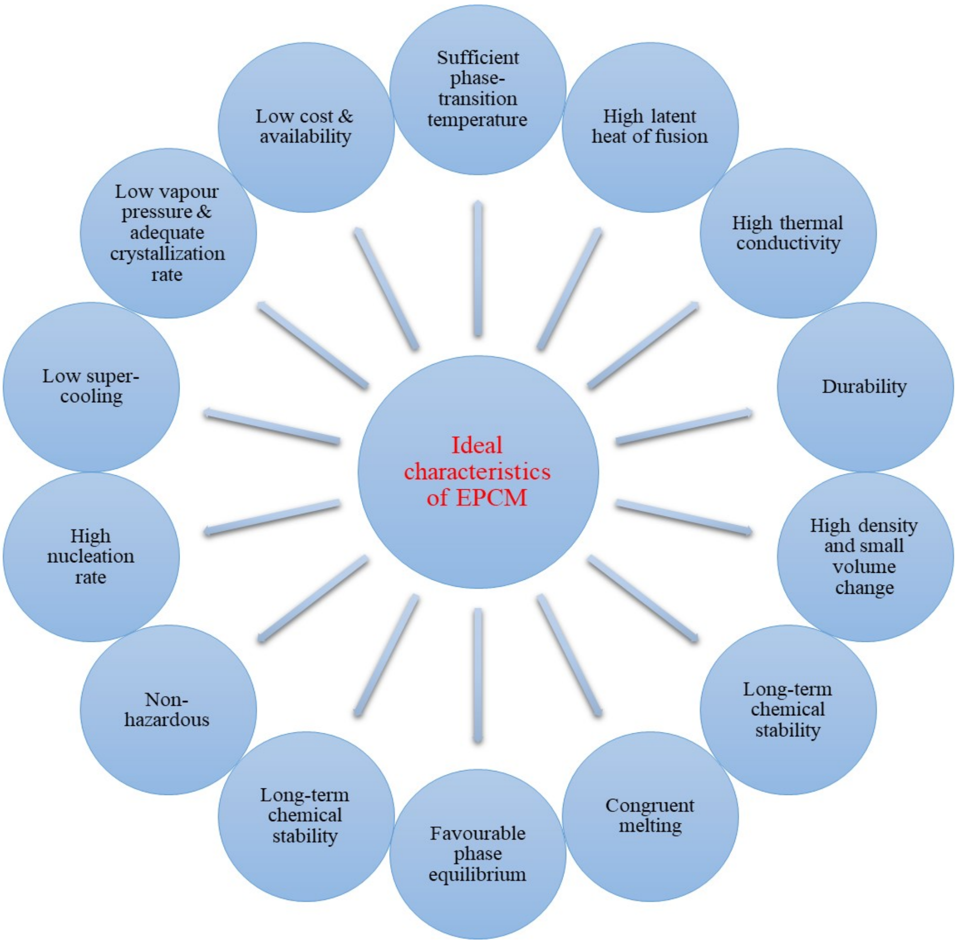


Figure 3: *Ideal characteristics of EPCM.*

3. The preparation technologies for EPCMs

The encapsulation techniques of PCMs are usually categories into four different methods; (i) physical–mechanical, (ii) physical–chemical, (iii) chemical–mechanical and (iv) chemical, which are based on synthesis of the EPCMs. Table 1 highlights a brief summary of above mentioned methods, their sub–relevant techniques and resulting formed size of capsules for the relevant type of PCMs.

3.1. Physical–mechanical methods

Generally, the physical–mechanical methods do not involve any chemical reaction resulting in formed the micro–capsules of not so much smaller size. The Table 2 summaries the properties of each technique of physical–mechanical method. The advantages and disadvantages of physical–mechanical methods are summarized in Table 3. The physical–mechanical methods include the following techniques forming micro–capsules.

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	Micro-fluidic Method	micro	organic
	Melt-coaxail electrospray method	micro	organic
Chemical	Interfacial polymerization	micro/nano	organic/inorganic
	Suspension polymerization	micro	organic
	Emulsion polymerization	micro/nano	organic/inorganic
	Miniemulsion polymerization	nano	organic/inorganic
	In-situ polymerization	nano	organic/inorganic

Table 2: *Advantages and disadvantages of physical–mechanical methods.*

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

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

3.1.1. Pan coating

The pan coating process is the oldest and widely used 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 melts the coating material, encloses the core of the capsule (e.g PCMs); and solidified by 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 resulting reduces the processing time as well energy and material consumption [62]. In this technique, the melting temperature of core material must be higher than the shell material melting temperature otherwise PCM encapsulation will not be eventuated effectively.

3.1.2. Air–suspension coating

Adopting air-suspension technique for micro–encapsulation gives more control and flexibility in comparison to pan coating by charging operation times of core material into the coating zone while processing [63]. Solid particle are suspended in an upward air stream after coating and drying in the solutions with both water and volatile organic solvents. During a cyclic process in 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 inter-particle agglomeration and surface layer.

3.1.3. Centrifugal extrusion

Southwest Research Institute (SwRI) [63] developed a mechanical process to produce the 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, flow through the annular around the tube. The key parameters which 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 the rotation or vibration of the tube the core and coating materials extrude from the orifice making spherical capsules due to surface tension forces. After then, the coated capsules are

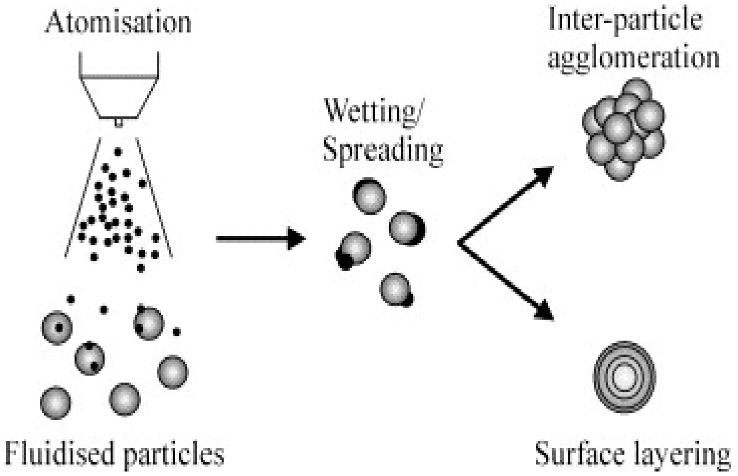


Figure 4: *Two particle growth mechanisms (inter-particle agglomeration and surface layering) in an air-suspension particle operation* [65], reused with permission from Elsevier license number 4385850236206.

solidified by heat or chemical reactions in a bath [45, 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 micro-granulation or matrix-encapsulation is normally carried out through a vibrating nozzle under laminar flow regime. The uniform capsules are formed due to vibration [68], however this method has been carried out for PCM encapsulation. Some studies were reported the uniform stable PCM composites prepared by this method but without vibration [69, 70, 71, 72, 73, 74, 75].

3.1.5. Spray drying

The spray drying encapsulation technique is an economical and easily scaled-up and controllable to produce homogeneous micro size capsules with efficient design of the atomizer [76, 77, 78]. The spray draying process is the most commonly used technique in food and pharmaceutical industries [79, 80, 81, 82] due to suitibility of encapsulation of heat–sensitive materials. This technique involves three major following steps [83]. Figure 5 presents the flow process of typical spray drying encapsulation technique [67].

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

The produced micro-capsules are usually poly-nuclear or matrix type and with increasing the production rate or flow rate, agglomerated and uncoated particles are obtained [45].

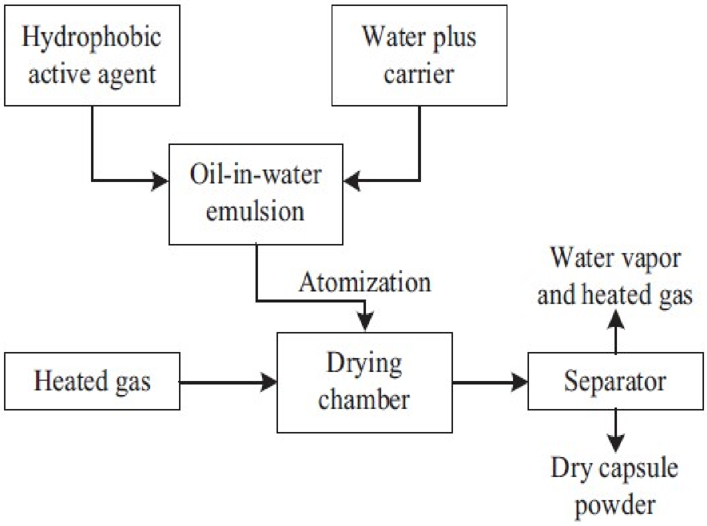


Figure 5: *Flow diagram of spray drying encapsulation technique*[67], reused with permission from John Wiley and Sons license number 4385841192579.

3.1.6. *Solvent evaporation/extraction*

Solvent evaporation or extraction is extensively used in pharmaceutical industries and it is liquid-liquid emulsification system. This technique is carried out in liquid manufacturing vehicle (LMV) and emulsification of polymer in a volatile solvent in water followed by a solvent removal. The basic steps of micro-encapsulation by solvent evaporation is shown in Figure 6 [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 solvent evaporation technique can be found in [84] .

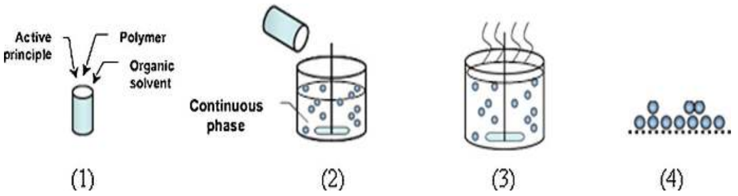


Figure 6: *Basic step of micro-encapsulation by solvent evaporation*[84], reused with permission from Elsevier license number 4385850567033.

3.1.7. *Vacuum impregnation*

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

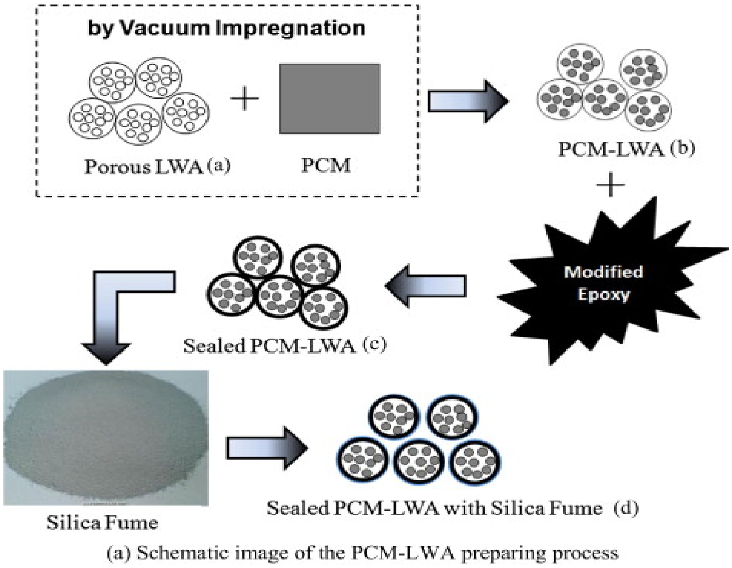


Figure 7: *Flow process of a macro-encapsulated TES LWA (a)schematic image of PCM-LWA preparation process; (b) LWA; (c) paraffin-LWA; (d) paraffin-LWA coated with a mixture of epoxy graphite powder; and (e) paraffin-LWA graphite powder sample coated with silica fume*[85], reused with permission from Elsevier license number 4385850945845.

Table 3: *Summary of prepared Micro–PCMs using physical–mechanical methods.*

Ref.	**Method**	**Core**	**Shell**	**Particle size** (μm)	**EE** (%)	T_m	**Latent heat** (J/g)
[78]	Spray drying	RT-27	LDPE, EVA	3.9	49.32	28.40	98.1
[86]	Spray drying	Paraffin wax	Gelatin and Gum arabic	~ 0.2	–	~ 60	145
[87]	Spray drying	N-octadecane	TiO_2	0.1–5	–	28.7	92–97
[88]	Spray drying	Green coffee oil	Lecithin and chitosan	1.35–3.70	86	–	–
[89]	Spray drying	Flaxseed oil	Gum arabic	~ 20	62.3–95.7	–	–
[90]	Spray drying	Lactobacillus plantarum	WPI with SA, WPI with FOS	53.99–105.07	87.92–94.86	–	–
[91]	Spray drying	Poppy-seed oil	Gelatin and Gum arabic	~ 5	76.8	185	–
[85]	Vacuum impregnation	Paraffin wax	LWA	$\sim 2 \times 10^5 (macro)$	70	27	102.5

Table 4: *Advantages and disadvantages of physical-chemical methods.*

Techniques	**Advantages**	**Disadvantages**
Ionic gelation	Low cost production Low temperature range	High wall permeability Difficulty in control
Coacervation	Controllable to produce Homogeoous particle size	Limited to scaled-up Agglomeration of particles Aldehyde as hardener
Sol-gel method	Suitable for encapsulation of inorganic shell High thermal conductivity capsules	Still need improvement

3.2. Physical-chemical methods

Generally, in physical-chemical methods include physical reactions such as, the phase separation, condensation, boiling and complexation etc. These include the following three main methods. The advantages and disadvantages of physical-chemical methods are summarized 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 pharmaceutical industries especially in drug supply systems and has not been carried out for the encapsulation of PCMs. In this method, the gel forming solution is dropped into droplet form in a gelation bath resulting hydrogel beads are formed. the gelation process may be occurred due the ionic bonding between the polymer chain such as the alginate solution is dropped in calcium bath which leads to the calcium alginate micro-capsules [92] or by cooling such as an agarose solution.

3.2.2. Coacervation

The coacervation word is derived form the Latin word "*acerus*" meaning "*heap*" [93]. Generally, the coacervation method is classified under two methods; (i) *simple coacervation* and (ii) *complex coacervation*. In simple coacervation method, the low-molecular substance is interacted dissolved polymer. The complex coacervation method, the interaction happens between two polymers who have the 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 the extra cost and more unyielding operation as compare to simple coacervation. However, complex coacervation method produces more smaller size micro-capsules of spherical shape with greater stability. Figure 8 represents the typical flow diagram of complex coacervation. The complex coacervation consists of three stages; (i) 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; (ii) the deposition of the shell material onto the core particles by adding second aqueous polymer solution of oppositely electric charge followed by adjusting the pH number, temperature or by dilution of the medium; (iii) finally, the mixture is cool down forming micro-encapsulation with stabilization by cross-linking and harvesting of the Micro-PCMs or thermal treatment [45, 94].

From complex coacervation, Konuklu et al. [95] produced micro-PCM using caprylic acid (octanic acid) using various wall materials (urea-formaldehyde resin, melamine formaldehyde resin and urea+melamine−formaldehyde resin) suitable for TES applications. The schematic of flow process and SEM image of produced particle size of mirco-capsules are shown in Figure 9 and Figure 10.

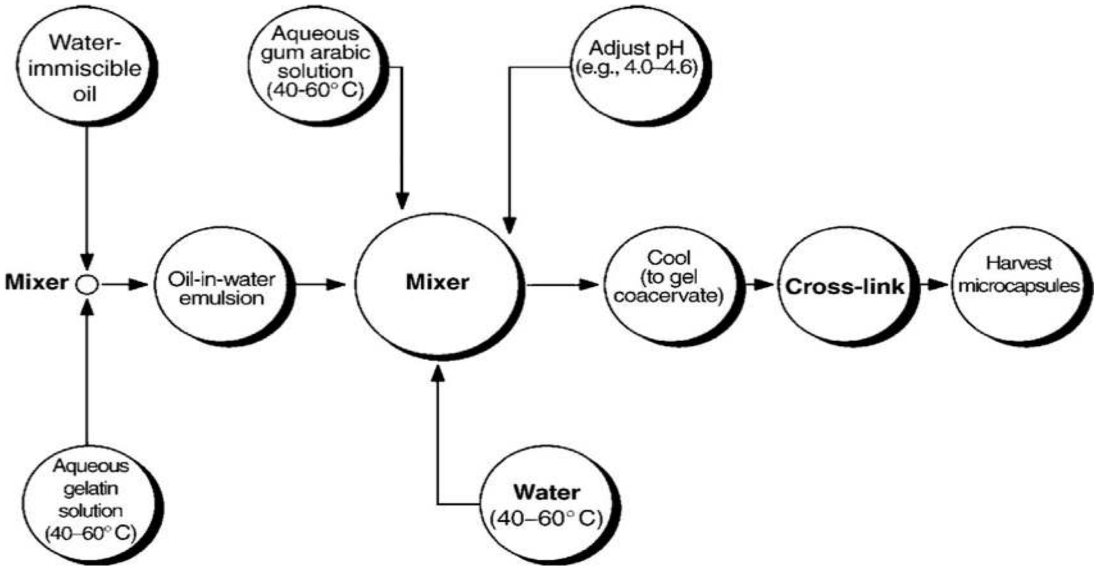


Figure 8: *Flow diagram of a typical complex coacervation method for encapsulation*[94], reused with permission from John Wiley and Sons license number 4385841192579.

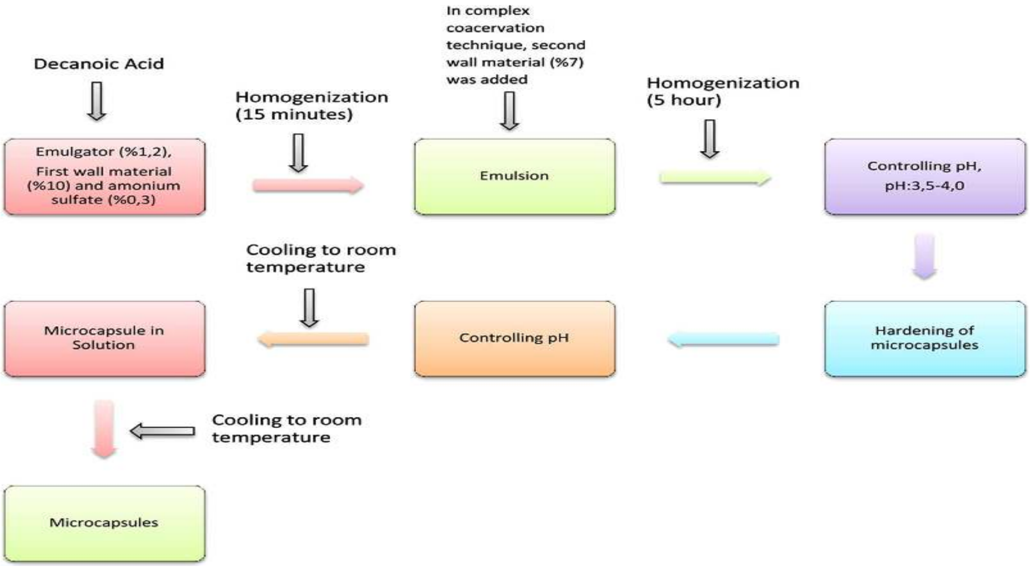


Figure 9: *Schematic formation of microCA with coacervation method*[95], reused with permission from Elsevier license number 4385860133315.

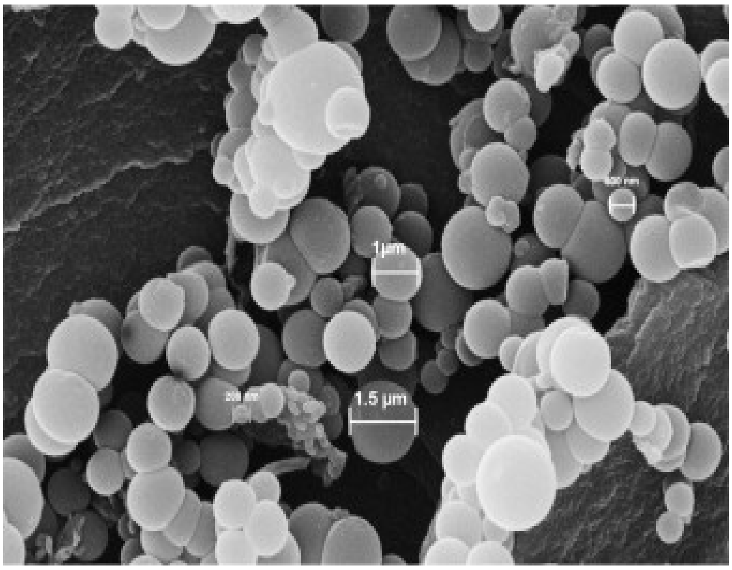


Figure 10: *SEM image of particle size of micro-capsules*[95], reused with permission from Elsevier license number 4385860133315.

3.2.3. Sol–gel method

The “sol–gel” is the abbreviation of “solution–gelling” and used largely to synthesis the inorganic materials. The sol-gel process is a familiar physico-chemical technique to develop NCs with an inorganic shell. It has capture attention in recent years as its inexpensive and need mild processing conditions. The sol-gel process followed as the poly-condensation 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 sol–gel method. In the sol–gel method, the processes are as follows; (i) the precursor (usually alkoxides and inorganics) is mixed uniformally with the solvent, catalyst and complex agent etc; (ii) then a stable and transparent colloidal solution is formed after hydrolysis and condensation chemical reactions; At this step, the condition of dispersion changes from solution to gel; that is why this method is known as the sol-gel method. (iii) the formed sol is further processed by aging to make three dimensional network structure; (iv) finally, micro and nano-PCM is formed after drying, sintering and curing processes [96, 97, 98]. Additionally the solgel method is mixed with the miniemulsion polymerization method to gain better thermophysical properties. For instance, Zhu et al. [99] prepared the nano-PCM using n-octadecane as PCM with organosilica shell via interfacial co-hydrolysis and co-polycondensation of functional SiO_2 precursors adopting mimiemulsion technique. The authors obtained the NCs of organosilica from $200-693nm$ of precise core-shell structure. Using mesoporous particles, the interfacial contact of EPCM with solid support enhances the nucleation sites in comparison of core-shell particles resulting reduced the super-cooling. 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.[101] confined stearic acid with a SiO_2 nanoshell with controlled shell density and improved the energy storage capacity of encapsulated PCM 36.9% likewise that of unconfined stearic acid, as shown in Figure 12. This improvement in latent heat is contributed

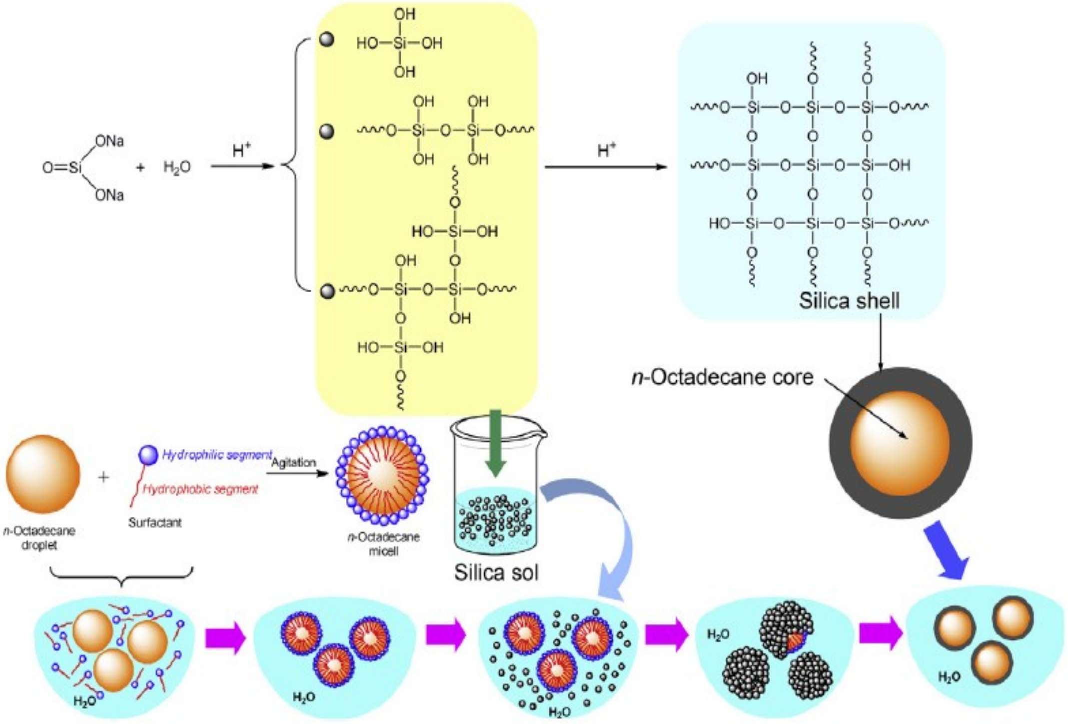


Figure 11: *Process scheme of sol-gel method*[100], reused with permission from Elsevier license number 4385860352467.

to the formation of a various stable hydrogen bonds network in high-superimposed stress on the encapsulated SA core from the SiO_2 shell, which considerably decreases the intermolecular spacing of the SA core in contrast to its unconfined state. This improvement in latent heat is contributed to the formation of a various stable hydrogen bonds network in high-superimposed stress on the encapsulated SA core from the SiO_2 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 experience phase transition. Further, this strong hydrogen bonding causes the rise of phase transition temperature of confined SA. Despite of the merits of the rigid shell, there are also some demerits. Rao et al. [102] investigated the melting mechanism of NEPCM of confined n-octadecane with free and constrained SiO_2 shell using molecular dynamic simulation method. The results sowed that the encapsulated n-octadecane was restrained with constrained SiO_2 futher the soft shell can increase the fluidity and eventually improve the heat transfer speed of the TES systems. As comparison organic based PCMs, IPCMs have also been confined within the SiO_2 shell. Zhang et al. [103] synthesized $Na_2SO_410H_2O$ encapsulated SiO_2 nanobowls via synchronous hydrolysis reactions of SiO_2 precursors. The authors proposed as well as validated that the microstress inside the liquid particles or nano droplets was the responsible of the formation of solid nanostructures. Furthermore, the SiO_2 wall, acting as a heterogeneous nucleator, reduces the degree of supercooling to 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 [104, 105]. Higher crystallinity and thermal conductivity reported in metallic PCMs. The silica shell can further reduce the corrosion and stop the leakage. Wu et al. [106] suspended bare indium and SiO_2 encapsulated indium nanoparticles in a base liquid, poly-α-olefin (PAO), for high-temperature heat transfer applications using 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 scientist to use as shell other than SiO_2. In comparison to SiO_2, the metal based materials have greater value of thermal conductivity, mechanical strength 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* solgel and emulsion polymerization, similar to SiO_2 shell formation. Till now, very few metal-based compounds have been utilised for encapsulation of PCMs [107, 108, 109]. Latibari et al. [110] utilized TiO_2 to prepare NCs of SA and using TiO_2 as a shell and found that the NCs present higher thermal conductivity and encapsulation efficiency up to 64.76% for NC of sizes $583.4nm$ and $946.4nm$. Pan et al. [111] used the boehmite ($\gamma - ALOOH$) 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 NCs was about $\sim 140kJ/kg$, 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 utilized 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.

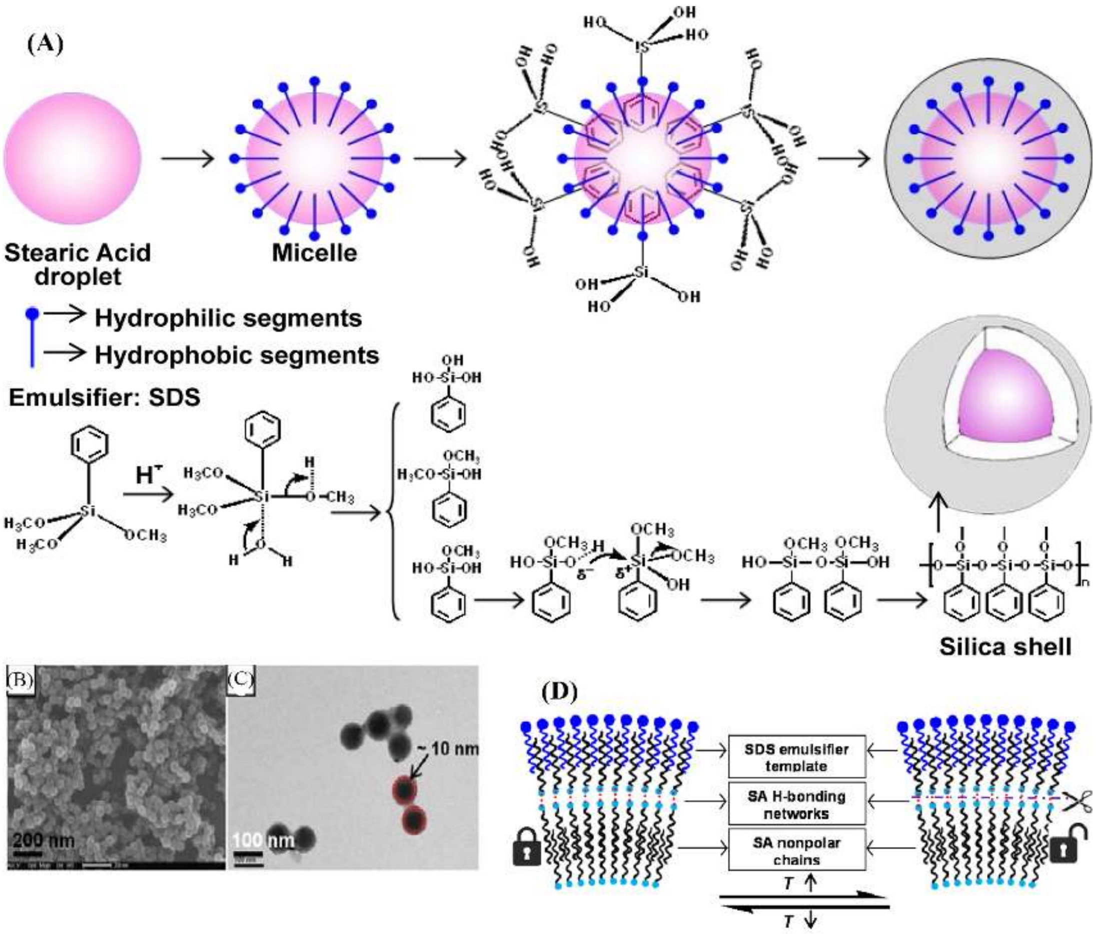


Figure 12: *(A) Schematic formation of the silica encapsulated strearic acid ($SA@SiO_2$) NCs; (B) and (C) SEM and TEM images, respectively; (D) illustration fo the formation and breaking of multiple stable hydrogen bonds under superimposed stress*[101], Reproduced with permission of the American Chemical Society.

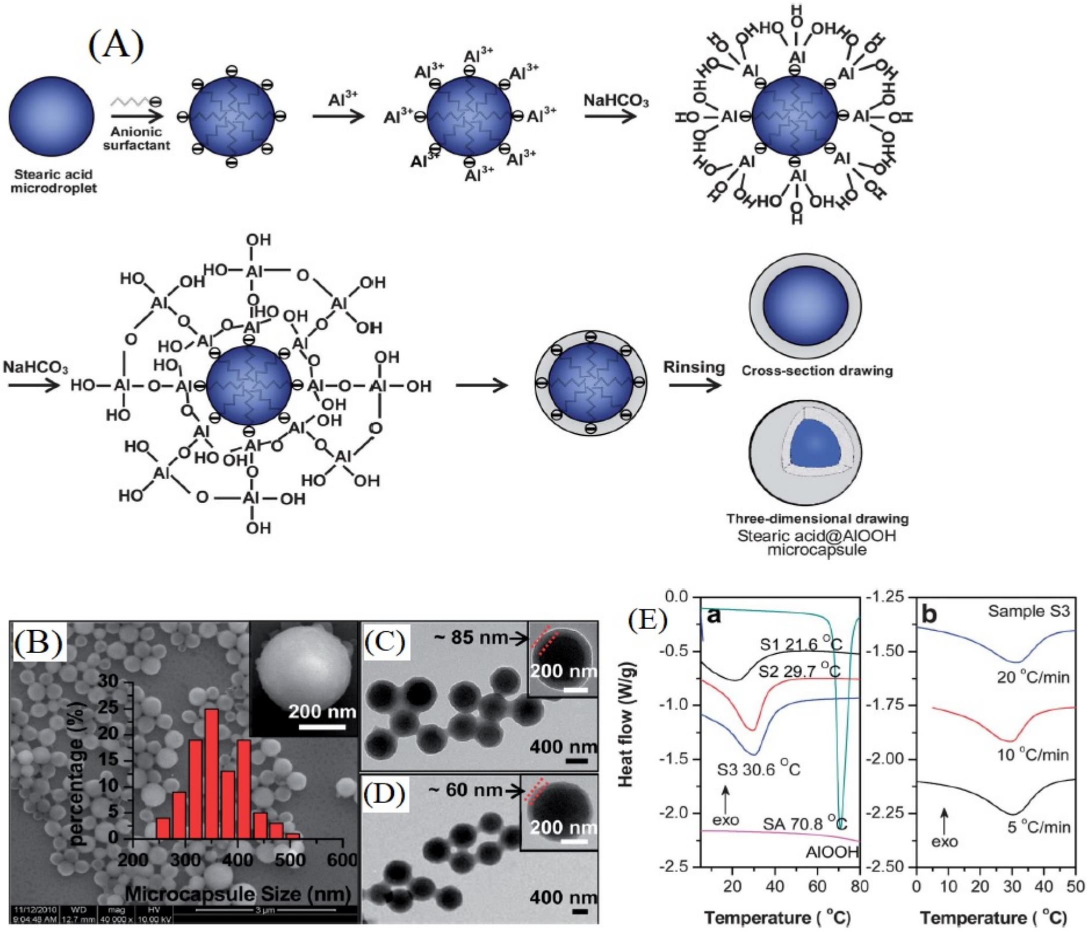


Figure 13: *(A) Schematic formation of* $SA@\gamma - ALOOH$ *NCs; (B) SEM image and size distribution of* $SA@\gamma - ALOOH$ *with 21.6% of SA; (C) and (D) TEM images of* $SA@\gamma - ALOOH$ *with 21.6% and 28.5% of SA, respectively; (E) DSA thermogram of pure SA,* $\gamma - ALOOH$ *and* $SA@\gamma - ALOOH$ *NCs with the same (left) and different (right) heating rate, respectively.* Reproduced from Ref. [111] with permission from The Royal Society of Chemistry.

Table 5: *Summary of prepared Micro/Nano-PCMs using physical-chemical methods.*

Ref.	**Method**	**Core**	**Shell**	**Particle size** (μm)	**EE** (%)	T_m	**Latent heat** (J/g)
[112]	Simple Coacervation	n-Hexadecane	Soy glycinin	∼ 101.7	65	–	–
[113]	Simple Coacervation	Holy basil essential oil (HBEO)	Gelatin	392.30	44.65–100.09	–	–
[95]	Complex Coacervation	Octanic acid	UF, MF, UMF	0.2–1.5	59.29	13.90	93.9
[114]	Complex Coacervation	Paraffin wax	Gelatin and Gum arabic	50–100	9.43–94.26	–	20–90
[115]	Complex Coacervation	Paraffin wax	Gelatin and Gum arabic	50–100	79.43–94.26	–	20–90
[116]	Complex Coacervation	Paraffin wax	Gelatin and Gum arabic	∼ 0.5	–	∼ 60	213
[117]	Complex Coacervation	Xylitol	Gelatin and Gum arabic	78.45–109.31	31–71	–	–
[118]	Complex Coacervation	Sunflower oil	Fish gelatin and arabic gum	40–240	–	–	–
[119]	Complex Coacervation	n-tetradecane	Gelatin	90–125	–	5.30	192
[120]	Complex Coacervation	Coco-fatty acid	Gelatin and Gum arabic	$1mm$	–	29–31	–
[121]	Complex Coacervation	n-Hexadecane, n-Octadecane, n-Nonadecane	Gelatin–Gum arabic mixture	–	–	11–38	19.70–165.80
[122]	Complex Coacervation	RT-27	Sterilized Galatine/Arabic Gum, Agar-Agar/Arabic Gum	9, 12	48, 49	298.3–301.3, 299.5–302.5	79, 78
[123]	Complex Coacervation	TMiglyol 812N	Chitosan and Gum arabic	5–10	–	–	–
[124]	Complex Coacervation	n-Eicosane	MF	1.89	53	36.9	134.3
[125]	Sol–gel method	n-Eicosane	Fe_3O_4/SiO_2	∼4–6	71.78	39.15	170.20
[126]	Sol–gel method	Tris	SiO_2	∼100–200	67.90	110–155	146
[127]	Sol–gel method	Paraffin wax	TiO_2	∼50	85.5	58.8	161.1
[128]	Sol–gel method	Palmitic acid (PA)	TiO_2	200–400(nm)	30.4	61.7	63.3
[129]	Sol–gel method	Stearic acid (SA)	SiO_2	20–30	90.7	52.6–53.5	162.0–171.0
[130]	Sol–gel method	Paraffin wax	SiO_2	40–60	82.2	57.96	156.86

[100]	Sol–gel method	n-Octadecane	SiO_2	2–4	41.45	27.96	87.46
[131]	Sol–gel method	n-Pentadecane	SiO_2	4–8	29.8–35.9	∼5–10	46.4–55.8
[132]	Sol–gel method	Paraffin wax	SiO_2	8–15	69.1–87.5	57.84–58.37	130.82–165.68
[133]	Sol–gel method	n-Octadecane	SiO_2	7–16	86.4	27.1	184.9
[55]	Sol–gel method	Palmitic acid (PA)	SiO_2	183.7nm, 466.4nm, 722.5nm	82.53, 84.28, 88.32	61.06, 60.92, 61.6	168.16, 172.16, 180.91
[110]	Sol-gel method	Stearic acid (SA)	TiO_2	317.6–946.4nm	30.36–64.76	58.23–59.14	58.12–123.96
[134]	Sol-gel method	n-Eicosane	TiO_2	1.5–2	49.90–77.97	42.73–43.88	97.60–152.50
[135]	Sol–gel method	Indium	SiO_2	200nm	–	155.3	19.6
[136]	Sol–gel method	RT 28	SiO_2, EG	5–20, 1–5	–	27.53, 27.72	112.84, 104.41
[137]	Sol–gel method	n-Octadecane	PMMA/SiO_2	10	–	–	178.9

3.3. Chemical–mechanical methods

In chemical–mechanical methods, mechanical machine is used to accomplished 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.

- Micro–fluidic technique
- Melt–coaxail electrospray technique

3.3.1. Micro–fluidic technique

In micro–fluidic technique, widely used in the medical and pharmaceutical fields [138], the capillary micro–fluidic device is utilized to form the mono–disperse double emulsion droplets following the flow motion geometry. Figure 14 illustrate the complete process of formation of mono–disperse double emulsion droplets developed by Sun et al [139]. The authors [139] 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 a co-flowing channels with different flow rates. The micro–PCM is obtained following washing and drying processes. Fu et al. [140] prepared the silicone/n-hexadecyl bromide micro–capsules by micro–fluidic technique selecting n-hexadecyl bromide as a 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.

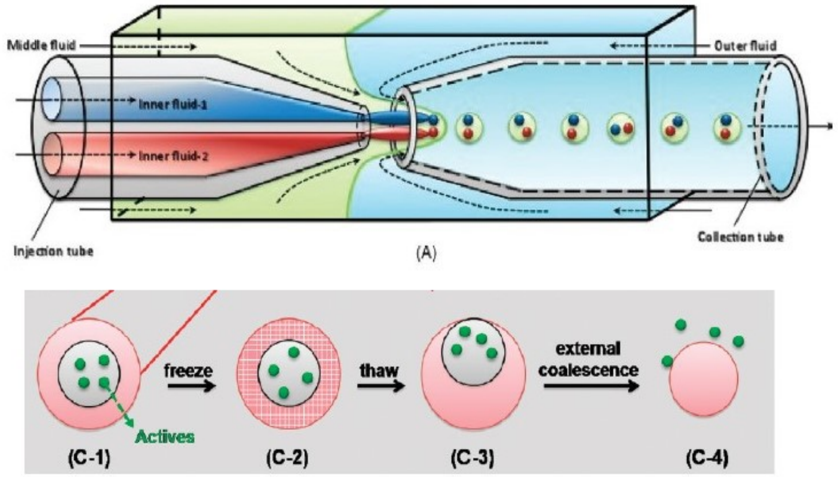


Figure 14: *(A)-schematic of capillary micro-fluidic device generating two-bore double emulsions; (C)-schematic illustrating the encapsulation and release of activities using the double emulsion-templated capsules*[139], Reprinted (adapted) with permission from ([139]). Copyright (2010) American Chemical Society.

3.3.2. Melt–coaxail 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. [141] who proposed a

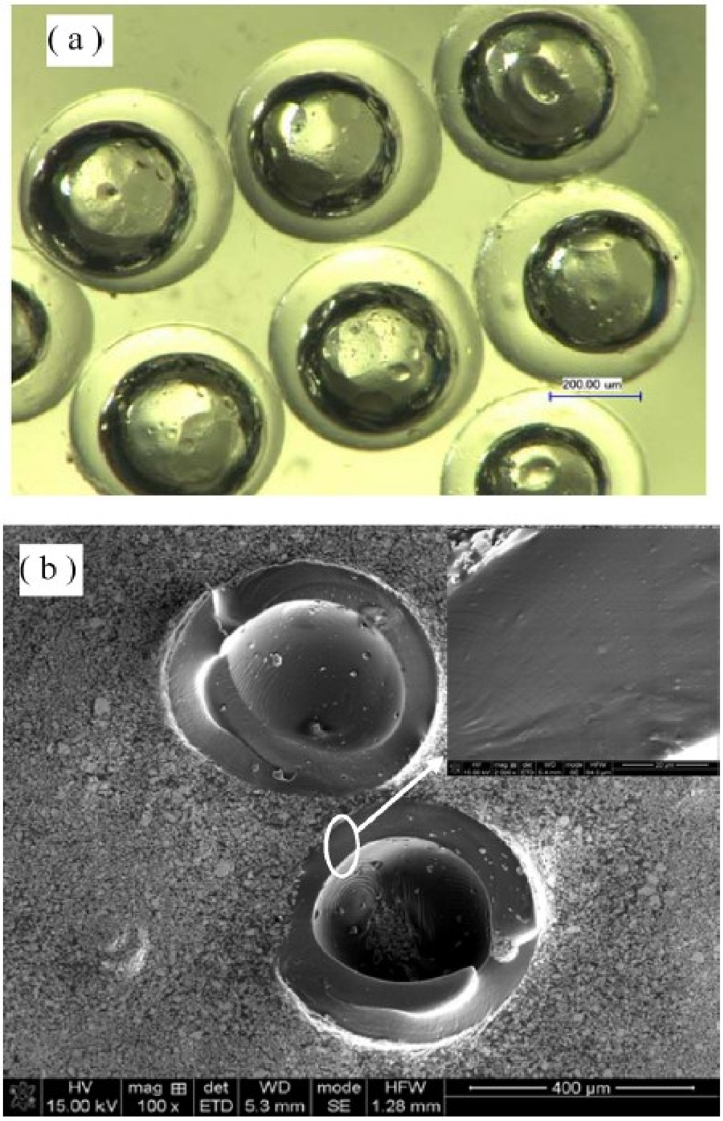


Figure 15: *(a)-Optical microscope; (b)-cross-sectional SEM image of mico-PCMs*[140], reused with permission from Elsevier license number 4385861063323.

method to generate steady coaxial jets of immiscible liquids having micrometer/nanometer diameter in size. The schematic diagram of melt coaxail electrospray technique used by Moghaddam et al. [142] is shown in Figure 16. The authors first time produced the micro–capsules using n-nonadecane and sodium alginate as core and shell materials, respectively.

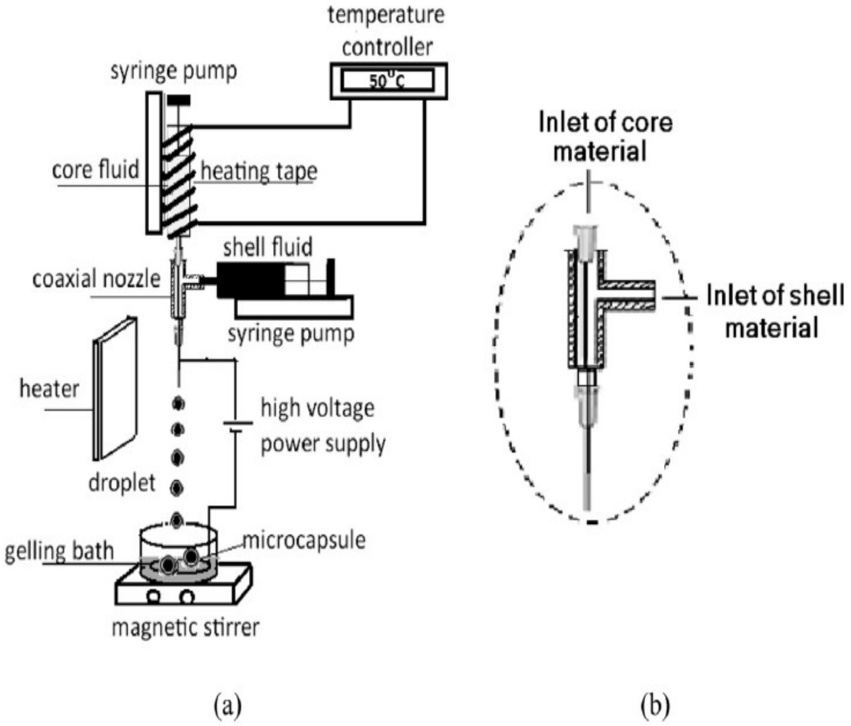


Figure 16: *(a)-Schematic of the melt coaxial electrospray setup; (b)-coaxial needle setup* [142], reused with permission from Elsevier license number 4385861260669.

Table 6: *Summary of prepared Micro/Nano-PCMs using chemical-mechanical methods.*

Ref.	**Method**	**Core**	**Shell**	**Particle size** (μm)	**EE** (%)	T_m	**Latent heat** (J/g)
[140]	Micro–fluidic technique	n-hexadecyl bromide	PDMS, PMHS	460	49	16.70	76.35
[143]	Micro–fluidic technique	Ascorbic acid	Solid lipid	170.2–342.5	73.4–96.6	–	–
[144]	Micro–fluidic technique	Silicone	PDMS	100–200	∼100	–	–
[145]	Micro–fluidic technique	Ceramic	Silsesquioxane	–	–	–	–
[142]	Melt–coaxail electrospray technique	n-Nonadecane	Sodium alginate	<100	56	31.12	81.67

Table 7: *Advantages and disadvantages of chemical methods.*

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

3.4. Chemical methods

The chemical methods ensures the production of smaller sizes such as nano-capsules 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 PCMs encapsulations. Table 8 represents the different approches and properties of micro/nano–encapsulated PCMs prepared by various chemical methods. The advantages and disadvantages of chemical methods are summarized in Table 7.

- Interfacial polymerization
- Suspension polymerization
- Emulsion polymerization
- Miniemulsion polymerization
- *In–situ* polymerization

3.4.1. Interfacial polymerization/polycondensation

In interfacial polymerization, 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 (i.e. OPCMs) by interfacial polymerization 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 [146], shows the synthesized micro-capsules via polycondensation. Park et al. [147] prepared the nano-PCMs using paraffin as a core and polyurea as a shell material via interfacial polycondensation. The SEM and TEM images of prepared Nano–PCM is shown in Figure 18 [147]. Pan et al. [148] 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.

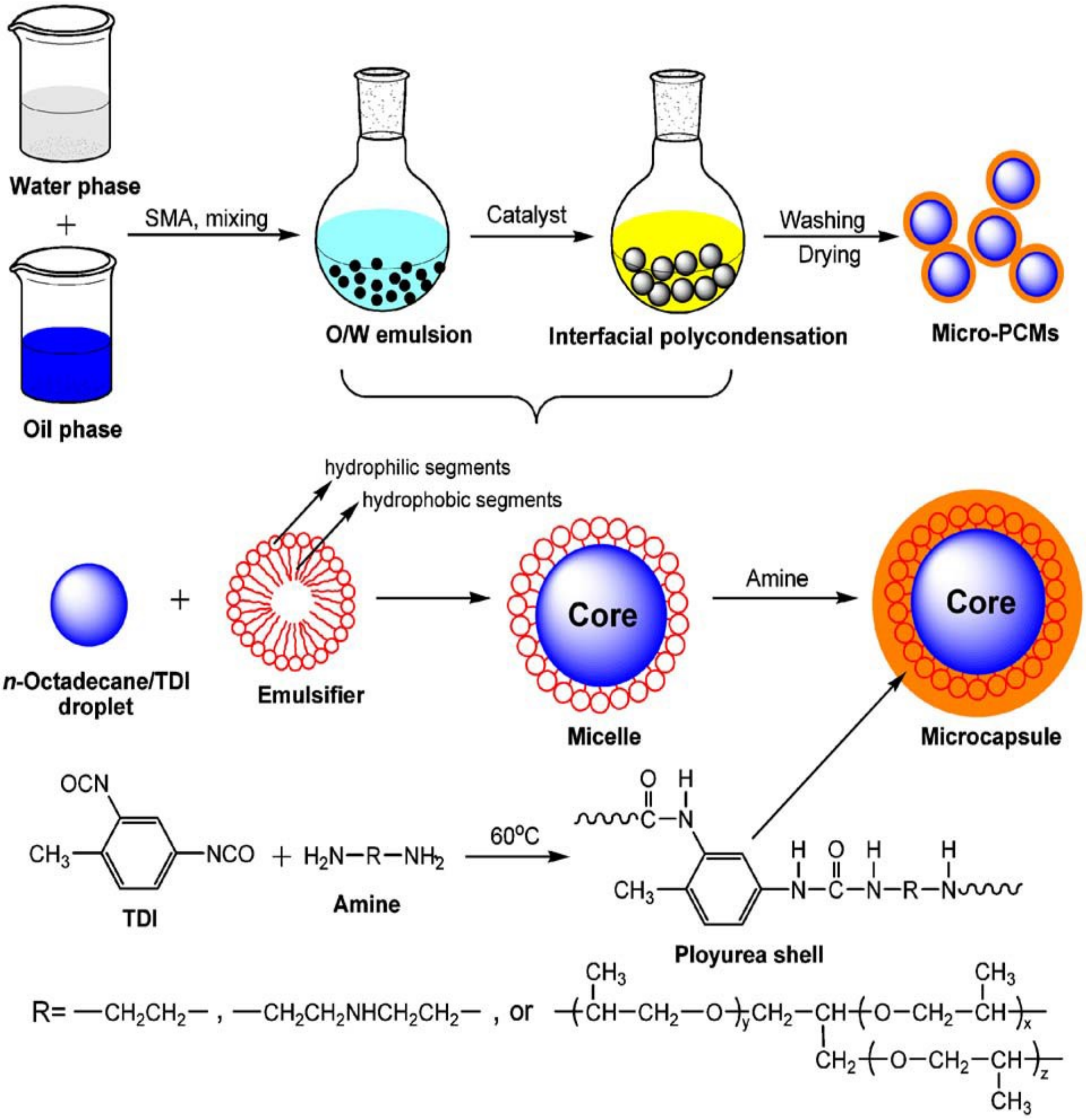


Figure 17: *Schematic formation of the micro-encapsulated n-octadecane with the polyurea shells containing different soft segments via interfacial polycondensation* [146], reused with permission from Elsevier license number 4385861412119.

3.4.2. Suspension–like polymerization

The suspension–like polymerization accomplishes on the system phases, (i) the discontinuous or dispersed phase, which contains the reagents of core material and monomers including initiator which prompt the chemical reaction; (ii) the continuous phase, which includes the reactants of shell materials and solvent [149]. The process of suspension-like polymerization consists of the following steps: (i) the dissolution of polymer monomers into core materials under stirring to obtain homogeneous oil solution; (ii) this homogeneous solution is then added to the continuous phase at constant temperature to produce the oil-water (O/W) emulsion; (iii) further an emulsifier is added to the O/W solution to make it more

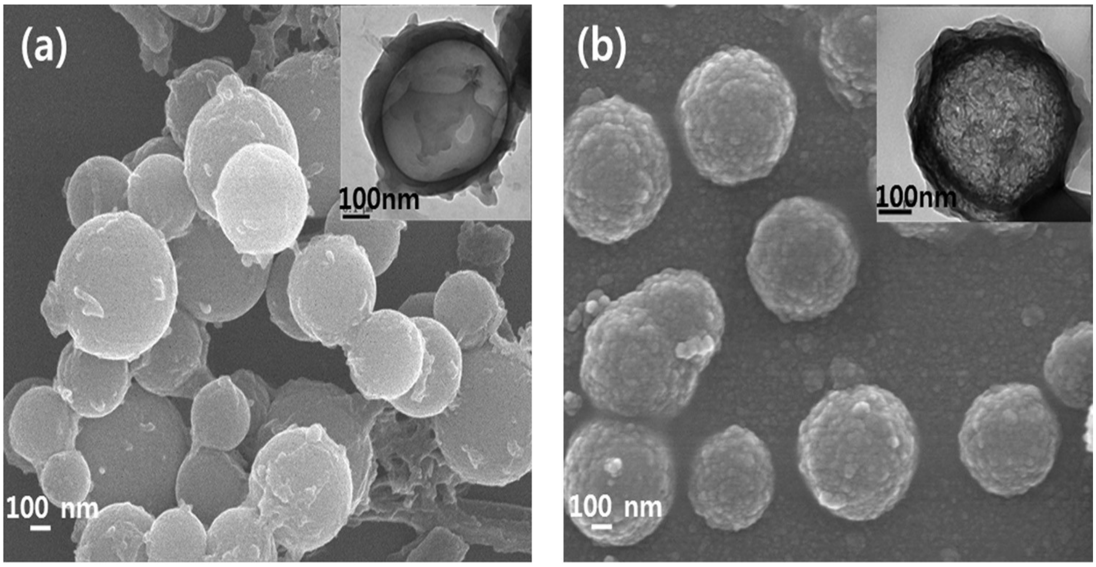


Figure 18: *The SEM and TEM images of nano-PCMs (a)-with and (b)-without Fe_3O_4 nano-particles* [147], reused with permission from Elsevier license number 4385870250913.

homogenized; (iv) then the prepared stable emulsion is stirred at constant high temperature for a period to give the proper polymerization reaction; (v) finally, the prepared encapsulated PCMs capsules are filtered, washed and dried. The schematic flow process of suspension–like polymerization is shown in Figure 19 [150].

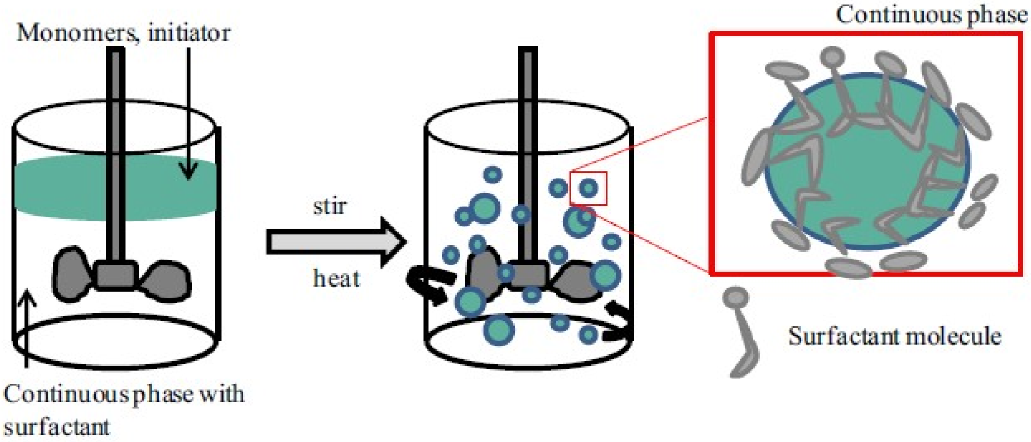


Figure 19: *Scheme of the suspension-like polymerization process*[150], reused with permission from Elsevier license number 4385870668358.

3.4.3. Emulsion polymerization

The emulsion polymerization method takes the mixing of the polymer in the presence of emulsifier in an oiled system. During the process, a number of thermal, chemical and physical processes occur to make the micro–PCM or nano-PCM. Unlike the suspension–like polymerization, in emulsion process the initiator is solved in the aqueous phase and the monomer is emulsified in the polymerization medium with the aid of a surfactant. Commonly, there are three steps on which the emulsion polymerization completes its process. Firstly (i) the insoluble monomer with emulsifier is dispersed in solvent reaction medium adding the surfactant and the mechanical stirring. Further (ii), the initiator is added which initiates the polymerization reactions resulting generates the polymer membrane on the surface of the core material. Finally (iii), the washing and removing of the oil to form the micro/nano-PCMs. Figure 20 shows the schematic of common emulsion polymerization method [150]. In emulsion polymerization method, commonly used materials for shell are polystyrene (PS) or polymethylmethacrylate (PMMA) and alkhane is used as a core material. Additionally, polymer polymerization is often carried by emulsion polymerization which used the liquid PCM as a core material to prepare the mico/nano-PCM. The properties of various studies adopting emulsion polymerization are listed in Table 8.

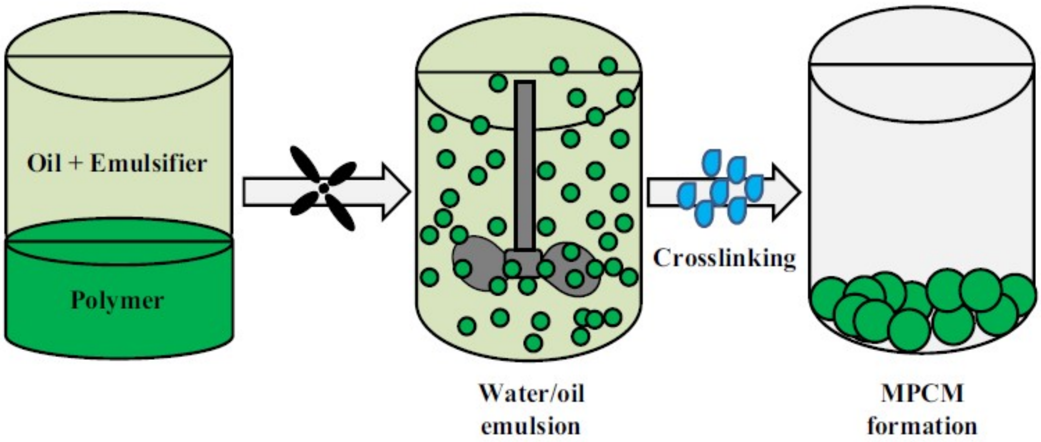


Figure 20: *Scheme of the emulsion polymerization method*[150], reused with permission from Elsevier license number 4385870668358.

3.4.4. Miniemulsion polymerization

The miniemulsion polymerization method is most commonly used method to prepare the nano–PCM because the smaller encapsulated capsules can be formed as compared to the emulsion polymerization method. Comparing to emulsion polymerization, miniemulsion polymerization occurs within the small droplet which requires the less input energy. Thus, this technique is employed under ambient reaction conditions which are necessary for the production of stable NCs. 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 homogenization. The scheme of miniemulsion polymerization is presented in Figure 21 [151]. The first step is miniemulsion process under the sheering effect small nanometer tiny droplets are formed in a size range of $30 - 500nm$ which are stable and contain the emulsifier, water, monomer, surfactant, initiator, the dispersed and continuous phase. The second step comprising on polymerization reaction in which these droplets are polymerized without changing their chemical composition, latex properties [152]. In miniemulsion polymerization, the monomers determines the morphological characteristics of prepared nano–capsules [153, 154]. The miniemulsion polymerization technique is further categorized into three classes; direct emulsion (oil in water, O/W), indirect emulsion (water in oil, W/O) and Pickering inverse emulsion. Classical emulsifiers e.g. amphiphilic oligo (methacrylic acid 41-*b*-methyl methacrylate 8), sodium lauryl sulfate, Tween 80, Span 20 and Span 85 are usually utilized in direct and indirect emulsions. Contrarily, in Pickering inverse emulsion, solid particles are employed as an emulsifier [46, 47, 155].

Cortazar and Rodrguez [48] employed the miniemulsion polymerization 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 $60wt.\%$ with latent heat capacity of $140.3J/g$ and obtained the capsule size of 439.4. Furthermore, the authors reported that NCs having a higher weight percentage of paraffin wax undergo the phase separation phenomenon. Chen et al. [156] adopted the miniemulsion polymerization 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 NCs fabricated by this method are $100 - 200nm$ in diameter and present a latent heat and encapsulation efficiency up to $98.8J/g$ and 82.2%, respectively. The authors also explored the effect of mount of emulsifier and co-emulsifier on latent heat, diameter, size distribution and encapsulation efficiency. Zhang et al. [157] encapsulated n-octadecane PCM with PEMA and PMMA with an average shell thickness of $50nm$, and a core/shell weight ratio of 80/20 and obtained an average particle size of NCs $140nm$ and $119nm$, 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. [158] designed a two-step Pickering emulsification technique to prepare the NCs of nonadecane as a PCM with a 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 materials and polystyrene (PS), polyurea (PU), styrene-buytl acrlate and polymethylmethacrylate (PMMA) as shell materials. In conclusion, miniemulsion is the most adopted polymerization technique in nano–capsules coating technology.

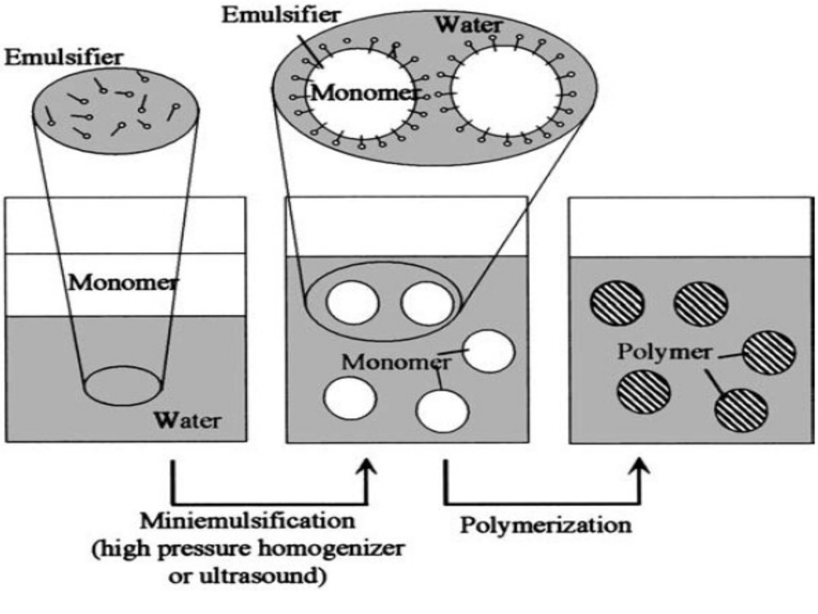


Figure 21: *Scheme of the miniemulsion polymerization method*[151], reused with permission from Springer Nature license number 4385871462764.

3.4.5. In–situ polymerization

The *In–situ* polymerization 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 polymerization. In preparation of micro/nano–capsules through *in–situ* polymeirztion, the monomers are dissolved in the continuous phase, however, the polymers are not soluble in continuous phase whereby the polymerization reaction occurs on the surface of the core materials. Commonly, there are four steps which complete the *in-situ* polymerization: (i) formation of the oil–water (O/W) emulsion; (ii) preparation of the prepolymer mixture liquid; (iii) mixing the O/W emulsion and prepolymer liquid to encapsulate the core materials; (iv) washing and drying of micro/nano–capsules. Figure 22 presents the example of *in–situ* polymerization method. Fang and his co-authors [159] employed the ultrasonic-assistant miniemulsion *in-situ* polymerization technique for coating of n-octadecane as a core with polystryrene as a shell material. The authors obtained the spherical shape nano–capsules of size ranging from $100-123nm$ in diameter. In another study [53], these authors coated the n-tetradecane with PS for cold energy storage of average diameter of $132nm$ and achieved the melting and freezing points and latent heats values of 4.04°C and −3.43°C, $98.71J/g$ and $91.27J/g$, respectively. With same core material n-tetradecane, Fang et al. [160] used the urea and formaldehyde as shell materials adopting *in-situ* polymerization technique with adding $1-3\%$ NaCl to improve the thermal stability of the prepared nano–capsules. To investigate the effect of various shell materials on thermophysical properties Konuklu et al. [95] used the urea-formaldehyde (UF), melamine-formaldehyde (MF) and urea+melamine-formaldehyde (UMF) resins to prepare the nano–capsules of caprylic acid. The authors found the UF resin as a best resin for shell material among others in term of stability of nano–capsules. So far now, generally, the OPCMs as core materials and urea-formaldehyde (UF), melamine-formaldehyde (MF), carboxymethyl cellose (CMC), polymethylmethacrylate (PMMA), poly(melamine-formaldehyde) (PMF), and poly (allyl methacrylate) (PAMA) are used as a shell materials.

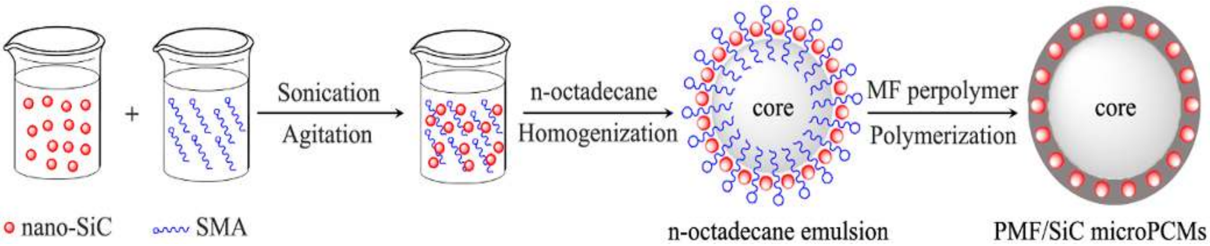


Figure 22: *Schematic formation of the micro-PCMs based on n-octadecane core and poly(melamine-formaldehyde)/silicon carbide (PMF/SiC) shell through in-situ polymerization*[161], reused with permission from Elsevier license number 4482000691089.

Table 8: *Summary of prepared micro/nano–PCMs using chemical methods.*

Ref.	**Method**	**Core**	**Shell**	**Particle size** (μm)	**EE** (%)	T_m	**Latent heat** (J/g)
[146]	Interfacial polycondensation	n-Octadecane	PU	11–20	87.4	27.04	188.9
[162]	Interfacial polymerization	Insecticide	PU	30–40	90	–	–
[163]	Interfacial polymerization	Xylitol	PUR	11.2–21.6	–	–	196.3
[147]	Interfacial polycondensation	Insecticide	PU	400–600nm	–	56.54	101.1
[164]	Interfacial polycondensation	Butyl stearate	TDI, EDA	20–35	–	29	80
[165]	Interfacial polycondensation	n-Hexadecane	TDI, EDA	–	–	–	–
[166]	Interfacial polymerization	n-Octadecane	TDI, DETA	1	–	30.8	112
[167]	Interfacial polymerization	n-Octadecane	TDI, DETA	7.3	92	–	–
[168]	Interfacial polymerization	n-Octadecane	TDI, DETA	5–10	94.7	–	117.5
[169]	Interfacial polycondensation	n-Pentadecane, n-Eicosane, Paraffin wax	UF	47, 79, 150	–	–	109, 148, 127
[170]	Interfacial polycondensation	n-Octadecane	SiO_2	4–30	–	–	–
[148]	*In-situ* emulsion interfacial polycondensation	Palmitic acid	AlOOH	100nm	69	16	27.8
[171]	*In-situ* emulsion interfacial hydrolysis and polycondensation	Paraffin wax	SiO_2	200–500nm	31.7	56.5	45.5
[172]	In-situ emulsion interfacial hydrolysis and polycondensation	n-Octadecane	SiO_2	169–563nm	49.3	27.35	109.5
[173]	Interfacial polymerization	Butachlor	PU	1–20	–	–	–
[174]	Interfacial polycondensation	Cyclohexane	PU	1.6	–	–	–
[175]	Interfacial polymerization	Migrin oil	PU	7.6–12.4	–	–	–
[176]	Interfacial polymerization	Ovalbumin	PU	50nm–8μm	–	–	–
[177]	Interfacial polycondensation	Octadecane	PU	1–2	–	31.9	54.8
[178]	Interfacial polymerization	n-Octadecane	PU	5–10	93.4–94.9	29.8–31.0	115.0–117.5

[179]	Interfacial polymerization	n-Hexadecane	PU	2–4	50.1	15.52	66.09
[180]	Interfacial polymerization	n-Eicosane	PU	–	74.6–77.6	35.7–36.5	29.34–63.55
[181]	Interfacial polymerization	Paraffin wax	Poly-amide	6.4	99	29–44	121.7
[182]	Suspension–like polymerization	$Na_2HPO_4.7H_2O$	PMMA	∼ 6.8	–	51	150
[183]	Suspension–like polymerization	n-Octadecane	BMA	1–46	–	20.9–21.6	116.4–144.3
[184]	Suspension–like polymerization	n-Octadecane	ODMA–MAA	0.5–4	–	21.1	93
[185]	Suspension–like polymerization	Paraffin wax	PS, MMA	380	–	40.66–41.81	83.70–96.47
[186]	Suspension–like polymerization	Paraffin wax, Tetradecane, PEG 800, PEG 1000, RT27, RT20, Nonadecane	PS	38.01, 11.24, 0.07, 0.07, 27.85, 64.87, 10.64	–	–	41.65, 48.92, 0, 0, 58.83, 12.01, 119.80
[187]	Suspension–like polymerization	Paraffin wax	PS	∼200	75.6	98–113	21.2–41.7
[188]	Suspension-like polymerization	RT27	PS	500	–	–	–
[189]	Suspension–like polymerization	n-Octadecane	PS–DVB	80	–	29	126
[190]	Suspension–like polymerization	n-Octadecane	PS–DVB	71–207	–	29	125
[191]	Suspension–like polymerization	n-Octadecane	PS, PSB, PSD, PSDB, PDVB	∼50	–	24.34–30.84	22.0–156.9
[192]	Microsuspension polymerization	n-Octadecane	PDVB	∼1.5	–	22.6	192
[193]	Suspension–like polymerization	n-Octadecane	BDDA, DVB, TMPTA, PETRA	0.72–0.75	–	29.3–35.2	83.7–156.4
[194]	Suspension–like polymerization	n-Octadecane	TPGDA	300–600nm	100	–	104
[195]	Suspension–like polymerization	Paraffin wax, Butyl stearate	Acrylate-based polymer	10–80	46–68	29.08–32.12	63.98–93.97
[196]	Suspension–like polymerization	Paraffin wax	PS	4.80	–	–	102.42
[197]	Suspension–like polymerization	RT31	PS	4.0–53.2	49.0–67.9	31.56	75.7–135.3
[198]	Suspension–like polymerization	Paraffin wax	PS	3.83, 3.97	43.6, 35.1	–	58.6, 79.0
[4]	Suspension–like polymerization	n-Octadecane	PBMA, PBA	2–75	47.7–55.6	29.1–31.6	96–112
[199]	Emulsion polymerization	Paraffin wax	PMMA	0.25	–	24–33	101
[200]	Emulsion polymerization	Paraffin wax, Palmitic acid	PScEA	0.166, 0.265	–	36.71, 59.12	49.03, 97.93

[201]	Emulsion polymerization	n-Octacosane	PMMA	0.25	–	50.6	86.4
[202]	Emulsion polymerization	n-Heptadecane	PMMA	0.14–0.40	–	18.2	81.5
[203]	Emulsion polymerization	Docosane	PMMA	0.16	–	41.0	54.6
[204]	Emulsion polymerization	n-Eicosane	PMMA	0.70	–	35.2	84.2
[205]	Emulsion polymerization	n-Hexadecane	PMMA	0.22, 1.05	–	15.69, 17.34	68.89, 145.61
[206]	Emulsion polymerization	n-Hexadecane	PMMA	140–466nm	–	17.23	148.05
[207]	Emulsion polymerization	n-Octadecane	PS	80nm	14.6–56.8	–	6.48–49.76
[208]	Emulsion polymerization	n-Heptadecane	PS	1–20	63.3	21.48	136.89
[155]	Emulsion polymerization	n-Nonadecane	PMMA	0.1–35	60.3	31.23	139.20
[209]	Emulsion polymerization	n-Heptadecane, n-Octadecane, n-Nonadecane, n-Eicosane, n-Tetracosane	PMMA	0.01–100	50.2–65.4	19.24–35.80	171.14–265.60
[210]	Emulsion polymerization	n-Tetracosane/n-Octadecane	PS	0.01–115	64.4	25.96	156.39
[211]	Emulsion polymerization	Capric/Stearic acid	PMMA	1.3	–	21.37	116.25
[212]	Miniemulsion polymerization	Paraffin wax	PS	<100nm	–	–	–
[156]	Miniemulsion polymerization	n-Dodecanol	PMMA	150nm	82.2	18.2	98.8
[213]	Miniemulsion polymerization	n-Dodecanol	SBA	100nm	98.4	27	109.2
[214]	Miniemulsion polymerization	n-Hexadecane	UF	270nm	–	16.15–16.36	114.6–143.7
[215]	Miniemulsion polymerization	RT80	SBA	52–112nm	78–80	77.7–84.1	4.9–23.9
[216]	Miniemulsion polymerization	n-Tetradecane	PS	132nm	89	4.04	98.71
[159]	Miniemulsion *in-situ* polymerization	n-Octadecane	PS	100–123nm	–	30–35	124.4
[217]	Miniemulsion *in-situ* polymerization	n-Octadecane	PS	108–126nm	–	–	88.35–124.4
[218]	Miniemulsion polymerization	n-Dotriacontane	PS	168.2nm	61.23	70.9	174.8
[219]	Miniemulsion *in-situ* polymerization	n-Octadecane	PS–MMA	102nm	–	29.5	107.9
[220]	Miniemulsion polymerization	Paraffin wax	PS	100nm	47.7–55.6	29.1–31.6	96–112

[157]	Direct miniemulsion polymerization	n-Octadecane	PEMA, PMMA	140nm, 119nm	89.5	32.2, 31.9	198.5, 208.7
[221]	*In-situ* polymerization	Paraffin wax	CMC–MF	50nm	63.1	24.4	83.46
[222]	*In-situ* polymerization	n-Octadecane	P(MMA–co–AMA)	577–693nm	64.0–71.6	24.7–27.4	129–151
[160]	*In-situ* polymerization	n-Tetradecane	UF	100nm	60	5.57–9.01	66.01–134.16
[223]	*In-situ* polymerization	n-Tetradecane	PVA, PS, PMMA, PEMA	23.15, 16.89, 18.59	–	2.06, 5.97, 5.68	$\sim$0, 66.26, 80.62
[224]	*In-situ* polymerization	Paraffin wax	UF	20	–	53.3–54.4	−98.5 to −200.4
[225]	*In-situ* polymerization	n-Octadecane	MF	0.9–9.2	–	30.4–30.5	169–172
[226]	*In-situ* polymerization	n-Octadecane	MF	2.2	59	40.6	144
[227]	*In-situ* polymerization	Migrin oil	MF	<10	–	–	–
[228]	*In-situ* polymerization	n-Hexadecane, n-Eicosane	MF	$\sim$10	70	–	163–170
[229]	*In-situ* polymerization	n-Octadecane	MF	20nm	92	26.91	146.25
[230]	*In-situ* polymerization	n-Octadecane	UMF	0.2–5.6	65–78	32.77–34.88	91.10–241.68
[231]	*In-situ* polymerization	n-Octadecane	MF	0.2–1.8	–	24.4–36.2	44–166
[232]	*In-situ* polymerization	n-Octadecane	MF	1–2	–	–	102–166
[233]	*In-situ* polymerization	Dodecanol	PEG modified MF	0.83 ± 0.23–14.4 ± 5.56	–	25.8	118.9
[234]	*In-situ* polymerization	Decanoic acid	PMUF	0.28	–	33	88
[235]	*In-situ* polymerization	Paraffin wax	MF	15 ± 3	–	129.4	157
[236]	*In-situ* polymerization	Paraffin wax	SiO_2, GO	$\sim$10	49.6	49.7	87.1
[237]	*In-situ* polymerization	n-Octadecane	MF	$\sim$1	20	–	160
[238]	*In-situ* polymerization	n-Octadecane, n-Nonadecane, n-Eicosane	MF	0.3–6.4	70	36.5, 219.3, 45.3	167, 161, 172
[239]	*In-situ* polymerization	n-Eicosane	MF	0.1–10	53	36.9	134.4
[240]	*In-situ* polymerization	n-Eicosane	MF	1.89	–	36.9	134.3
[241]	*In-situ* polymerization	P1–S, RT25, RT40	Amino–aldehyde	5.91, 2.78	–	–	–

[12]	*In-situ* polymerization	n-Octadecane, n-Eicosane, n-Hexadecane	MF	1-500	–	17.7	44.6
[242]	*In-situ* polymerization	n-Docosane	MF	10	–	–	150
[243]	*In-situ* polymerization	n-Docosane	MF	5–20	68–135.4	55.69–56.72	17.74–57.81
[244]	*In-situ* polymerization	PETMP	PMF	1–10	–	–	–
[245]	*In-situ* polymerization	n-Dodecanol	MF	30.6	93.1	21.5	187.5
[246]	*In-situ* polymerization	n-Octadecane, n-Hexadecane	MF	5–20	–	–	150–210
[226]	*In-situ* polymerization	n-Octadecane, n-Hexadecane	MF	2.2	59	40.6	144
[247]	*In-situ* polymerization	n-Docosane	MF	3.6	–	–	–
[248]	*In-situ* polymerization	Paraffin wax	Aniline (C_6H_7N)	300–500nm	49.7	53.4	65.1

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 fulfil the industrial and end-users requirements to meet the clean energy demands. The characteristics of EPCMs are performed using various quantitative and qualitative techniques per the evaluation of the property. Table 9 presents the list of various characterization 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 crystalloid phase, material structure, crystallite atomic arrangement and size, crystal orientation or texture and parameters such as crystallinity, 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 of the scattering mechanism. This technique ensures the crystalline structure of micro/nano capsules preferably suitable for inorganic shell materials. For instance, Zhang et al. [286] presented the XRD results of Ag/SiO_2 double-layered micro-PCM with 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 n-eicosane core. Zhao et al. [250] presented the XRD patterns of Ag-paraffin@Halloysite microspheres and obtained the consistent crystalline structure of Ag nanoparticles onto surface of paraffin@Halloysite. Additionally, the crystalline structure of paraffin was not affected in Ag-paraffin@Halloysite while encapsulation process.

4.1.2. 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 micro/nano–capsules 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 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 spectrum arises due the singles which 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 collecting an interferogram of a sample using an interferometer. Further, Fourier Transform (FT) is applied on the interferogram resulting spectrum is obtained. The FT–IR spectrometer collects and digitizes the interferogram performing the FT function and then displays the spectrum. For example, various researchers presented the FT–IR peaks to represent the chemical composition of micro/nano-PCMs. Presented FT–IT results by Zhang et al. [270] showed the excellent chemical composition of encapsulated $KNO_3@SiO_2$ microcapsules. Kahraman et al. [299] synthesized microcapsules using PS

Table 9: *Characterization techniques used by the various researchers for characteristics evaluation of EPCMs.*

Characterization Technique	**References**
X–Ray diffraction (XRD)	[176, 237, 238, 54, 72, 87, 224, 132, 135, 75, 247, 103, 249, 130, 111, 55, 250, 251, 157, 171, 128, 127, 42, 221, 37, 125, 219, 172, 107, 252, 218, 134, 110, 126, 91, 236, 99, 253, 161, 254, 255, 256, 257, 258, 149]
Fourier transformed infrared spectroscopy (FT–IR)	[175, 176, 166, 97, 180, 259, 225, 230, 169, 231, 238, 120, 178, 131, 207, 226, 168, 260, 87, 224, 243, 244, 203, 164, 261, 44, 74, 70, 245, 146, 229, 206, 132, 135, 199, 185, 69, 133, 205, 204, 190, 163, 262, 170, 103, 213, 156, 136, 148, 193, 249, 157, 130, 129, 194, 53, 215, 263, 171, 264, 111, 4, 55, 248, 181, 123, 155, 128, 127, 42, 218, 265, 100, 221, 125, 234, 95, 235, 266, 195, 147, 155, 209, 208, 184, 219, 267, 43, 268, 134, 200, 269, 172, 85, 142, 210, 211, 110, 126, 91, 236, 99, 253, 233, 161, 36, 254, 255, 270, 251, 256, 271, 272, 273, 149]
Scanning electron microscopy (SEM)	[175, 176, 251, 79, 223, 97, 116, 237, 112, 73, 225, 230, 232, 240, 169, 238, 231, 178, 131, 274, 207, 226, 242, 186, 12, 167, 275, 276, 260, 72, 87, 224, 243, 244, 203, 137, 160, 261, 44, 70, 277, 189, 245, 146, 229, 206, 122, 132, 135, 199, 185, 202, 75, 139, 69, 133, 205, 204, 78, 247, 191, 197, 190, 262, 170, 103, 156, 136, 148, 193, 14, 249, 157, 89, 192, 130, 129, 278, 48, 215, 263, 182, 171, 264, 111, 4, 248, 55, 181, 101, 123, 279, 128, 127, 88, 155, 42, 143, 265, 96, 125, 252, 100, 221, 37, 234, 95, 195, 235, 266, 147, 183, 155, 209, 208, 81, 184, 267, 268, 134, 200, 269, 172, 85, 107, 280, 90, 210, 211, 110, 158, 126, 91, 236, 99, 253, 233, 281, 161, 36, 254, 282, 255, 283, 256, 284, 257, 258, 271, 272, 273, 149]
Transmission electron microscopy (TEM)	[285, 212, 207, 276, 72, 87, 261, 70, 135, 75, 103, 213, 136, 157, 194, 53, 215, 171, 55, 101, 279, 125, 147, 219, 134, 172, 107, 251, 111, 218, 110, 158, 99, 253, 161, 254, 283, 148]
Energy-dispersive X-ray spectroscopy (EDS)	[275, 103, 55, 125, 268, 107, 280, 110, 126, 286, 161, 251, 283, 287, 288, 289, 271, 149]
X-ray photoelectron spectroscopy (XPS)	[163, 249, 263, 128, 125, 134, 280, 286, 161, 283, 256, 257]
Optical microscopy (OM)	[144, 42, 140, 100, 125, 268, 142, 158, 290, 255, 291]
Thermal conductivity analysers	[134, 292, 293, 269, 281, 268, 268, 282, 257, 149]
Differential scanning calorimeter (DSC)	[176, 294, 114, 223, 295, 285, 237, 180, 73, 225, 230, 169, 238, 119, 178, 131, 274, 207, 226, 242, 186, 12, 168, 260, 72, 87, 224, 243, 203, 160, 164, 164, 44, 74, 70, 189, 146, 229, 206, 122, 132, 199, 185, 202, 75, 69, 133, 205, 204, 78, 247, 191, 163, 197, 190, 262, 170, 103, 213, 156, 136, 148, 193, 14, 249, 157, 192, 130, 129, 194, 53, 278, 263, 171, 111, 4, 248, 55, 181, 296, 101, 155, 128, 127, 42, 218, 140, 100, 37, 125, 234, 95, 235, 266, 195, 183, 155, 209, 208, 184, 219, 219, 267, 43, 268, 134, 200, 269, 172, 85, 142, 107, 210, 211, 110, 158, 126, 91, 270, 236, 99, 233, 253, 281, 161, 36, 254, 282, 255, 252, 257, 244, 245, 283, 256, 258, 271, 272, 273]
Thermogravimetrical analysis (TGA)	[176, 180, 230, 232, 178, 226, 275, 276, 72, 224, 243, 244, 203, 137, 160, 44, 189, 245, 146, 122, 132, 199, 185, 202, 75, 69, 133, 204, 191, 163, 190, 262, 170, 156, 148, 193, 14, 249, 157, 192, 130, 129, 194, 53, 215, 263, 171, 4, 248, 55, 181, 296, 155, 128, 127, 42, 218, 140, 265, 100, 221, 37, 125, 266, 195, 252, 234, 235, 147, 183, 155, 209, 208, 219, 268, 134, 200, 269, 172, 107, 210, 211, 110, 126, 91, 236, 99, 253, 233, 281, 161, 36, 254, 255, 283, 256, 257, 297, 271, 272, 149]
Atomic force microscopy (AFM)	[298, 263, 265, 200, 85, 233, 254, 255]
Brunauer, Emmett and Teller (BET)	[263]
Raman Spectroscopy	[244, 236]
Small Angle X-Ray Scattering (SAXS) and Wide angle X–ray Scattering (WAXS)	[146, 229, 133, 170, 100, 268]

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 or chemical characterization 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, EDS technique is carried out in conjunction with scanning electron microscopy (SEM). Zhang et al. [286] 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. [251] 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. [283] presented the EDS results with SEM of silver coated microcapsules found the equal proportion of silver 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 characterization of a sample material. XPS can measure the elemental composition, empirical formula, 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. [286] through XPS technique and observed the elemental characteristic peaks of Ag/SiO_2 double-layered microcapsules. Geng et al. [283] presented the XPS peak spectrum of silver coated microcapsules and observed the existence of face-centred cubic metallic silver. Advincula et al. [256] 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 utilized for the measurement of thermal conductivity of micro/nano capsules such as laser flash apparatus (LINSEIS LFA1000) [134], TC 3020 thermal conductivity meter [292], TC3000 thermal conductivity meter [293], Sweden Hot Disk thermal conductivity meter [269, 281], EKO HC-110 thermal conductivity meter [268]. The encapsulated capsules are pressed in a tablet form to measure the thermal conductivity of micro/nano-capsules. The thermal conductivity of single a capsule can be predicted theoretically based on composite sphere approach as follows [300, 301, 262, 302]:

$$\frac{1}{k_p d_p} = \frac{1}{k_c d_c} + \frac{d_p - d_c}{k_s d_p d_c} \tag{1}$$

Here, k_p, k_c, and k_s are the thermal conductivities of micro/nano-capsule, core material, and shell material, respectively. Additionally, d_p and d_c are the diameter of micro/nano-capsule and core material, respectively. As the most the PCMs especially OPCMs exhibit the low thermal conductivity which reduces heat transfer performance. The sole purpose to encapsulate the PCM is to enhance their thermophysical properties to utilize 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 reduces the rate of heat transfer while thermal energy storage and release. However, coating of inorganic nanomaterials such as Fe_3O_2[147, 125], TiO_2[127, 128, 134], SiO_2[171, 172, 125, 149], GNP [292], Al_2O_3[269], $CaCO_3$[268], Cu_2O[161], and $MWCNT$[254]. 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) [283]. During DSC analysis the amount of energy absorbed or released upon heating or cooling is measured providing qualitative and quantitative data while endothermic (heat absorption) and exothermic (heat rejection) phase transitions. In DSC analysis, the change of heat flux is recorded with respect to time, however, the heating rate and sample mass is the most important because the changing heat rate and sample mass will give temperature–heat flow responses [299, 303].

4.2.3. Thermogravimetrical analysis (TGA)

The thermogravimetry or thermogravimetrical analysis (TA) 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 [252]. The change in the mass of sample material of micro/nano capsules are examined under the various thermal modes such desorption, absorption, sublimation, vaporization, oxidation, reduction and decomposition [304].

4.3. Physical Analysis

4.3.1. Performance parameters

In 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 [161]:

$$C_{th} = \frac{m_{core}}{m_{core} + m_{shell}} \times 100\% \tag{2}$$

$$C_{act} = \frac{m_{core} - m_{shell}}{m_{core}} 100\% \tag{3}$$

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 [250, 251, 305]:

$$ER = \frac{\Delta H_{m,EPCM}}{\Delta H_{m,PCM}} \times 100\% \tag{4}$$

$$EF = \frac{\Delta H_{m,EPCM} + \Delta H_{s,EPCM}}{\Delta H_{m,PCM} + \Delta H_{s,PCM}} \times 100\% \tag{5}$$

$$TESC = \frac{\Delta H_{m,PCM}(\Delta H_{m,EPCM} + \Delta H_{s,EPCM})}{\Delta H_{m,EPCM}(\Delta H_{m,PCM} + \Delta H_{s,PCM})} \times 100\% \tag{6}$$

$$TCP = \frac{\Delta H'_{m,EPCM}}{\Delta H_{m,PCM}} \times 100\% \tag{7}$$

Here, $\Delta H_{m,EPCM}$ and $\Delta H_{s,EPCM}$ are the change in enthalpies of melting and solidifications, respectively of EPCM, $\Delta H_{m,PCM}$ and $\Delta H_{s,PCM}$ 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 utilization of EPCMs in various applications, the shell of the encapsulated micro/nano-capsules possesses a crack or porous structure resulting in the leakage of the core PCM. So the core percentage or leakage rate in micro/nano-capsules at various times is usually used to define the leakage-performance [286, 255]. 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:

$$L_r = \frac{m_0 - m_t}{m_0} \times 100\% \tag{8}$$

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.

4.3.2. Optical microscopy (OM)

To evaluate the particle size, morphology, transparency color and fixation a few researchers have been presented the images of EPCMs using optical microscopy (OM) technique [140, 100, 291]. Wang et al. [291] 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, showed the $10\mu m$ size of microcapsules using OM technique.

4.3.3. Scanning electron microscopy (SEM)

The SEM technique, based on the scattered electrons, is used to determine the particle size and shape using electron microscope of the micro/nano capsules. The SEM uses a higher–energy beam of electron on the surface of the sample which generates the various signals showing the image of sample surface. These variety of signals reveal the various characteristics information of the sample including topography (the surface features or texture)[273, 271], morphology (the shape and size)[284, 273, 272], composition (elements and compounds)[291, 272] and crystallography (atoms arrangement)[149, 271]. Various researchers have been presented SEM images to represent chemical composition, morphology, and crystallography of EPCMs mentioned in Table 9.

4.3.4. Transmission electron microscopy (TEM)

TEM, based on the transmitted electrons, is used to measure at high resolution than SEM such as nano level closer to the atomic structure. So the morphology and PSD of micro/nano-capsules can also be determined by TEM at more smaller level (e.g nano-meters) which is beyond the limit of SEM [251]. 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. [283] presented the TEM images of Ag-MMF coated micro-capsules of 1-tetradecacanol with diameter of $100nm$.

4.3.5. Atomic force microscopy (AFM)

The atomic force microscopy (AFM) is a surface topography measuring technique which measures the surface images near nanometer 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 micro/nano–capsules. Zheng et al. [297] evaluated the highest elastic modulus of CNTs coated n-eicosane micro-capsules. Huang et al. [254] evaluated the surface profile of CNT coated n-octadecane micro-capsules and obtained the average roughness and root-mean-square roughness with CNT were $17.12nm$ and $21.09nm$, respectively, which were approximately three times of microcapsules without A-CNTs/PSS multilayers.

4.3.6. Brunauer, Emmett and Teller (BET)

The BET techniques 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 [306]. The most commonly used BET equation is described below, see Equation 9.

$$\frac{x}{V(1-x)} = \frac{1}{V_m.c_{BET}} + \frac{x.(c_{BET}-1)}{V_m.c_{BET}} \tag{9}$$

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 micro/nano–capsules at a range of $0.02 - 10°$ [307]. 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 $2\theta > 1°$. The Bragg peaks (diffraction peaks) are analysed by function of scattering angles which arise by scattering from the subnanometer-size crystal structures [308]. A few researchers have utilized SAXS and WAXS techniques for EPCMs [170, 100, 268].

5. Stability of EPCMs

The stability of ECPMs is the real challenge for the current industrial revolution. Stability of EPCMs mainly concerns with the 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 thermo-physical properties. The quality of the encapsulated PCMs is evaluated by assuring that there is no geometrical variation, leakage of micro/nano capsules, sedimentation, aggregation and crystallization of inter layer materials and so far. 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 enhance 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 anti-osmosis test in which sealing performance of encapsulated capsules of PCMs is determined. Anti-osmosis test determines the weight loss of the extracted micro/nano capsules, and it can be used to evaluate the durability of the encapsulated capsules[133, 146, 168]. Zhang et al. [133] 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 micro–capsules of 50/50 weight ratio had the best anti-osmosis performance as compared to others weight ratios. Further, the they evidenced that the release rates of micro–capsules were depended on the thickness of the silica shell. The more the thickness of the shell, lesser the release rate of the encapsulated capsules. Similar method to determine the leaking performance or durability of micro–encapsulated *n*-octadecane by Zhang and Wang [146, 229]. The authors (In Ref. [229]) used the styrene-maleic anhydride (SMA), sodium dodecyl sulfate (SDS) and polyvinyl alcohol (PVA) as an emulsifiers and results showed that by using SMA and SDS, shown in Figure 23. The Figure showed that the release rate of the micro-capsules increased with increasing with the weight percentage of the core materials. Further, the authors reported that release rate of micro-capsules prepared by using SDS is was much higher than that of micro-capsules using SMA at the same weight ratio. Su et al. [168] 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 polyurethane-shell, shown in Figure 24. Further they suggested that this releasing phenomena might be attributed to the emulsion effect and shell polymerization.

5.2. Thermal stability

The thermal stability of the encapsulated micro/nano capsules 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 [294, 309]. Silakhori et al. [248] conducted the thermal cycles tests using TGA and DSC methods up to 1000 cycles for paraffin wax/polyaniline nano–capsules and found

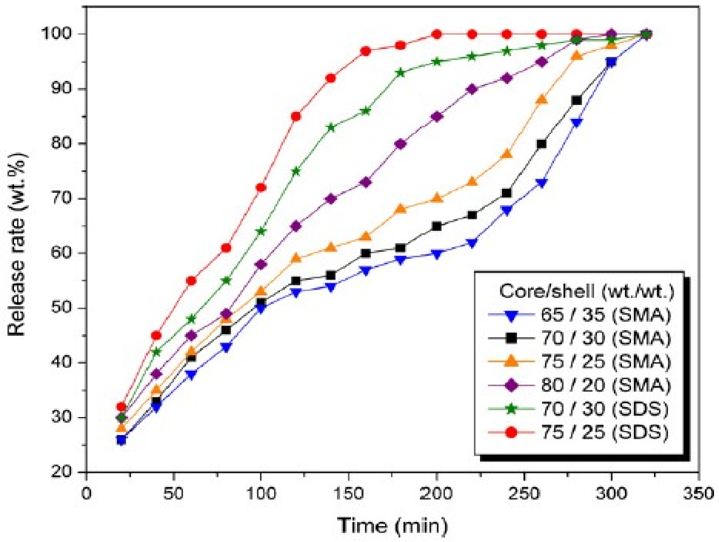


Figure 23: *Release curves of micro–EPCMs capsules with different weight ratios of core/shell materials*[229], reused with permission from Elsevier license number 4385880183182.

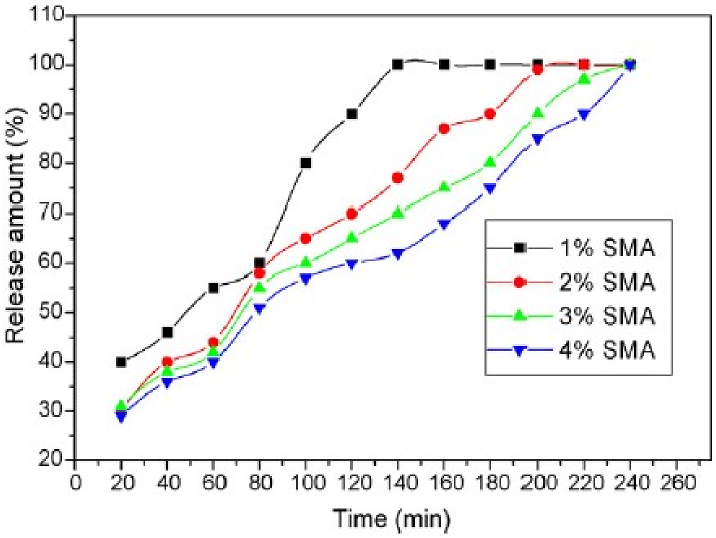


Figure 24: *Release curves of micro–EPCMs samples prepared by* 1.0, 2.0, 3.0 *and* 4.0% *of SMA*[168], reused with permission from Elsevier license number 4385881263849.

the chemical and thermal structure of the capsules remained unchanged. Similarly, Hawlader et al. [115] claimed that encapsulated capsules of paraffin wax maintained their original geometrical profile and energy storage capacity even after 1000 thermal cycles. Fortuniak et al. [278] used DSC for 50 cycles of fusion and crystallization and reported the proof of thermal stability of micro–capsules of n-eicosane coated with polysiloxane. Sar et al. [201] performed the FT-IR, TGA and DSC analysis of PMMA/n-octadecane micro–capsules 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 79.9J/g and 81.7J/g, respectively, after 5000 thermal cycling. The authors concluded that there was good thermal and chemical stability of

PMMA/n-octadecane micro–capsules in terms of changing of its thermal properties. Alkan et al. [203] 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 $40.1 - 41.4$°C and crystallizing point changed from $41.6 - 41.7$°C, moreover, the latent heat of melting and crystallization were 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 micro–capsules after thermal cycling tests, shown in Figure 26. Sharma et al. [295] 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 the good thermal stability regarding phase change temperature and latent heat of fusion, however, the stearic acid showed the melting over a wide range of temperatures.

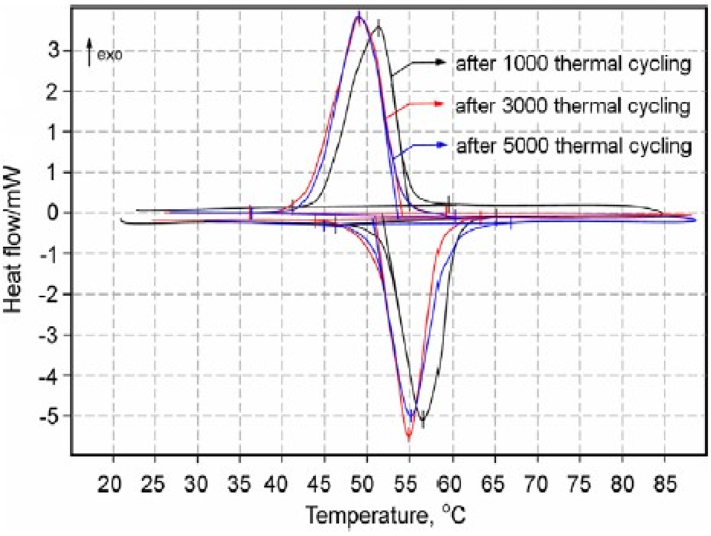


Figure 25: *DSC thermogram for PMMA/n-octadecane micro–capsules after thermal cycling*[201], reused with permission from Elsevier license number 4385881396518.

6. Application of micro/nano–PCMs

The utilization of developed micro and nano EPCMs have been categorized by exhibiting their new chemical and thermophysical properties. Moreover, the unique properties such as (i) suitable solid–to–liquid phase transition, (ii) higher amount of energetic changes, (iii) chemical and thermal stabilization, (iv) variations in conduction and convection heats during phase transformation define the employability of EPCMs for a specific application. In this section, we reviewed the 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 potential requirement in the sight of researchers and industrialist. Nature has gifted us such a fundamental, unlimited and economic

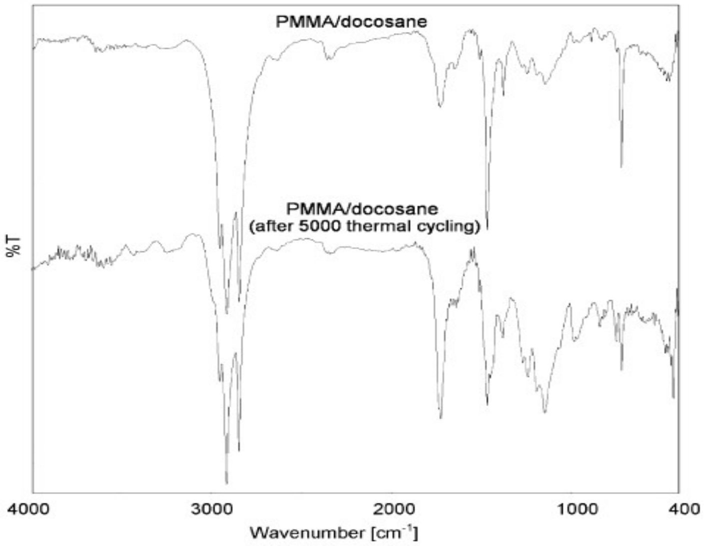


Figure 26: *FT-IR spectra for PMMA/docosane micro–capsules before and after thermal cycling*[203], reused with permission from Elsevier license number 4385890037722.

energy source in the form of sun. From the creation of this universe, the sun has been providing us a huge amount of energy in the form of solar energy on the earth. Here, the question is that how to utilize this energy in an efficient and longer time period to meet the energy requirement for both in day and night times. As, more heat and electricity are required at night because of the absence of sun. To address this challenge, the novel smart energy storage materials are needed to be developed which can efficiently store this renewable solar energy source along with reducing the global warming and climate changes issues. Therefore, EPCMs have been gaining the promising attention in recent era to absorb solar thermal energy in form of latent heat and release it later on to meet the energy demands. The utilization of micro– and nano–PCMs have been under investigation for photo–thermal conversion, solar cells, direct absorb solar collector, photo catalyst, storage tank or container, heat exchanger, minichannel and so on to harvest and convert the solar energy directly and indirectly [303, 292]. Zeng et al. [310] synthesized the core–shell nanoparticles using $Sn/SiO_2/Ag$; where Sn was used the as core material to store the thermal energy, SiO_2 was used as a shell material to provide containment and Ag shell was used to enhance the light absorption intensity.They found the good optical absorption and TES capabilities of $Sn/SiO_2/Ag$ composite nanoparticles which improved the volumetric absorption efficiency of DASC from medium–to–high temperature range. Zheng et al. [297] 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. [311] synthesized the SiO_2/D-Mannitol micro–PCMs using sol–gel technique for solar energy harvesting and storage systems. Fundamental thermophysical properties were studied and found the enhancement in thermal conductivity of $1.77 W/m.K$. Additionally, they found the 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%, respectively. Xu et al. synthesized the micro–PCMs consisting of paraffin@$Cu - Cu_2O$ 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 results summarized that paraffin@$Cu - Cu_2O$ 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. [312] found the melting temperature and latent heat of 59.28°C and 91.94J/g, respectively, of SA/MWCNTs prepared by vacuum absorption method. Further estimated the photo–thermal conversion efficiency by suspending the SA/MWCNTs into water making a stable suspension. They 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. [250] developed innovative hybrid micro–PCMs consisting Ag–Paraffin@Halloysite to store the 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 6mins compared with one without heat storage with conversion of 71.1% in 6mins for catalytic reduction of 4-nitophenol. The efficiency (η) of solar–to–thermal energy conversion and storage systems confined with EPCMs can be determined from Equation 10:

$$\eta = \frac{m\Delta H}{AIt} \tag{10}$$

Here, in Eq. 10 m is the mass of confined EPCMs, ΔH is the latent heat enthalpy while phase transformation, A is the effective surface area of solar system, I is the intensity of solar irradiation, and t is phase transition completion duration. Recently, Kahraman et al. [299] encapsulated the various n–alkanes eutectics such as n-heptadecane, n-octadecane, n-nonadecane, n-eicosane, and n-tetracosane and their mixtures with PS to harvest the solar energy. They found that micro–PCMs eutectics mixtures had reversible and isothermal phase transition temperature between 21°C and 35.9°C and latent heat of enthalpy between 61.2J/g and 146.1J/g which are highly suitable for a wide range of solar thermal applications.

6.2. Electrical–to–thermal energy storage

The energy harvesting and conversion from electrical to thermal is a very emerging area to store the heat for beneficial usage. The fundamental evaluation parameter is the enhanced or reduced temperature at a certain input power which encourages the researchers to develop the practical devices or systems of higher energy conversion efficiency. From the last three decades, the researchers have been putting keen interests on the solar–to–thermal energy harvesting and conversion using PCM which stores the heat through absorption only in the sunshine duration. Contrarily, there is a huge challenge for the countries located at the North–Pole of the globe which experience the lack of sunlight mostly in winter season. To overcome this challenge few studies are available who developed the electrical conductive micro/nano–PCMs to convert and store the energy from electrical–to–thermal. The conductive EPCMs converts the electrical energy into heat on applying the small input voltage and store that heat in form

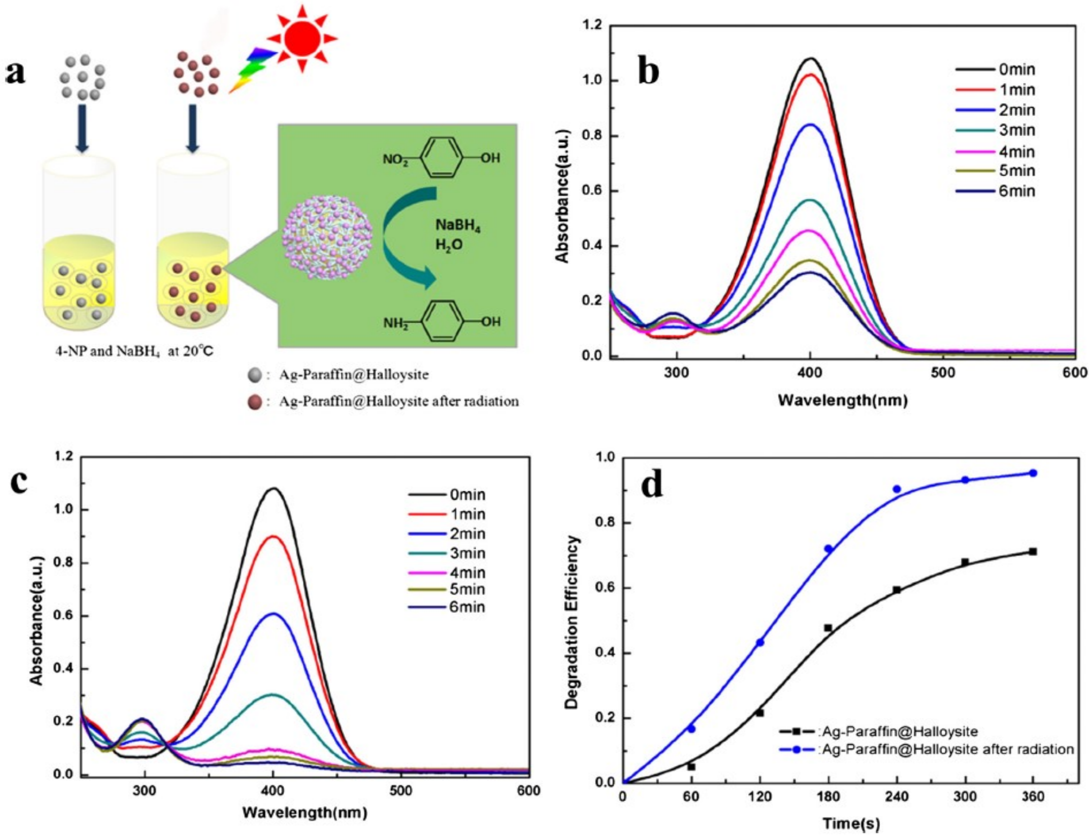


Figure 27: *(a) Schematic catalysis mechanism of Ag-Paraffin@Halloysite under different treatment processes. Time evolution of UVvis absorbance spectra for successive reduction of 4-nitrophenol by* $NaBH_4$ *with Ag-Paraffin@Halloysite catalyst (b) without radiation and (c) after solar radiation treatment, (d) Degradation efficiency of Ag-Paraffin@Halloysite with and without solar radiation treatment* [250], reused with the permission from Elsevier license number 4444690967317.

of latent heat while melting of the PCMs within the micro– and nano–capsules. Zheng et al. [313] presented a joule heating system to reduce the convective heat transfer from electrothermal system to surrounding by inserting the highly conductive and stable micro–capsules of docosane and GO-CNT as core and shell material, respectively. The results shown in Figure 28(a-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 [314]:

$$\eta = \frac{m\Delta H}{VIt} \tag{11}$$

Here, m and ΔH 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. [305] synthesized the bifunctional nano–PCMs consisting oleic acid (OA)-PEG core and SiO_2/SnO_2 shell materials to store the thermal and electrical energies.

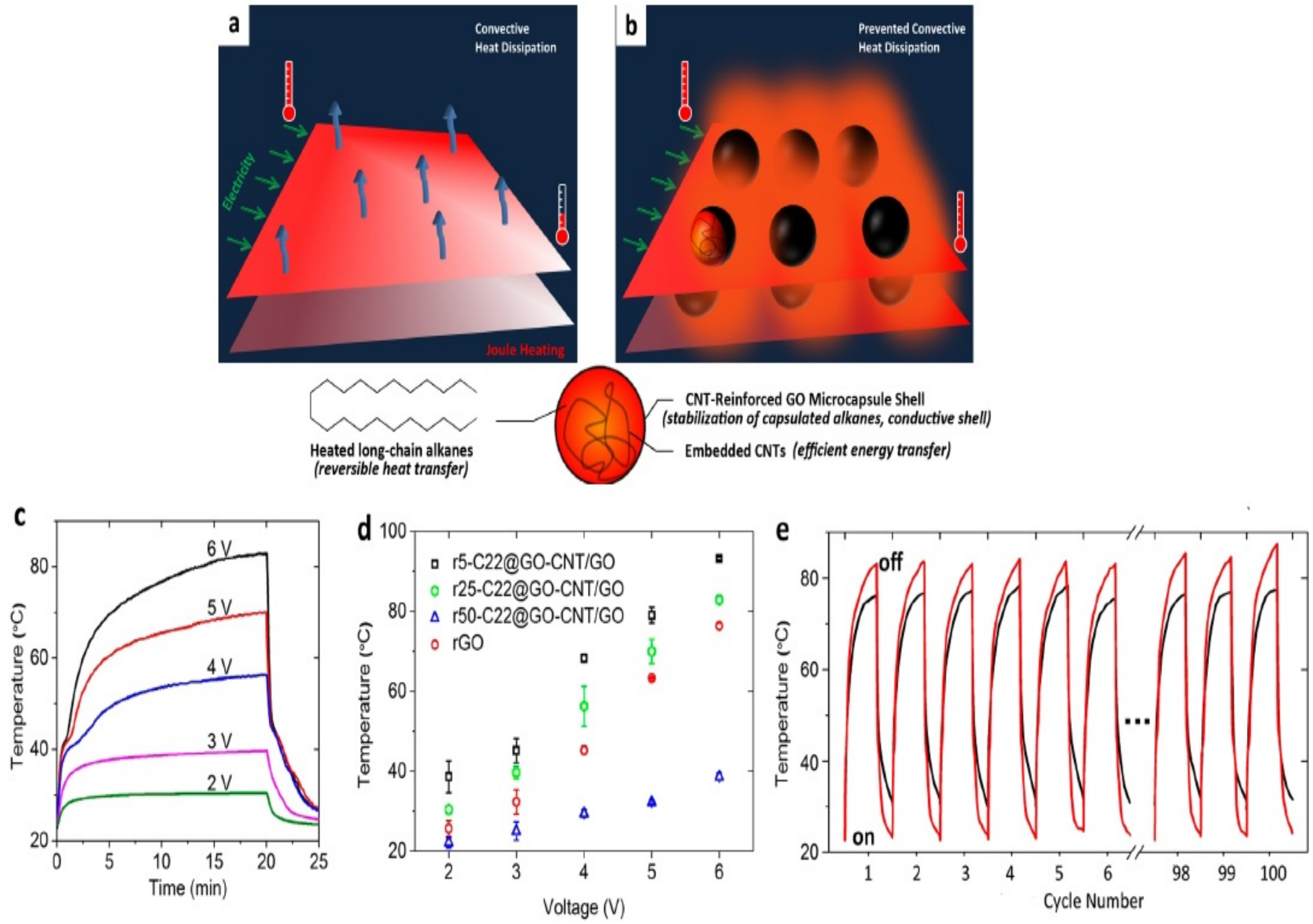


Figure 28: *(a)-Illustration of convective heat dissipation in a Joule heating structure composed of nanocarbons, (b)-illustration of prevented heat dissipation in a PCM capsule incorporated system, (c)-Temperature evaluation curves of an electrothermal structure containing* 25*vol.% micro-PCM capsules, (d)-As a function of voltage, the balanced surface temperatures obtained at 20min heating are demonstrated, and (e)-A collection of temperature evolution curves of an electro-thermal structure containing* 25*vol.% micro-PCM and a neat electro-thermal heater under* 6*V repeated for* 100 *cycles* [313], Reproduced with the permission of the American Chemical Society.

The authors reported the thermal and electrical conductivities of $0.7053W/mK$ and $1.08 \times 10^{-7}S/cm$, respectively. Additionally, it was suggested that OA-PEG/SiO_2/SnO_2 nano–PCMs can been used to as electrode material for electrochemical energy storage.

6.3. Thermal management

Thermal management is highly emerging and keen requirement for the efficient performance of thermal systems. The effective thermal management requires a highly conductive media to transfer the heat flux from hot source towards the sink. The 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 [315, 316]. For cooling of each system, it requires confine amount of PCM and range of operating temperature. Overall, cooling techniques of are classified as *active cooling* and *passive cooling.* Here, we summarize the active cooling technique based on single–phase and multi–phase 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 base on its viscosity and heat transfer capacity. The heat transfer capacity of single–phase fluid (e.g. water) is very low to ensure the efficient thermal performance maintaining the device temperature on comfortable level. In order to enhance the heat transfer capacity of HTF, the micro/nano–capsules are dispersed into the base fluid. The prepared fluid after adding the micro/nano–capsules is called *slurry* which has the capability to enhance the high heat transfer and high heat storage capacities by combing the latent heat of micro/nano–capsules and sensible heats both base fluid and micro/nano–capsules. This, EPCMs slurry (consisting on solid/liquid mixture), also called multi–phase fluid, has a multifunctional characteristics to serve as both heat HTFs and energy storage fluids (ESFs) [317]. The emulsion of macro– and micro–PCMs in base fluids under high pressure causes the fracture of capsules. Thus, increases the viscosity of slurry resulting reduces the heat transfer capacity and requires higher input power needed for pumping the slurry. Therefore, to address these issues, nano–PCMs have been dispersed into the base fluid. The effective specific heat (C_{eff}) of EPCMs slurry as a function of volume fraction (ϕ) of encapsulated capsules can be defined as:

$$C_{eff} = C_o + \phi H_{EPCM}/\Delta T \tag{12}$$

Here, C_o is the specific heat of base fluid, H_{EPCM} is the latent heat of dispersed EPCM per unit volume, and ΔT 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. [135] synthesized the SiO_2-encapsulated In nanoparticles and polymer–encapsulated paraffin wax nanoparticles using colloid method and then slurry was prepared by dispersing into poly-α-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 nano–capsules by mass are 1.6 and 1.75 times, respectively, higher than of 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. [220]. The enhancement in heat transfer coefficient was found by 50% and 70% for jet impingement and spray cooling , respectively, compared to base fluid. Later, the authors prepared the 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 [106]. 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 2 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 in ducts, 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

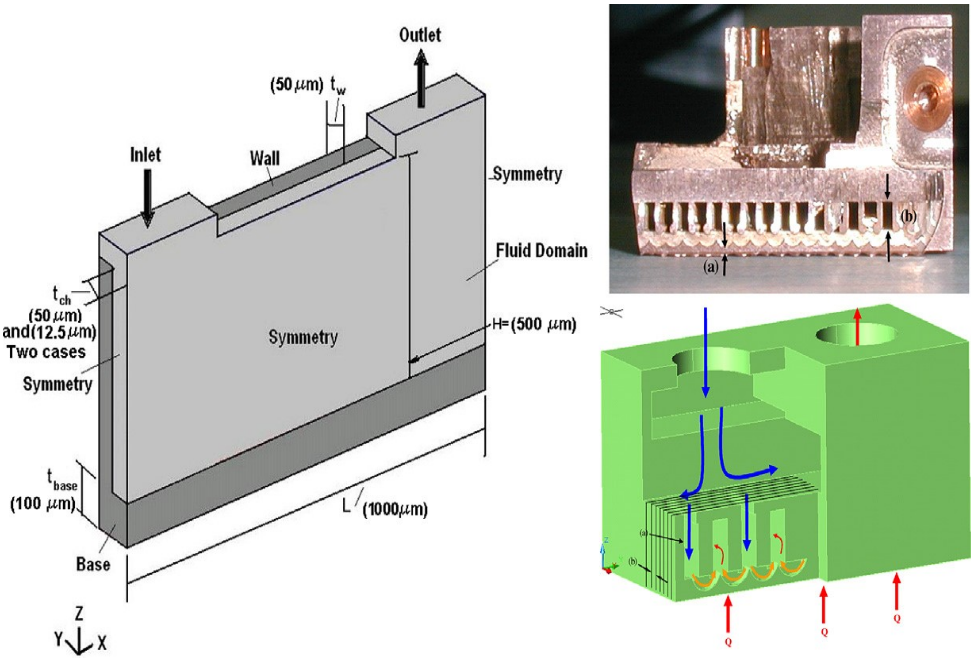


Figure 29: *Design concept and cross-sectional view of microchannel heat exchanger* [106], reused with the permission from Elsevier license number 4444700260609.

or systems. The hybrid water–based suspensions consisting of Al_2O_3 nanoparticles (nanofluid) and micro–PCMs particles (slurry) were prepared and then heat transfer characteristics were studied flowing through a circular tube [318] and minichannel heat sink [319]. 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. [320] 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 the more pumping power. Liu et al. [293] 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 are 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 thermal boundary layer [321].

6.4. Building

The micro and nano EPCMs 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 which requires for heating, cooling, air conditioning and ventilation, water heating and lighting [322]. The embedment of EPCMs have significant potential to increase the thermal inertia at constant mass in buildings especially mixing with concrete which influence the thermophysical and mechanical properties of concrete [323]. Additionally, the embedment of micro– and nano–PCMs in concrete increase the thermal and acoustic insulation of walls. Giro-Paloma et al. [324] reported the mechanical properties of micro–PCMs synthesizing 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 micro–capsules and also better stability was achieved with less short–emission of volatile organic compounds. Aguayo et al. [325] 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 depended on the mechanical properties of micro–PCMs. Cao et al. [326] 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 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.

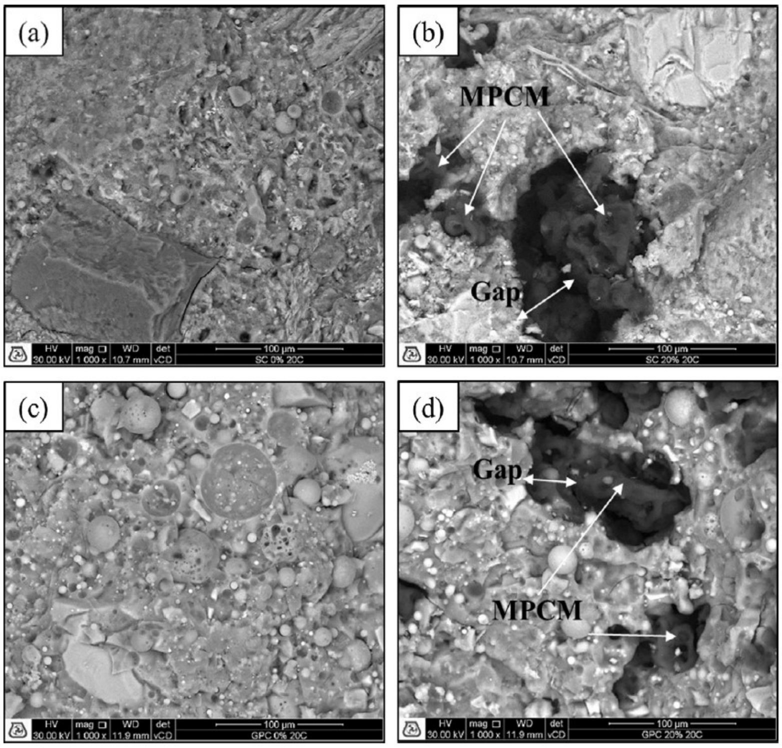


Figure 30: *SEM images of (a)-PCC without micro-PCMs, (b)-PCC containing* 3.2*wt.*% *micro-PCMs, (c)-GPC without micro-PCMs, (d)-GPC containing* 2.7*wt.*% *micro-PCMs* [326], reused with the permission from Elsevier license number 4444700728610.

Wei et al. [327] 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. [328]. 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 [329], gypsum plaster [330, 331], sandwish panels [332], and slabs [333] which could lead to reduce the energy demand both in 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 woolen, durable fragrances and skin softeners. Meanwhile, micro–PCMs have been utilized for waste yeast cells, coating on the surface of fabric or embedded within fibre Nelson [334]. Sarier and his co-authors [12, 121] firstly reported the thermal regulation or thermal comfort of four different micro–PCMs capsules of containing n-octadecane, n-octadecane/PE600, n-eicosane/n-hexadecane, and PEG/$Na_2CO_3.10H_2O$/n-hexadecane as a core materials coated with PUF. The energy absorption capacities were enhanced from $2.5-4.5$ times relative to the reference fabric at a particular temperature. Later on, authors found the higher thermal conductivities of micro–capsules which can be employed for thermal cooling of clothing fabrics, medical and automobile textiles and building materials. Additionally, the phase change enthalpies of $137 J/g$ and $168 J/g$ for n-hexadecane and n-octadecane, respectively, were achieved using silver nanoparticles. Alay et al. [205, 206, 335] synthesized the micro–PCMs of n-hexadecane/PBE and n-hexadecane/PMMA with the aim to increase the physical interaction between the micro–capsules 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 microfiber polyester fabrics were capable to absorb heat of $6.56 J/g$ and $28.59 J/g$ with n-hexadecane/PBE [335], $4.95 J/g$, $10.02 J/g$, and $8.38 J/g$, respectively, with n-hexadecane/PMMA [205]. Moghaddam and his co-authors [142, 336] prepared the micro–capsules of n-nonadecane 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 30-31°C which was the suitable for thermal regulation in textile. Aksoy and his co-authors [337, 290, 338] synthesized the micro–PCM of n-eicosane/PMMA-co-AA, n-eicosane/sodium alginate, and n-eicosane/PMMA-co-MAA 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 micro–capsules incorporated fabric homogeneously onto the surface which are mainly located between the fibers and fiber spaces, as shown in Figure 31. The heat storage enthalpy of $97-114 J/g$ 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 micro–capsules 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 micro–capsules.

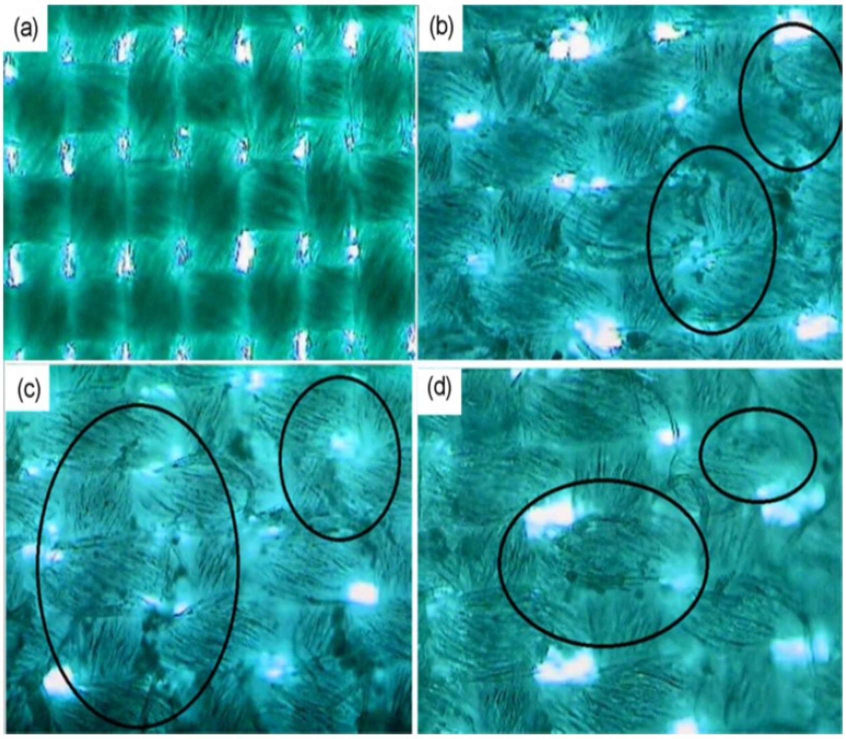
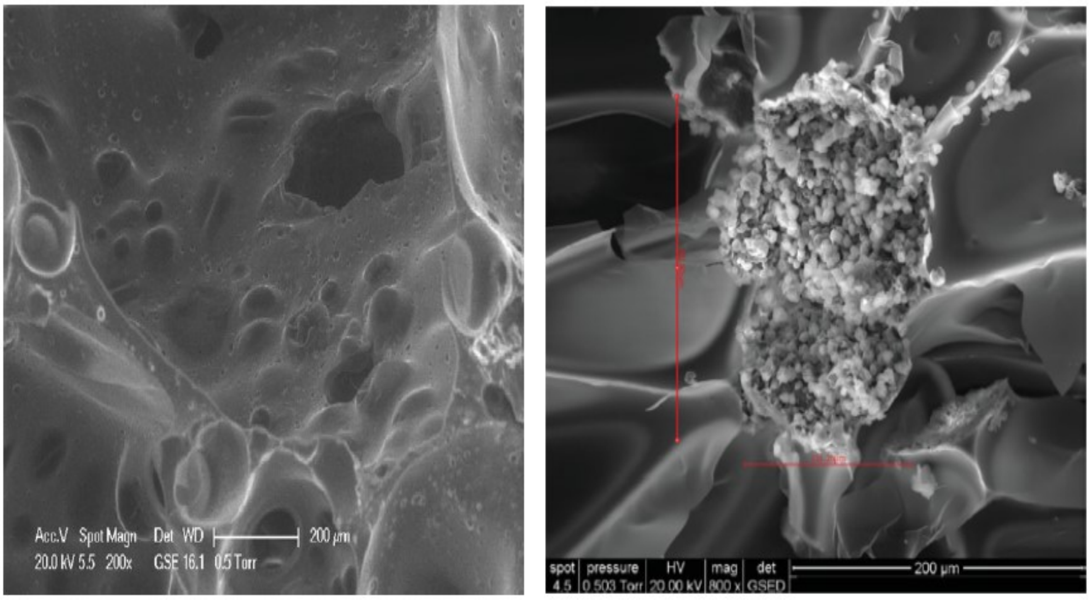


Figure 31: *Optical microscopy images of the fabrics (a)-untreated, (b)-treated with microcapsule-1, (c)-treated with microcapsule-2, and (d)-treated with microcapsule-3* [290], reused with the permission from Springer Nature license number 4444701208637.

Recently, Sun and Iqbal [339] synthesized the 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 to 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 a insulating material. Mostly PS and PU are applied with micro– and nano–PCMs in building structures such as wall, windows roofs and flours, automotive and aerospace interiors and biomedical applications. You et al. [340] 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 micro–capsules i.e. 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 [341, 342] 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 micro–capsules enhanced the TES capacity meanwhile along with sustaining the mechanical properties without addition of fillers. Whereas at higher content of 21 wt.% of micro–capsules 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$^{\circledR}$ DS 5001X [343]. Figure 32a and 32b exhibit the SEM of PU foams containing 18 wt.% of mSP-(PS-TR27) and Micronal$^{\circledR}$ 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 micro–capsules caused the strut rupture and damaging the mechanical properties.



(a) (b)

Figure 32: *(a)-SEM images with* 200× *magnification of PU foam containing 18 wt.% of mSP-(PS-TR27) and (b)-SEM images with* 800× *magnification of PU foam containing 18 wt.% of Micronal*$^{\circledR}$ *DS 5001X.* [343], Reproduced with the permission from John Wiley and Sons license number 4444710857803.

Recently, Serrano et al. [344] developed the rigid PU of varying the weight percentage from 0% to 50% of micro–capsules of named mSD-(LDPE.EVA-RT27) and found the $40wt.\%$ optimum weight percentage of micro–capsules to produce thermal regulating foams having latent heat of $34.4J/g$ 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 CO_2 leaving to the atmosphere can be reduced as well as saving the energy. Qiu et al. [345, 346, 347, 348] prepared the PS foam with micro–capsules containing paraffin wax and DEEP as core and P(MAA-co-EMA as a shell materials, and found that micro–PCM had good thermal regulation potential and TES capacity treated with foam. Later, they synthesized the micro–PCM of hybrid shell materials of PMMA and UF coated on n-tetradecane and found the higher enthalpy of $175.5J/g$. Additionally, the authors reported that the foam treated with micro–PCMs has the better thermal regulating properties than raw foam [348].

6.7. Medical industry

The antibacterial effectiveness of EPCMs has been paid an 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. [349] devepoled the silvermodified 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 aureous* (Gram-positive bacteria). Zhang et al. [286] synthesized 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 *Escherichia coli*, *Staphylococcus aureus*, and *Bacillus subtilis*. The antibacterial effectiveness, shown in Figure 33, revealed that bacterial activities for *Escherichia coli*, *Staphylococcus aureus*, and *Bacillus subtilis* were inhibited up to 64.6%, 99.1%, and 95.9%, respectively, when contacting the micro–capsules for 2hrs.

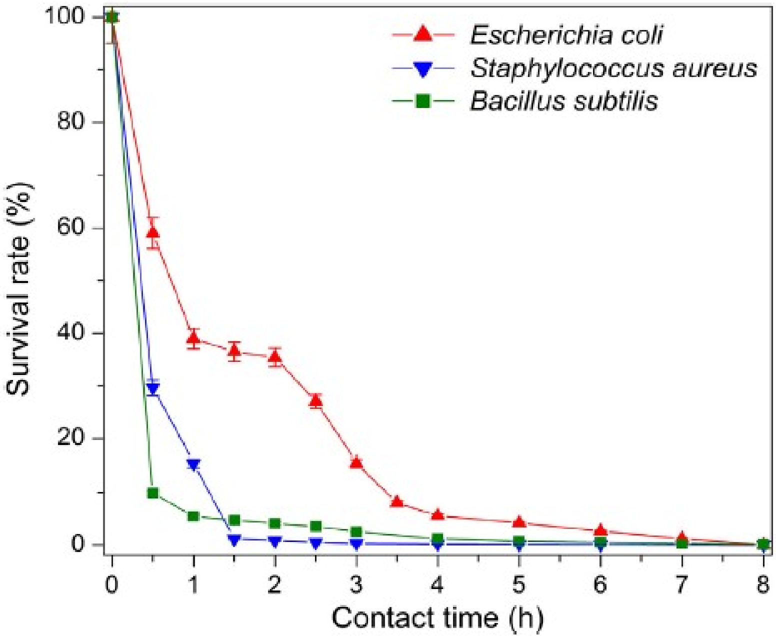


Figure 33: *Plots of the survival rates of different bacteria as a function of contact time for the n-Eicosane/silver/silica microcapsules obtained at the reaction time of 20hrs* [286], reused with the permission from Elsevier license number 4444720694482.

7. Future research on EPCMs

The 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 researcher are currently working on the preparation and characterization 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 the high latent of fusion during phase transformation, so they have more potential in TES applications e.g. active and passive heating and cooling through solar energy. However, they can degrade in moisture environment. Till yet, the research is focusing on the OPCMs to use as a core materials. Therefore, there is need mico/nano–encapsulation of molten salts and salt hydrates to use a core materials.

- Sub–cooling or super–cooling: The super–cooling 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: The encapsulation of PCMs, it has been reported the melting temperature latent heat of fusion are decreased as compared to pure PCMs. The purpose of PCMs is to use as energy storage materials in TES systems without losing 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 macro–, micro– and nano–meter encapsulated capsules. Additionally, thermophysical properties such as thermal conductivity, latent heat of enthalpy, encapsulation ratio and encapsulation efficiency are summarized 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 summarized 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 polymerization 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 polymerization 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 while 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 and environment of use and selection of shell material. As a specific shell material has its own merits and demerits regarding to thermophysical properties point of view.
- IPCMs as a 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, sub–cooling 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* polymerization technique is found better 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–mini–channels, heat pipes, heat exchangers, wallboards, panels and slabs and so on.

Conflict of interest

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

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