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Review

A Comprehensive Review of Microencapsulated Phase Change Materials Synthesis for Low-Temperature Energy Storage Applications

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Abstract: Thermal energy storage (TES) using phase change materials (PCMs) is an innovative approach to meet the growth of energy demand. Microencapsulation techniques lead to overcoming some drawbacks of PCMs and enhancing their performances. This paper presents a comprehensive review of studies dealing with PCMs properties and their encapsulation techniques. Thus, it is essential to critically examine the existing techniques and their compatibility with different types of PCMs, coating materials, and the area of application. The main objective of this review is to describe each microencapsulation process and to determine different factors that influence the performance of resulting microcapsules. Microencapsulation efficiency, as well as the limitation of each technique, are investigated, and optimum operating conditions of each process are highlighted. Furthermore, up-to-date studies of multifunctional PCMs microcapsules development with enhanced performances and new application directions are also presented. This review aims to be a useful guide for future researches dealing with low thermal energy storage applications of PCMs microcapsules.

Keywords: phase change materials (PCMs); energy storage; PCMs encapsulation; multifunctional PCMs; thermal conductivity enhancement

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1. Introduction and Background

Solar energy is one of the green alternatives to fossil energy that could meet the growing energy demand [1]. However, as with many renewable energy sources, solar energy is limited by its fluctuating nature, known as intermittence in daily and seasonal cycles [2]. There are various forms of energy storage, such as mechanical, electrical, thermal, and chemical [3]. Thermal energy storage (TES) was early recognized as a solution to managing the solar irradiation excess and the energy demand with no known environmental damage [4]. Thermal energy storage can be achieved according to three physical principles, i.e., (i) sensible heat thermal energy storage (SHTES) based on raising the temperature of the material (solid or liquid) without involving a phase change [5]; (ii) thermochemical storage (TCS), which refers to the heat absorbed or released during a reversible chemical reaction [6]; and (iii) latent heat thermal energy storage (LHTES) based on the phase change of the material. Each form is characterized by a specific capacity, storage period, efficiency, rate of charge and discharge, and its cost [7].

Phase change materials (PCMs) are recognized as promising LHTES materials that allow absorbing and releasing latent heat during phase change transition [8]. Energy absorption occurs in three consecutive stages ranging from storage by sensible heat and latent heat. As the temperature increases below the phase transition temperature, the material's specific heat (Cp) is absorbed as sensible heat. During the phase change, energy storage occurs isothermally by absorbing heat in the form of latent heat. Finally, above

this transition, the temperature of the material increases, and storage by sensible heat takes place [9]. PCMs remain mainly selected for their thermal properties. For a specific application, the phase change temperature should be suitable for the operating one. At the same time, they should present high latent heat to ensure maximum latent heat storage capacity by using a small material amount [10]. PCMs exhibiting high thermal conductivity have a higher heat absorption and release rate than other materials [11].

Moreover, chemical stability is an essential criterion in the selection of PCMs. Therefore, chemically stable materials allow PCMs to operate at the desired temperature without degradation or damage after several heating/cooling cycles [12]. The chemical composition of PCMs and the phase change temperature must be selected in function of the operating conditions to avoid possible reactions with other materials through the application. In addition, the used material can be neither hazardous nor flammable to prevent toxic emissions that can be harmful to the environment and/or humans during its preparation and use. Moreover, the vapor pressure should be as low as possible during the phase change at the operating temperature, and preferably, the volume change during solidification is negligible [13]. PCMs having a small degree of supercooling does not impact the phase transition temperature. Finally, PCMs with suitable crystallization and nucleation rates are expected to be potential material candidates for energy storage [14,15].

Despite many desirable properties, most PCMs undergo leakage issues during the phase change process and have significant volume change and low thermal conductivity, limiting their direct application [16].

Many efforts have been made to improve the heat transfer of PCMs to overcome these drawbacks. Since 2005, several studies have been focused on the thermal conductivity improvement of PCMs. Different materials are used as heat transfer enhancers, such as copper, nickel, aluminum, and carbon fibers [17]. Qureshi et al. reviewed different thermal conductivity enhancement techniques, such as developing PCMs composite materials using thermal conductors (e.g., expanded graphite, metallic foams, etc.) or by encapsulation with high thermal enhancer shell materials such as inorganic materials and carbon-based materials [18].

Encapsulation techniques are assumed to be an efficient way to stabilize PCMs' shape [19]. The incorporation of PCMs into a protective shell leads not only to limiting undesired interaction and preventing their leakage but also to an increase in the specific surface contact area, and therefore, improve the thermal transfer [20].

The encapsulation corresponds to all technologies that aim to envelop a solid, liquid, or gaseous active principle within a coating material. The objectives of encapsulation are multiple and depend on the desired specific application [21]. Primarily, encapsulation aims to protect the active substance from the external environment (reactivity with other materials, pH, temperature, etc.) during the application. Secondly, it prevents the oxidation of the core material and increases its durability. Thus, the core material's thermal, physical, and chemical stability can be improved, whereas their volatility and flammability can be reduced [22]. Capsules resulting from different encapsulation techniques are termed according to their size, i.e., macroencapsulation refers to the encapsulation of PCMs in any type of containers such as tubes, spheres, or panels where the size of these containers is usually larger than 1 cm; the microcapsules range from less than 1 µm to 1000 µm in diameter size, and the nanocapsules are synthesized at the nanoscale [23].

Microencapsulation techniques are based on two steps: preparing an emulsion or a suspension of the active ingredient and forming a shell. The emulsion preparation determines the size distribution of the capsules, which depends on the operating conditions (the rate and time of agitation, viscosity, the mass ratio of different phases, etc.) [24]. The formation of the shell depends upon many factors (pH, temperature, solubility, and concentration of shell materials) that should be adapted to the encapsulation method and the employed core material [24]. The main application fields of the encapsulation process are the pharmaceutical [25], cosmetic [26], and food industries [27]. PCMs encapsulation is achieved through different methods.

According to the literature survey, PCMs have been gaining research interest since the 1980s [28,29], including the direct and indirect applications (Figure 1). The number of publications has been steadily increasing until 2016. From 2016 to 2020, extensive efforts were devoted to exploring sustainable PCMs technologies to face the growing demand for energy consumption. It can be depicted by the number of PCMs publications, which reached 17,111 publications in 2019. Indeed, scientific publications concerning PCMs microencapsulation reached 17,615 publications in 2020. In the last few years, there has been a growing interest in the research on storage materials since green energy has become required to respond to the various IPCC (Intergovernmental Panel on Climate Change) reports. They have highlighted the impending problems leading to the acceleration of climate change and have urged immediate action toward renewable energy, efficiency, and limiting greenhouse gas emissions. Therefore, the increase in publications carrying out the enhancement of PCMs performances has allowed their application areas, such as building [30], smart textile [31], micro electro mechanical system [32], air conditioning [33], etc.

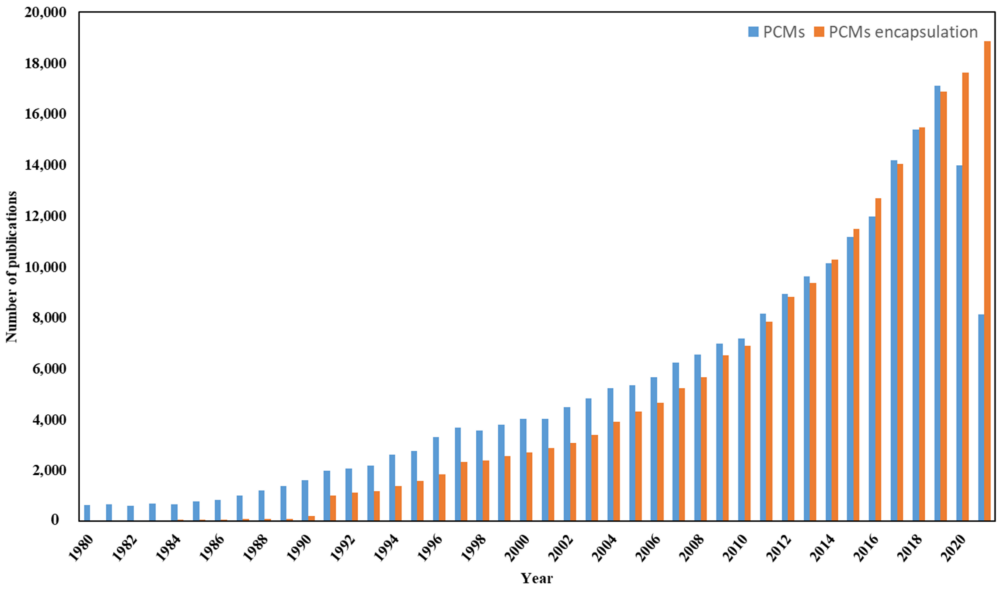


Figure 1. Trends in scientific articles on phase change materials and their encapsulation techniques (realized on Web of Science in 2021, advanced search): TS = (microcapsule OR microencapsulation OR nanoencapsulation OR encapsulation AND Phase AND Change AND Materials) TS = (PCM OR Phase Change Materials).

Microencapsulation of PCMs has been widely studied by several researchers [34–37]. Several reviews focused on PCMs encapsulation and its properties for energy storage applications. However, recent researches concerning PCMs encapsulation are focused on developing innovative microcapsules with additional functionalities (e.g., pollutants degradation by photocatalytic activity, antibacterial for medical application, photoluminescence for thermosensitive and photosensitive sensors, etc.). Therefore, this article aims mainly to highlight the innovation and particularity of the new types of microcapsules.

Firstly, this review summarizes the main studies related to PCMs classification, their characteristics, and drawbacks, which can assist researchers in selecting the appropriate type for a targeted application. Several microencapsulation techniques exist, and the choice of suitable routes is not always obvious. To bridge this gap, the compatibility between different encapsulation routes and raw materials is investigated. Moreover, this paper gives a clear overview of studies dealing with PCMs encapsulation and points out different factors that influence the performance of resulting microcapsules (e.g., temperature, types of solvent, rate of stirring, etc.). Microencapsulation efficiency, as well as limitations of each technique, are investigated. The optimum operating conditions of each process are also deeply studied, which can serve as a guide for researchers in their future works.

Finally, particular emphasis is given to possible challenges and future directions of research and development about microencapsulated PCMs with improved performances and additional activities.

2. Classification of Phase Change Materials (PCMs)

PCMs can be categorized according to their applications based on their phase change temperatures [38]. Those that melt below 0 °C are primarily used for cold thermal energy storage applications. Materials with a melting temperature between 0 and 65 °C are suitable for construction applications. At the same time, they will be used in cooling systems when the melting temperature is between 80 and 120 °C, but above 120 °C, they can be used in high-temperature processes such as waste heat recovery systems. Apart from these applications, phase change materials suitable for textile thermoregulation applications have a melting temperature between 16 and 35 °C [39]. Moreover, PCMs are classified as solid-solid, solid-liquid, solid-gas, liquid-gas, and vice versa. Solid-gas and liquid-gas phase transitions are not very interesting for LHTES applications due to the significant volume change and the low latent heat of PCMs for phase change [40]. The study by Sharma et al. showed that solid-liquid PCMs, whether organic or inorganic in origin, exhibit a wide range of phase change temperatures and high energy storage densities, making them suitable candidates for TES applications [21]. Therefore, the most common way to identify solid-liquid PCMs is to regroup them into three categories: organic [41], inorganic [42], and eutectic PCMs [35] (Figure 2).

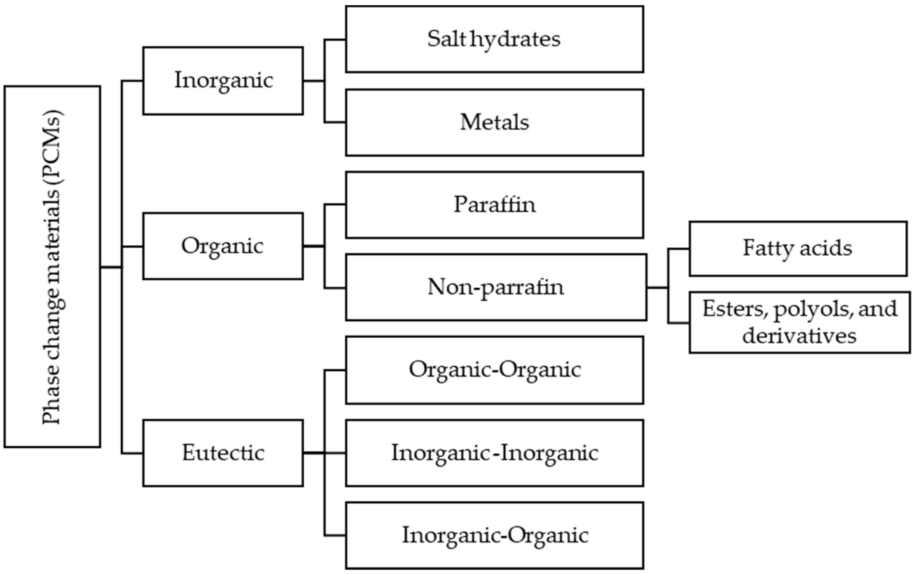


Figure 2. PCMs classification [43].

2.1. Inorganic PCMs

Several inorganic PCMs are employed thanks to their high latent transition heat, high density, and low cost. They are grouped into two categories, i.e., salt hydrates and metals.

2.1.1. Salt Hydrates

Salt hydrates are crystallized solids formed by inorganic salt and water. Their general formula is A. $n$$H_2O$, where A is the salt compound, and n is the number of H_2O molecules. The salt hydrates reveal attractive properties, such as high latent heat from 150 to 300 ($J \cdot g^{-1}$) and suitable thermal conductivity of approximately 0.5 $W \cdot m^{-1} \cdot K^{-1}$ [39]. However, most of them are corrosive to most metals and present supercooling issues [44].

2.1.2. Metals

Metals and metals alloys are used as latent heat energy storage materials due to their suitable thermal stability, low specific heat and vapor pressure, and higher thermal conductivity compared with other PCMs [44].

The employment of metallic PCMs is not only restricted to high-temperature energy storage applications [45]. Ge et al. investigated the advancements of using low melting temperature liquid metals such as mercury, lithium, rubidium, etc. [46]. The low melting point liquid metals materials revealed the same thermal properties as other metals, including high thermal conductivity, large heat of fusion, and suitable stability. The main drawback of metallic PCMs is the low heat of fusion per unit weight [38].

2.2. Organic PCMs

The organic types are considered more adapted for energy storage applications thanks to their wide range of temperature transitions. They are recommended due to their satisfying properties, such as non-toxicity, chemical stability, and availability [47]. The organic solid-liquid PCMs are paraffin and non-paraffin materials such as fatty acids, esters, alcohols, polyols, etc.

2.2.1. *n*-Alkanes

The paraffin materials are saturated hydrocarbons (C_nH_{2n+2}). In general, the melting temperature depends on the hydrocarbon chain length. They remain the most used due to many desirable properties, such as their excellent thermal stability and high latent heat. Moreover, they are inexpensive and widely available [48]. They are derived from gasoline, diesel, or fuel, etc. Nevertheless, some shortcomings such as high volume change during the phase transition, low density, and low thermal conductivity restrict their use [38].

2.2.2. Fatty Acids, Esters, Polyols, and Derivatives

Non-paraffin materials are the most extensive group of PCMs for latent heat storage, and the most commonly used are fatty acids, alcohols, esters, and polyols. Sharma et al. considered that among the different groups of PCMs, the non-paraffin materials are the most suitable for energy storage applications [49].

Among non-paraffin materials, fatty acids have recently attracted attention due to their excellent properties, including suitable chemical and thermal stability, high latent heat of transition, lower vapor pressure, appropriate melting temperature range, low volume change, little or no supercooling during phase transition, non-toxic, and non-corrosive [50].

Fatty acids are bio-based compounds derived from vegetable oils and animal fats by separation techniques or produced by specified processes from triacylglycerols [51]. Fatty acids are widely used as surfactant and co-surfactant agents for emulsification and gelation in food, cosmetic and pharmaceutical applications. They are also used as thermal energy storage materials in buildings [52], air conditioning [53], and smart textiles [54].

The results of some studies that investigated the phase change temperature and latent heat of the most known fatty acids are listed in Table 1. The thermal analysis results of the same fatty acids are slightly different in the literature. This difference is probably due to the operating conditions such as experimental temperature, the purity of materials, and different measurement techniques. In addition, the phase change temperature of fatty acids and fatty acid esters depends on the skeleton's number of carbon atoms.

However, fatty acids have low thermal conductivity. This shortcoming is overcome when composite materials were prepared by combining fatty acids with materials exhibiting high thermal conductivity, such as expanded graphite (EG), silica fume (SF), and activated montmorillonite (a-MMT). Moreover, the phase change temperature could be adjusted by mixing two or more materials for low-temperature heat storage applications [55].

Table 1. Thermal properties of some fatty acids.

Fatty Acids	Melting Temperature (°C)	Melting Latent Heat ($J \cdot g^{-1}$)	Density ($kg \cdot m^{-3}$)		Specific Heat ($kJ \cdot kg^{-1} \cdot °C^{-1}$)		Thermal Conductivity Liquid ($W \cdot m^{-1} \cdot °C^{-1}$)	Ref.
			Solid	Liquid	Solid	Liquid		
Stearic acid (SA) $CH_3(CH_2)_{16}COOH$	69	202	965	848	1.6	2.2	0.172	[56]
	60	178	-	-	-	-	-	[57]
	69	223	-	-	-	-	-	[58]
Palmitic acid (PA) $CH_3(CH_2)_{14}COOH$	64	185	989	850	1.9	2.8	0.162	[56]
	60	233	-	-	-	-	-	[59]
Myristic acid (MA) $CH_3(CH_2)_{12}COOH$	58	187	990	861	1.7	2.4	0.150	[56]
	54	187	-	-	-	-	-	[58]
	52	211	-	-	-	-	-	[59]
	52	178	-	-	-	-	-	[60]
	52	205	-	-	-	-	-	[61]
Lauric acid (LA) $CH_3(CH_2)_{10}COOH$	44	177	1007	862	1.7	2.3	0.147	[56]
	42	190	-	-	-	-	-	[59]
	44	184	-	-	-	-	-	[62]
Capric acid (CA) $CH_3(CH_2)_8COOH$	32	153	1004	878	1.9	2.1	0.153	[56]
	30	140	-	-	-	-	-	[63]

2.3. Eutectic PCMs

Several publications indicated that the comfortable indoor temperature is recognized in the range of 16–25 °C in the building sector. Boulard et al. considered that only PCMs having a melting temperature between 20 and 28 °C could be used in greenhouse applications [64]. Mondal reviewed PCMs for smart textile applications and indicated that the PCMs with a melting point in the range of 15–35 °C are the most suitable materials for temperature regulation and insulation of textiles [65].

Therefore, the development of eutectic mixtures by combining two or more components expand the phase change temperature ranges of PCMs. The eutectic mixture is characterized by its eutectic point, representing the mixture's lowest melting temperature. Moreover, it exhibits the same stability as a single material with a melting temperature lower than the phase change temperature of each of its compounds. There are three categories of eutectic mixtures: organic-organic, organic-inorganic, and inorganic-inorganic.

Two methods were commonly adopted to determine the mass ratio of the different components of a eutectic mixture, i.e., theoretical calculation or proportioning test [66].

2.3.1. Theoretical Method

Theoretical calculations determined the mass ratio of a eutectic mixture were based on Schroder's equation. It is derived from the phase equilibrium theory and the second law of thermodynamic to describe the relationship between the physical properties of different compounds of the eutectic mixture (molar fraction, melting temperature, enthalpy) and the melting temperature of their mixtures (Equations (1) and (2) [67]).

$$T = \frac{1}{T_{m,A}} - \frac{R \ln x_A}{\Delta H_{m,A}} \quad (1)$$

$$T = \frac{1}{T_{m,B}} - \frac{R \ln x_B}{\Delta H_{m,B}} \quad (2)$$

where T is the onset melting point of the eutectic mixture, and x_A and x_B are the mole fractions of the components A and B in the mixture ($x_A + x_B = 1$), respectively. $\Delta H_{m,A}$, $\Delta H_{m,B}$, $T_{m,A}$, and $T_{m,B}$ are the components A and B's heat enthalpies and melting temperatures. R is the gas constant (8.314 $J \cdot K^{-1} \cdot mol^{-1}$).

It is reported that the calculated results could be affected by the presence of impurities that influence the data obtained by differential scanning calorimetry (DSC) measurements.

2.3.2. Experimental Method

The eutectic mass ratios can be determined by preparing and testing a series of PCMs mixtures with different proportions and comparing their DSC analysis results to determine the eutectic mass ratio [68]. In the case of binary mixtures, multiple samples are obtained by combining two PCMs. The different mass ratios of solid PCMs are weighed, melted, and stirred for 15 min to homogenate the mixture. Then, the phase change temperature and latent heat of prepared samples are investigated by DSC. The eutectic mixture point is identified by plotting the phase diagram based on DSC results. The multiple numbers of DSC tests and the time required for samples preparation make the experimental method more complicated than the theoretical one, especially for eutectic mixtures containing several components.

In recent studies, the most reported eutectic mixtures are organic-organic ones, particularly fatty acids eutectic mixtures due to their advanced properties compared to inorganic materials, such as high latent heat and minimal volume change suitable thermal stability. Moreover, fatty acid mixtures present an excellent homogeneity, and no chemical degradation was noticed after repeated thermal cycles. On the other hand, the most used fatty acids have higher melting temperatures than the recommended temperature range for low latent heat storage (Table 1). For this purpose, mixing two or more components ensures temperature adjustment. Several types of eutectic mixtures (binary, ternary, etc.) exist, and their phase change temperature is adjusted by changing the weight ratio of the selected components (Table 2). A wide variety of eutectic mixtures with excellent thermal properties was used for several applications such as buildings insulation [69,70], solar heating and cooling systems [71], and thermoregulating textiles [72].

Table 2. Examples of PCMs eutectic mixtures and their properties.

Eutectic Mixture	Mass Ratio wt%	Onset Melting Temperature (°C)	Melting Latent Heat ($J \cdot g^{-1}$)	Ref.
CA-LA	64:36	19	163	[73]
CA-MA	78.39:21.61	25	123	[74]
CA-PA	89:11	28	145	[74]
CA-SA	94.47:5.53	30	156	[74]
LA-PA	77.51:22.49	38	151	[74]
MA-SA	76.29:23.71	48	148	[74]
LA-MA	63.63:36.37	34	130	[74]
LA-SA	86.51:13.49	41	164	[74]
MA-PA	64.96:35.04	45	152	[74]
PA-SA	62.99:37.01	54	179	[74]
MA-SA	64:36	44	182	[75]
CA-PA	76.5:23.5	23	156	[76]
CA-MA-SA	72.5:22.5:5.0	24	159	[66]
CA-PA-SA	79:13:8	20	129	[71]
SA-PA-LA	6.77:20.97:72.26	32	159	[74]
LA-MA-SA	57.5:34.3:8.2	29	140	[77]
SA-PA-LA-MA	11.86:18.54:45.6:24	27	128	[72]
Tetradecane-octadecane	-	-4	228	[38]
Tetradecane-docosane	-	2–6	234	[38]
Tetradecane-hexadecane	-	2	156	[38]

3. Shell Materials

The use of PCMs in their crude form has several drawbacks, such as low thermal conductivity and liquid leakage during solid-liquid phase changes, which limit their applications. Thus, many encapsulation techniques were developed to overcome these disadvantages and improve heat transfer. This approach allows not only to transform a

liquid into a pseudo-solid and thus protect it during its use but also improve its thermo-mechanical and morphological properties. The performance of microcapsules is greatly influenced by the chemical and physical properties of the shell, and therefore, the selection of raw materials depends on desired characteristics and the application. There are three different types of shell materials, i.e., organic, inorganic, and organic-inorganic hybrid shells.

Organic materials are mainly melamine-formaldehyde (MF) resin, urea-formaldehyde (UF) resin, polyurea (PU), and acrylic resins poly(urea-urethane).

Microcapsules with organic shells are characterized by their suitable structural flexibility and suitable reliability after repeated thermal cycles [78]. However, they exhibit poor chemical and thermal stabilities and undergo some shortcomings such as toxicity, flammability, and poor heat transfer performance [23]. The selection of the techniques depends on the physicochemical properties of core and coating materials (Figure 3), required properties, and the application fields.

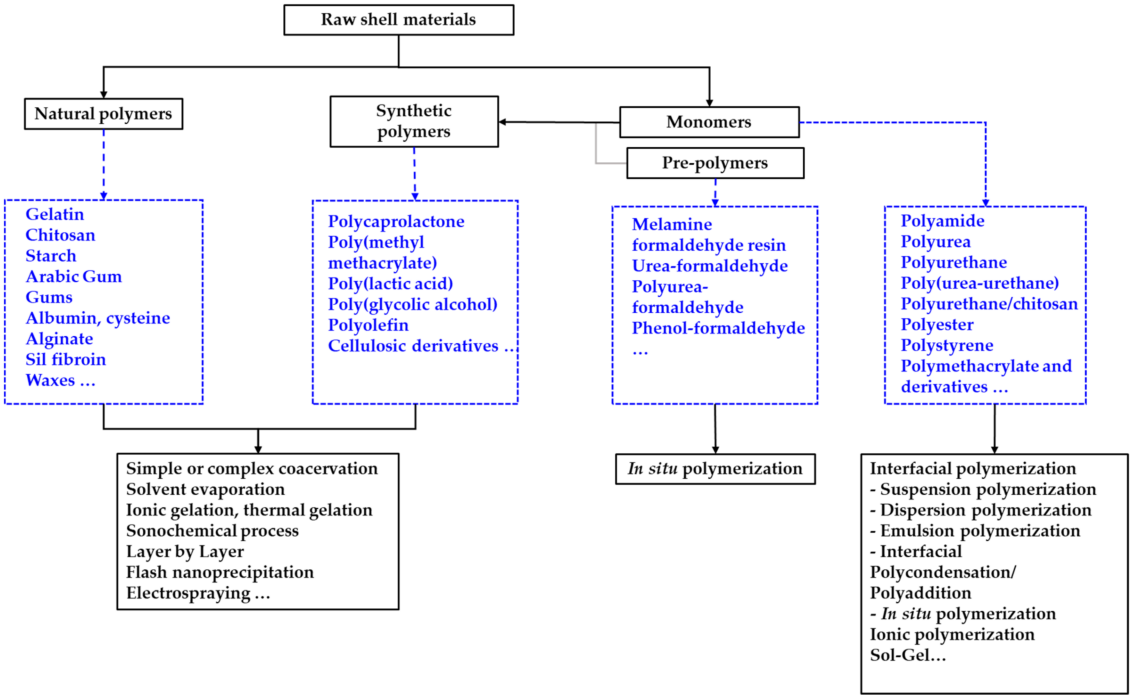


Figure 3. Microencapsulation processes based on raw materials.

Recently, inorganic shell materials have gained more attention, including silica, titania, calcium carbonate, zinc oxide, and polystyrene (PS). Inorganic shell materials are recognized by excellent thermal stability, high thermal conductivity, mechanical durability, chemical inertness, and non-toxicity [44].

The employment of hybrid shells consists of mixing organic and inorganic materials. The hybrid shells not only lead to overcoming the drawbacks but also combine the advantages of organic and inorganic materials. Therefore, the use of inorganic materials enhances mechanical rigidity, thermal stability, and thermal conductivity, while organic materials offer structural flexibility to microcapsules.

4. Microencapsulation Techniques

The synthesis of encapsulated PCMs is achieved by three different methods, i.e., (i) physical, (ii) chemical, and (iii) physicochemical. Microencapsulation consists of three basic steps, i.e., principal active inclosing, microparticles formation, and hardening.

4.1. Chemical Process

The chemical method is employed for the encapsulation by lipids, wax, or polymers coating materials. This method involves in situ formation of the polymeric coating material using monomer, prepolymer, or polymer as a starting material. The chemical routes include suspension, precipitation, dispersion, and emulsion polymerization or interfacial and in situ polycondensation. Therefore, the performance of polymeric shell materials depends strongly on the parameters of each process. Moreover, the selection of the polymerization process relies on the solubility of monomer, prepolymer, and resulting polymer [79].

4.1.1. Microencapsulation by Heterophase Polymerization

- Suspension polymerization

The suspension polymerization includes two phases, i.e., (i) the dispersed phase containing the active agent, water-insoluble monomers, and initiator; (ii) the continuous phase involving solvent and reactant of shell materials (Figure 4) [37]. PCM droplets are obtained by vigorous agitation of the mixture and dissolution of stabilizers in aqueous phases such as poly(vinyl alcohol), polyvinyl pyrrolidone, or cellulosic derivative. This method is mainly used to encapsulate with polystyrene, poly(methyl methacrylate), and poly(vinyl chloride) shells [80].

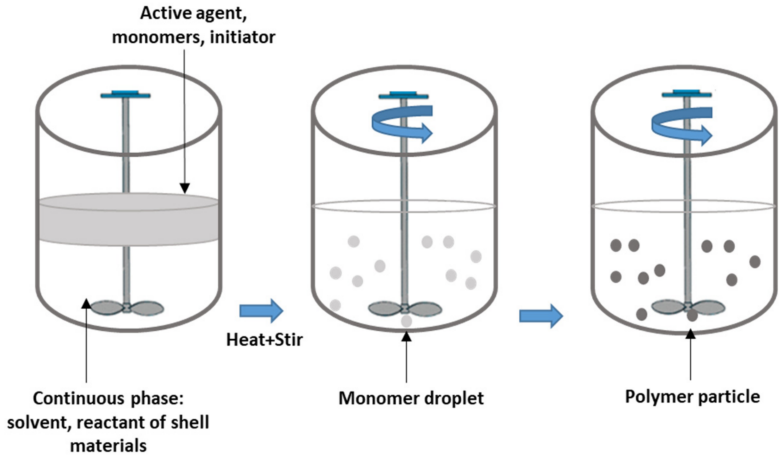


Figure 4. Schematic representation of the microencapsulation by suspension polymerization.

The advantages of this method are the formation of uniform spherical particles, excellent heat control of the reaction, and its cost-effectiveness. The main drawback is the coalescence of particles during polymerization [81]. The complex interaction between the polymer system and the continuous phase on the surface of the droplets defines the efficiency of encapsulation and particles properties and depends on several factors. It was reported that the thermal energy storage capacity depends strongly on surfactant concentration and core/polymer ratios. In addition, the polymerization temperature has a significant effect on particle morphology without impacting the particle size [82]. Moreover, the loading content and particle size depend on the nature of core materials [83].

To improve polystyrene shell properties, Sánchez Silva et al. studied the development of paraffin microcapsules by using copolymerization of styrene (St) and methyl methacrylate (MMA) [84]. They observed that the MMA/St mass ratio affects the polymerization rate and that the particles size decreased with the increase in MMA amount. In addition, the weight ratios MMA/St of 4 and monomers/paraffin of 4 and 3 were established as suitable conditions to favorite paraffin microencapsulation. Furthermore, Tanwar et al. employed this method to entrap caprylic acid in a PMMA shell with a mean particle diameter of 4 µm [85]. The microcapsules exhibited enhanced thermal properties for thermo-responsive textile fabrics, PCMs slurries, and thermo-responsive functional coatings.

- Emulsion/miniemulsion polymerization

The emulsion polymerization involves emulsifying monomers and generating a cross-linked system in chemical, thermal, or enzymatic ways. The mean diameter of the resulting particles is between 50 nm and 1 µm and is influenced by the mass ratio of monomer/aqueous phase, surfactant and initiator concentration, and polymerization temperature [86]. In emulsion polymerization, unlike suspension polymerization, the initiator is soluble in the aqueous phase. The first step consists of the formation of monomers micelles with the aid of a surfactant. Monomers are insoluble or scarcely soluble in the polymerization medium. The polymerization starts by introducing water-soluble initiators leading to free radical formation and diffusion through the swollen monomer micelles [87] (Figure 5).

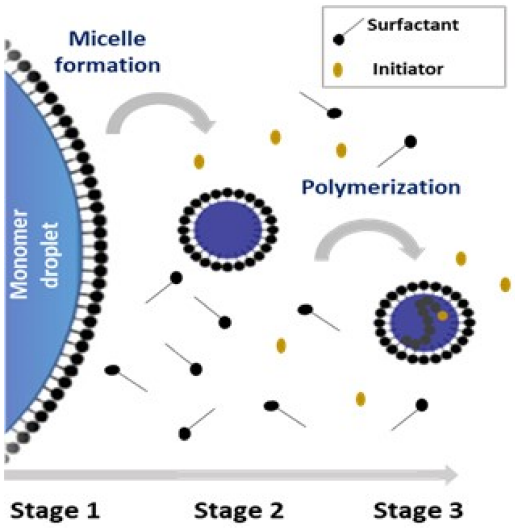


Figure 5. Schematic representation of different stages of emulsion polymerization.

The advantage of this method is the possibility of employment of high molecular weight polymer. The main drawback is the necessity of an additional step to remove polymerization adjuvants and surfactants that remain in the polymer [37]. Polymethyl methacrylate (PMMA), polystyrene, polyvinyl acetate, poly(ethyl methacrylate) are widely used for PCMs encapsulation because of their excellent chemical resistance, non-toxic and easy handling. Sari et al. worked on the preparation of *n*-alkanes/PMMA microcapsules using *n*-octacosane [88], docosane [89], *n*-nonadecane [90] as core materials. PCMs microcapsules with a loading content of 43, 28, and 60 wt% were obtained, respectively. They indicated that the type of *n*-alkanes, the weight ratio of monomer/PCMs, and the crosslinker agent significantly influence the morphology, particle size, and encapsulation efficiency. The resulting microcapsules exhibit relative thermal performances and can be employed for textile, building, or food packaging materials, in thermal fluids. Alay et al. obtained a higher *n*-hexadecane encapsulation ratio, smaller size, and enhanced morphology by using glycidyl methacrylate or ethylene glycol dimethacrylate as a crosslinker agent [91].

The ultraviolet (UV) light initiating polymerization is improved technology for preparing PCMs/PMMA microcapsules due to its significant advantages compared to the traditional thermal initiated polymerization, such as the temperature independence of the radical formation higher reaction rate. The light-induced polymerization limits the colloidal particle destabilization as the reaction is conducted at ambient temperature. In addition, the reaction rate of polymer can be maintained by varying intensity of light and time of irradiation [92].

The efficiency of this approach has been established by Ma et al. to prepare paraffin/PMMA microcapsules [93]. They obtained a loading content of 61% wt with the use of Photocure® 2959 as a water-soluble photoinitiator. Zhang et al. prepared mPCMs using

2-hydroxyl-2-methyl-1-phenyl acetone [94], or iron (III) chloride as photoinitiator [95]. They demonstrated that the types of surfactants affect thermal properties and particle size distribution, even if cationic and nonionic emulsifiers are suitable for preparing nanocapsules. In addition, the particle size distribution narrowed with the addition of crosslinking agent and the reduction in initiator and monomer concentration. The latent heat of nanocapsules decreased with the increase in monomer and initiator concentration.

Sami et al. developed paraffin wax/polystyrene microcapsules. The average size of obtained microcapsules was about 18 μm [96]. The particle size decreased by increasing the amount of surfactant and the stirring rate, enhancing the microencapsulation efficiency. Four parameters of this microencapsulation process were optimized to encapsulate lauric acid (LA), i.e., LA/polystyrene, and surfactant/polystyrene weight ratios, stirring rate, and temperature; to obtain an encapsulation efficiency about of 92% [97].

The miniemulsion polymerization method is employed to form PCMs nanocapsules (50–500 nm) following the same process of emulsion polymerization. This technique is a simple method for the preparation of PMMA nanocapsules. The core/monomer mass ratio and crosslinking agents such as ethylene glycol dimethacrylate are the principal factors that influence the size, morphology, thermal stability, and thermal storage behavior of nanocapsules. Encapsulation efficiency and heat transfer rate can be improved by the application of ultrasonic radiation [98]. This method was used for the encapsulation of *n*-eicosane/PMMA microcapsules [99].

Traditional low molecular weight emulsifiers are physically adsorbed on the polymer and influence the stability of particles. Zhou et al. demonstrated that the employment of reactive emulsifiers such as alkyl vinyl sulfonate stabilizes the emulsion, participates in polymerization with monomers, and is integrated into the polyacrylate shell [100]. In addition, the morphology of nanocapsules could be enhanced using a comonomer. Yu et al. reported the development of *n*-dodecanol/PMMA nanocapsules using butyl acrylate, acrylamine, and acrylic acid as comonomers. They concluded that the comonomer's hydrophilicity increased the polymer chain's hydrophilicity, which affected the encapsulation of oil-soluble PCM *n*-dodecanol efficiency. They also noticed that the type and amount of comonomers had a significant influence on the thermal properties and morphology of the nanocapsules [101].

- Dispersion polymerization

The dispersion polymerization involves a single step, and all reactants are dissolved in the continuous phase to form a homogeneous solution. The process depends on stabilizer concentration, initiator, type and amount of monomer, and reaction time. Khakzad et al. employed this method to encapsulate hexadecane by a melamine-formaldehyde shell. They observed that the morphology of the resulting microcapsules was strongly affected by the type and amount of stabilizer or surfactant and the homogenization speed [102]. Disrupted microcapsule formation was obtained by using inappropriate stabilizer compounds such as Arabic gum or starch. The aggregation of particles was related to hydrogen or secondary bonding between the molecules of stabilizers around the dispersed droplets. Thus, the optimization of the microencapsulation should take into account the working and formulation parameters.

4.1.2. Microencapsulation by In Situ Polymerization

Encapsulation by in situ polymerization consists of the presence of the monomer or prepolymer in a single phase (continuous or dispersed phase) rather than in two phases, as in interfacial polymerization. The formation of coating materials occurs when the monomers or the pre-condensates diffuse at the interface of the two immiscible phases. An amino resin such as urea-formaldehyde (UF) or melamine-formaldehyde (MF) is the most common shell material used in this method. The polycondensation of the amino resin occurs in the continuous phase; the separation phase is controlled by adjusting the pH and the modification of melamine/formaldehyde or urea/formaldehyde ratios [87].

The encapsulation of PCMs carried out by in situ polymerization is based on three steps, i.e., (i) formation of tiny PCM droplets into the water phase with the adding of UF or MF under acidic conditions; (ii) primary shell formation by the self-deposition of amino resins onto the PCMs droplets; and (iii) crosslinking of the amino shell due to the increase in the amino resin concentration at the interface. The shell formation mechanism is based on the activation of the pre-polymers, yielding etherification reactions. Hence, the water solubility of pre-polymers decreases leading to the separation of materials from the continuous phase. The obtained materials are collected after filtration and drying [103]. In situ polymerization microencapsulation process using melamine-formaldehyde is described in Figure 6.

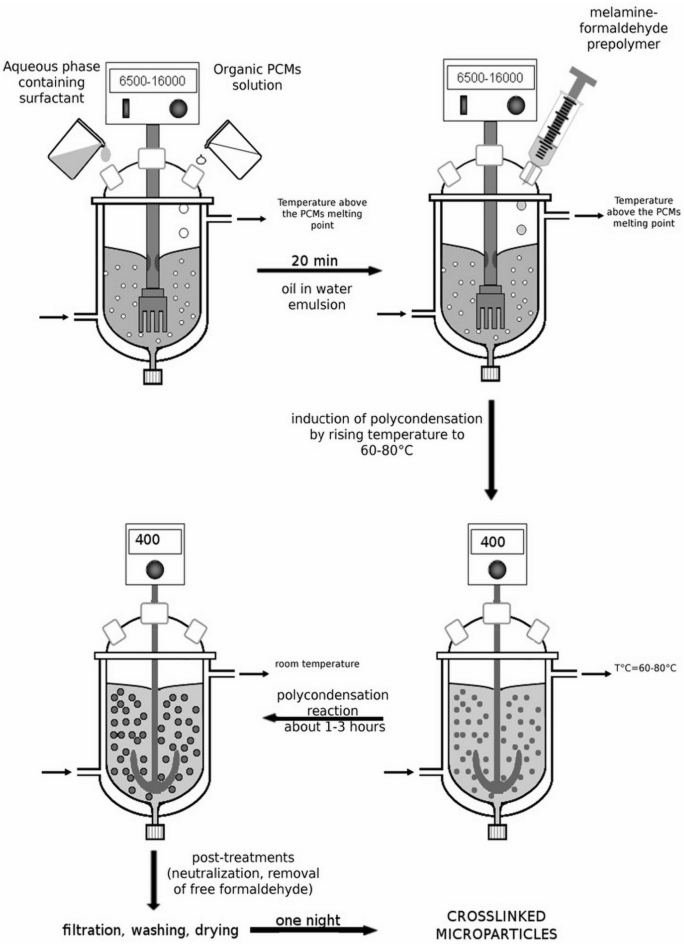


Figure 6. Schematic representation of the microencapsulation process by in situ polymerization [39].

Several studies investigated the optimization of process parameters to reduce free formaldehyde content. For example, Wang and Zhao encapsulated *n*-octadecane by MF and analyzed the influence of the pH value, temperature, and MF dropping rate on the particle morphology and encapsulation yield [104]. Thus, they observed that well-defined microcapsules with the highest encapsulation efficiency were obtained at a moderate pH (between 4 and 8), at 75 °C, and with a medium dropping rate of MF (0.75 mL·min^{-1}). Naikwadi et al. encapsulated *n*-tetracosane by MF by switching the pH of the emulsion from acidic (pH = 4) to alkaline (pH = 9) to complete the polycondensation reactions to control the encapsulation efficiency [105].

The influence of the type and amount of surfactant in the formation of mPCMs was investigated by Yin and al. [106]. They selected *n*-hexadecanol, MF, and anionic styrene-maleic copolymer (SMA) as core, shell, and surfactant materials. NaOH was used to enhance the solubility of SMA in water. They reported that 8% SMA to the core

material and a weight ratio of 3.3:10 between shell and core material are the optimal polymerization conditions to obtain spherical mPCMs with smooth surface and high encapsulation efficiency. Kumar et al. encapsulated 1-dodecanol by MF shell [107]. They noticed that the encapsulation efficiency was lower than other studies, probably due to nonionic emulsifiers (Tween® 20 and Span® 60) and the pH value in the range of 5–6.

MF resin has several advantages, such as high prepolymer reactivity and short-time reaction, and a high weight ratio between the core and the shell compared to UF resins [108]. However, the strong tendency of MF to self-polymerization due to its high solubility leads to the formation of mPCMs with poor morphology. The washing and filtration steps are more difficult and toxic due to the presence of free formaldehyde. Modified MF resin by hydroxyl-terminated polydimethylsiloxane (HTPDMS) [109], carboxymethyl cellulose (CMC) [110], resorcinol [111] were used as an alternative to traditional MF resin. In addition, melamine-urea-formaldehyde (MUF) copolymers were used to enhance mPCMs stability. Kanuklu et al. encapsulated decanoic acid with Poly(UF) (PUF), Poly(MF) (PMF), and Poly(MUF) (PMUF) as shells [112]. The microcapsules using PUF present a higher thermal storage capacity, but they were easily broken at around 95 °C due to their thin shell. In addition, mPCMs/PMF present low-capacity storage. The higher encapsulation ratio was attributed to the mPCMs with PMUF and was about 53%. The mean diameter and the dispersion stability were also affected by the type of surfactant and the use of cosurfactants (Tween® 40 and Tween® 80).

Wu et al. investigated the influence of surfactants on the synthesis of mPCMs [113]. SMA, Tween® 20, and polyethylene glycol p-isooctylphenyl ether (OP-10) were used as emulsifiers agents. They indicated that SMA as an anionic emulsifier is more suitable for preparing MUF mPCMs, leading to regular spherical mPCMs. In addition, the phase change enthalpy increases with the increase in the SMA amount.

Methyl/butanol etherified MF prepolymer was identified as an excellent modifier providing a relatively simple and effective way to prepare mPCMs. *n*-dodecanol was encapsulated by Zhang et al. using a mixture of methanol-modified MF (MMF) and traditional MF as shell materials using SMA as an emulsifier [114]. The influences of operating parameters such as PCMs/shell ratio, MF/MMF ratio, amount of surfactant, rate, and agitation time were investigated. They concluded that more stable spherical microcapsules were obtained with minor deformation within a more extended growth period due to the increasing amount of self-polymerized nanoparticles. Hence, complete in situ shell formation was achieved within 60 min under 70 °C. They observed that the size distribution of mPCMs depends on SMA concentration and emulsifying stirring speed. Moreover, decreasing the core/shell ratio results in an excessive amount of shell material adsorbed onto the surface of the microcapsules. In addition, the degree of aggregation and absorption of self-polymerized was reduced by decreasing MF/MMF ratio.

In other studies, MF was etherified by methanol or/and *n*-butanol to reduce the number of amino groups, allowing its reactive activity and polymerization control. Huang et al. employed methylated melamine-formaldehyde (MMF) and butylated melamine-formaldehyde (BMF) pre-polymers as a hybrid shell to encapsulate *n*-dodecanol [115]. They mentioned that the morphology of mPCMs with MMF/BMF was smoother than microcapsules with MF and MMF ones. They related this observation to the high solubility of the MF and MMF pre-polymers in the aqueous phase, leading to an increase in the self-polymerized nanoparticles deposited on the surface of microcapsules. The 1:1 mass ratio of MMF/BMF was considered as the optimum condition. The heat storage capacity and the encapsulation efficiency increased with the increase in the MMF/BMF ratio.

The amino resin was also modified with high thermal resistance materials, such as graphene oxide [116], silver [117], and metal oxide, to improve the heat transfer and thermal stability. Thus, Daou et al. used metal oxide (Fe_2O_3, ZnO, and TiO_2) to develop a modified inorganic-organic hybrid UF shell to encapsulate paraffin. They observed that the thermal performances were improved, and the decomposition of UF polymer was delayed to a higher temperature level [118]. Wu et al. indicated that MF modified by

cellulose nanofibers (CNFs) prevents breakage during application [119]. They mentioned that only 3.4 wt% of CNFs is required to improve the mechanical strength of the MF coating. Moreover, the encapsulation efficiency increased with the increase in the amount of CNFs.

Therefore, the emulsion stage governs the average diameter and size distribution of the particles [120]. The use of an SMA improves the stability of the emulsion rather than a nonionic surfactant. Shell formation and particle surface morphology are related to pH adjustment, preferably around 4, with a low prepolymer drop rate. Controlling these parameters can suppress particle flocculation to achieve a smooth surface [121].

However, even if these microcapsules are currently used at the industrial scale, the main drawback of the process is the release of free formaldehyde during the synthesis steps. Several regulations in many countries prohibit the use of formaldehyde, which limits its application.

4.1.3. Microencapsulation by Interfacial Polycondensation

The microencapsulation of phase change materials by interfacial polycondensation or polyaddition consists of their solubilization in the dispersed phase containing solvent and multifunctional monomers before emulsification in the continuous phase containing emulsifiers and stabilizers (Figure 7). The primary shell is formed through the precipitation of the insoluble polymeric materials on the droplet's surface after adding a complementary monomer in the continuous medium. In most cases, the membrane growth in the organic side and is achieved by crosslinking reactions.

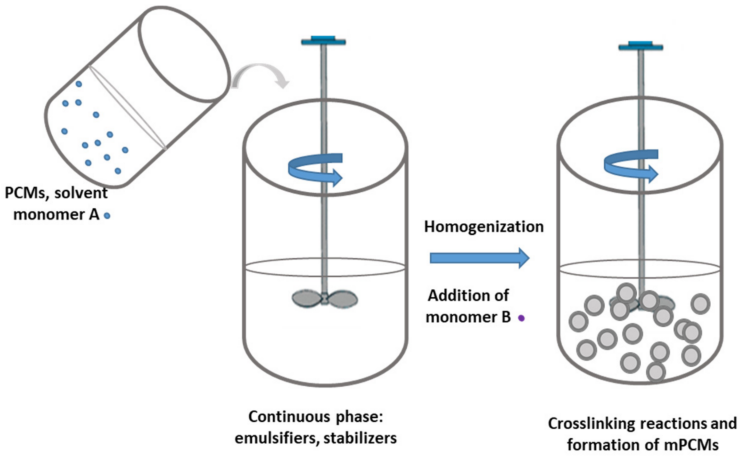


Figure 7. Schematic representation of the microencapsulation process by interfacial polycondensation.

The aggregation of particles during encapsulation is one of the main drawbacks of this method. To overcome this shortcoming, many parameters should be studied, such as stirring speed during the formation of droplets and during the addition of the second monomer, time and temperature of encapsulation step, and the influence of catalysts. It was reported that the polymerization process could be improved by increasing the temperature and time of encapsulation and adding catalysts. Moreover, the decreasing stirring rate before the addition of the second monomer suppresses the aggregation of particles. However, it was also necessary to deposit the initial coating layers at a higher stirring speed to avoid coalescence and the formation of unstable microcapsules [122].

Polyurea is commonly synthesized in encapsulation by interfacial polycondensation due to its excellent mechanical properties [123] but poor thermal stability and compactness [124,125]. Cyclohexane, as a solvent, is employed to promote the diffusion of monomers from the oily phase to the interface. However, a high proportion of solvent in the dispersed phase decreases the PCM's loading content in microcapsules and the encapsulation efficiency. Thus, Siddhan et al. preconized using a small volume of cyclohex-

ane and a weight ratio PCM to cyclohexane about 6 to ensure the formation of the shell material [122].

The double-layered shell polyurea/polyurethane was employed in the encapsulation of *n*-octadecane by Lu et al. to improve the thermal stability and compactness of the microcapsules [126]. The formation of the shell requires the use of polyisocyanate, aromatic and aliphatic monomers. The use of methylene diphenyl diisocyanate (MDI) or toluene diisocyanate (TDI) leads to the formation of an undesirable phenylamine compound [127], whereas this is not obtained with isophoronediisocyanate (IPDI) [128].

The use of a solvent allows adapting the physicochemical properties of the dispersed phase to ensure the formation of a stable emulsion and optimize the chemical reaction at the interface. Nevertheless, in the frame of development of the microencapsulation process without organic solvent, some studies were realized to adjust the formulation of the PCMs to ensure the total miscibility of the isocyanate monomer in this phase. Therefore, the PCMs formulation was based on fatty acid. For instance, butyl stearate was used as co-PCMs to paraffin to allow the miscibility of TDI [129] or IPDI [130] for the formation of polyurea/polyurethane double shell or polyurea microcapsules. Furthermore, using aliphatic isocyanate allows controlling the polycondensation rate, obtaining a uniform and compact microcapsule shell. Yin et al. used ethyl palmitate to solubilize IPDI and tetraethylorthosilicate (TEOS), at 30 °C, as monomer or precursor for the shell formation through interfacial polycondensation [131]. The presence of TEOS led to the formation of a polyurea-polyurethane-SiO_2 shell, allowing to enhance the thermal stability of the mPCMs. Cai et al. studied the encapsulation of fatty acid ester as PCM material to justify that the solvent-free process was more straightforward and effective [132]. The formation of polyurea membranes by interfacial polycondensation is not limited to the use of amine monomers. For example, the use of chitosan, a bio-based polymer, as a complementary monomer to isocyanates has been developed in recent years, as described in the work of Gao et al. for the encapsulation of PCMs [133].

Commonly shell materials used in chemical processes and the properties of developed mPCMs are illustrated in Table 3.

Table 3. Commonly used shell materials in chemical process and mPCMs properties.

Method	Shell	Core	T_m mPCMs (°C)	LC (%)	ΔH_f (J·g^{-1})	Size (µm)	Ref.
Suspension polymerization	St/MMA	Paraffin	42	43	88	-	[84]
	PMMA	Caprylic acid	14	66	98.7	2–10	[85]
	TiO_2-PMMA	*n*-Octadecane	25	73	84–142	10–20	[134]
	OMA/MMA	*n*-Octadecane	26	21	93	1.6–1.7	[135]
Emulsion polymerization	PMMA	Paraffin	24–33		101	0.5–2	[93]
	PMMA	SA-Eicosanoic	57	69	126	0.046	[94]
	PMMA	SA	55	52	102	0.29	[95]
	PMMA	Paraffin wax	52–55	88	115	18	[96]
	Polystyrene	LA	44		167	1.32	[97]
Dispersion polymerization	MF	Hexadecane	-	79	162	3.9	[102]
In situ polymerization	MF	*n*-Octadecane	-	40	120	4	[104]
	MF	*n*-Tetracosane	53	25	135	2–20	[105]
	MF	*n*-Hexadecanol	51	79	171	10–60	[106]
	MF	1-Dodecanol	20	41	79	0.49	[107]
	PUF	CA	30	-	129	0.66	[112]
	PMF	CA	29	-	34	0.32	[112]
	PMUF	CA	29	54	61	0.29	[112]

Table 3. *Cont.*

Method	Shell	Core	T_m mPCMs (°C)	LC (%)	ΔH_f (J·g^{-1})	Size (μm)	Ref.
	MUF	*n*-Dodecanol	21	91	131	38	[113]
	MF/MMF	*n*-Dodecanol	28	50–83	110–181	0.71–6.28	[114]
	MMF/BMF	*n*-Dodecanol	24	50	100	2–5	[115]
	CNFs/MF	1-Dodecanol	26	50	100	1–3	[119]
	PNDA/MF	*n*-Dodecanol	32	-	110–141	0.08–0.14	[136]
Interfacial polycondensation	Polyurea	*n*-Octadecane	-	70	-	7.3	[122]
	Polyurea/polyurethane	*n*-Octadecane	29	-	143	3–5	[126]
	Polyurea/polyurethane	Butyl stearate paraffin	28–35	40–60	58–87	5–15	[129]
	Polyurethane	Butyl stearate	22	-	80	10–35	[130]
	Polyurea	Ethyl palmitate	19	62	123	10	[131]
	Polyurethane	Ethyl palmitate	17	55	110	10	[131]
	SiO_2/polyurea	Ethyl palmitate	22	59	120	10	[131]
	SiO_2/polyurethane	Ethyl palmitate	17	61	122	10	[131]
	Polyurethane	Dodecanol dodecanoate	32	54–74	103–140	10–40	[132]
	c-PU	Butyl stearate	24	-	106	4.46	[133]

4.2. Physical Process

In the physical process, the shell is mechanically condensed above the principle active without any chemical reaction, leading to microcapsules with a mean diameter above 100 μm. The commonly used physical methods are pan-coating, fluidized bed, air-suspension coating, spray drying, centrifugal extrusion, and electrohydrodynamic processes [23].

4.2.1. Spray Drying

Spray drying consists of dispersing PCMs in an aqueous coating medium into a heated chamber where solvent evaporation takes place to rigidify the microcapsules shell. Firstly, the emulsion is sprayed in tiny droplets with an atomizer. Then, sprayed droplets are carried by the gas stream at an adequate temperature for the solvent's complete evaporation. Finally, solid particles treated by the gas phase are collected using a cyclone, filter bag, or electrostatic precipitator [37].

The benefits of this process are its low cost, high yield production, and partial versatility [137]. Meanwhile, the main drawbacks are particles aggregation and the use of high temperature [138]. Borreguero et al. encapsulated paraffin Rubitherm®RT27 using polyethylene-ethyl vinyl acetate (LDPE-EVA) as a copolymer [139]. They obtained homogeneous microcapsules with small particle sizes and high microencapsulation efficiency. The shape of microcapsules collected from the collection vessel was more defined and homogeneous than those collected into the drying chamber (Figure 8). Nevertheless, one of the main drawbacks of this process is the aggregation taking place in the drying chamber, which can be minimized by controlling the temperature or using a high stream of the gas carrier.

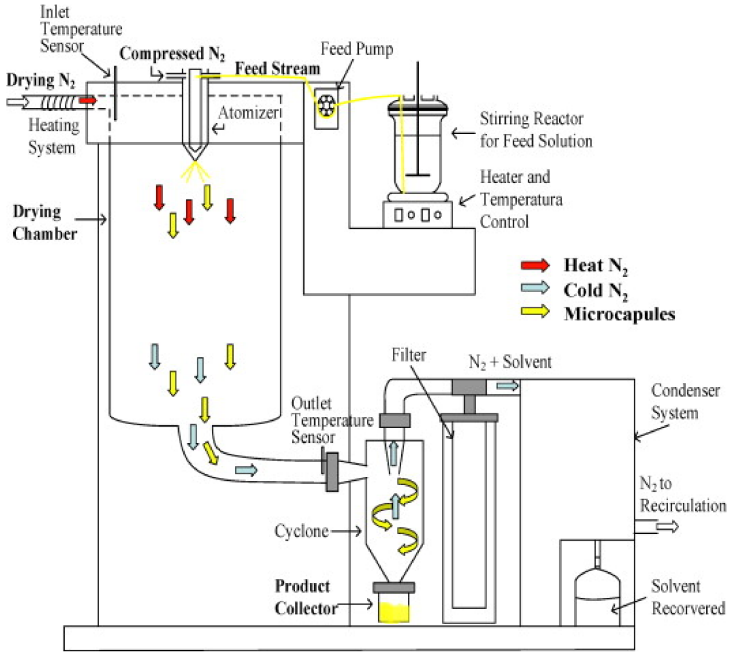


Figure 8. Schematic representation of the principle of spray-drying process [139].

Zuo et al. employed a spray-drying method to prepare polylactic acid (PLA)/sodium monofluorophosphate microcapsules [140]. They obtained porous microcapsules with lower encapsulation efficiency due to the low viscosity of PLA. The spray pressure regulation influenced the particles size.

4.2.2. Electrohydrodynamic Encapsulation

The electrospraying process is one-step electrohydrodynamic atomization. The polymeric solution is polarized by applying electrical forces. Then the charged liquid is stretched and accelerated into a jet of charged droplets by the electrostatic force generated at the droplet surface. Then, the charged jet breaks up into tinier charged droplets by coulomb repulsion forces. Finally, the micro/nanoparticles are collected after the evaporation of the solvent.

Electrospraying has become a promising technique of PCMs microencapsulation due to its advantages, such as high encapsulation efficiency, high core loading content, and easy handling. Moreover, this method does not include any toxic chemical additives or surfactants; thus, it is considered a sustainable method.

Furthermore, the morphology of particles could be controlled by optimizing different parameters and choosing nozzle geometry. The single nozzle is employed in the preparation of simple core/shell microcapsules. In contrast, using a coaxial double or tri-capillary nozzle allowed double-layered shell microcapsules to enhance properties (Figure 9) [141].

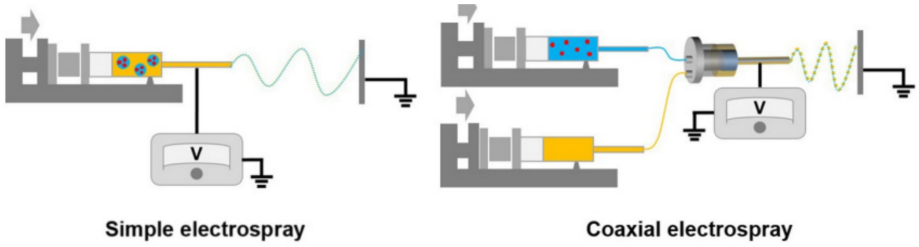


Figure 9. Schematic representation of experimental setup for simple electrospray (**left**) and coaxial electrospray (**right**) [141].

Electrospinning is widely used with the phase change materials to prepare core-sheath structure nanofibers via a coaxial system as an electro atomization method. For instance, a coaxial spinneret was performed by Rezaei et al. to prepare polyethylene glycol and cellulose acetate as PCMs and shell solutions for the fabrication of nanofibers [142].

Nevertheless, the encapsulation of PCMs by electrospraying is scarcely reported in the literature. Moghaddam et al. synthesized *n*-nonadecane/sodium alginate by coaxial electrospraying process [143]. They observed that the size distribution increased with the increase in alginate concentration and the increase in the volumetric flow rate of the core/shell solution. The diameter of microcapsules was lower than 100 μm, and the loading of contained *n*-nonadecane was about 56 wt%. Following the same method, they encapsulated *n*-nonadecane using sodium alginate and calcium chloride as shell materials. They concluded that the mean diameter of microcapsules increased with alginate concentration, feeding rate, needle-to-collector distance, and stirrer rate, and decreased with needle gauge and needle-to-tip collector length. Nonetheless, they indicated that optimizing operating conditions leads to alginate/PCMs in the nanoscale (80–350 nm) [144].

Zhang et al. encapsulated *n*-hexadecane and *n*-eicosane in a polycaprolactone matrix [145]. Ethyl acetate (EA) and chloroform (Chl) were employed as solvents. They denoted that the mean diameter depends on the nature of core materials and the type of solvent. The morphology of the microcapsules and the loading content were affected by the solvent evaporation and the phase separation between the PCM and poly(caprolactone) (PCL) matrix. They also used the coaxial system to prepare microparticles using *n*-hexadecane/polycaprolactone (PCL) [146]. They demonstrated that the increase in *n*-hexadecane and PCL concentration led to a change in the particle size distribution from a poly-disperse to monodisperse size distribution and a modification in the surface state from porous to non-porous. This study leads to the preparation of spherical microcapsules with a mean diameter of 10–20 μm and high encapsulation efficiency (96%).

4.3. Physicochemical Process

4.3.1. Coacervation

The coacervation involves a reaction between two or more oppositely charged polyelectrolytes (polycation and polyanion). The polycation is usually gelatin, while the polyanion is Arabic gum (acacia). There are two techniques of coacervation, the simple and the complex one.

The complex coacervation involves three steps carried out under continuous agitation, i.e., (i) the preparation of emulsion by dispersing PCMs into an aqueous phase containing polycation; (ii) the formation of coating material by the addition of an aqueous solution containing oppositely charged polyanion (in this step the medium pH should be adjusted in a way to induce the separation phase and to ensure the deposition of coating materials on the oil interface), and; (iii) the stabilization of the microcapsules by crosslinking, desolvation or thermal treatment (Figure 10).

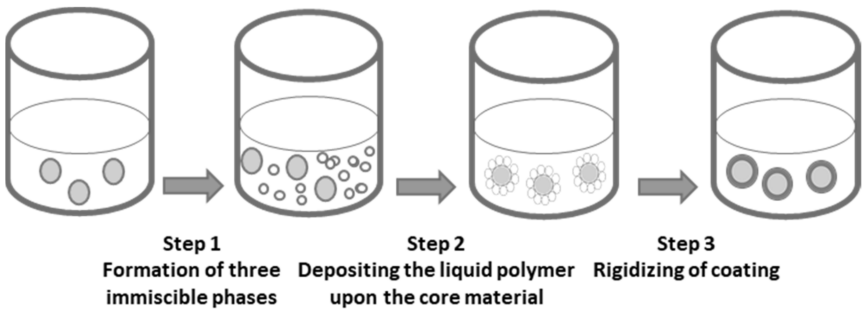


Figure 10. Schematic representation of the different stages of the microencapsulation process by coacervation process.

Microcapsules morphology and stability could be improved by adjusting pH and introducing an adequate amount of surfactants at higher stirring rates [147]. In addition, microencapsulation efficiency is affected by the operating parameters such as PCMs/polymers weight ratio, emulsion time and the chemical nature, and the amount of crosslinking agent [148].

Complex coacervation is based on the interactions between two oppositely charged polyelectrolytes to undergo a liquid-liquid phase separation. Gelatin/gum Arabic, gelatin/sodium alginate [149], chitosan-co-poly(methacrylic acid) copolymer [150], or gum Arabic/chitosan [151] were selected to encapsulate PCMs.

Demirbağ et al. reported developing with enhanced flame-retardant properties by coacervation technique [149]. They encapsulated *n*-eicosane as PCMs, and they used different shells such as aluminum oxide nanoparticle doped gelatin/gum Arabic and gelatin/sodium alginate. They observed a significant enhancement in their thermal stability and flame-retardant performance. Clay nanoparticles (clay NPs) doped gelatin/sodium alginate shells were also used as shell materials. They obtained a well-defined core-shell structure with a smooth surface. The presence of clay NPs improved the thermal stability of the microcapsules compared to microcapsules containing only gelatin/sodium alginate shell materials.

Tan et al. employed this process to encapsulate hexadecane-eicosane mixture using chitosan-co-poly(methacrylic acid) copolymer [150]. The acrylic copolymer was not only one of the polyelectrolytes but also acted as an emulsion stabilizer during the coacervation process to obtain an encapsulation efficiency of about 84% for loading PCMs content 66%. Butstraen and Salaün prepared gum Arabic/chitosan microcapsules containing a commercial blend of triglycerides as core material [151]. They optimized the process parameters (phase volume ratio, stirring rate and time, pH, reaction time, biopolymer ratio, and crosslinking agent), affecting a stable emulsion and shell formation during the microencapsulation process. The optimal conditions, in this case, are pH = 3.6, a weight ratio of chitosan to acacia gum of 0.25, a volume ratio of the dispersed and continuous phases of 0.1, and an emulsion time of 15 min at 11,000 rpm.

4.3.2. Sol-Gel

Sol-gel is the abbreviation for "solution-gelling". It is a process by which essentially inorganic materials are synthesized. Sol (solution) is a stable dispersion of polymers or colloidal particles with diameters of (1–100 nm) in a solvent prepared at low pH. This solution is prepared through polycondensation reactions of monomers (or precursors) already hydrolyzed to polymerize and form sol nanoparticles. To maintain the resulting particles suspended, they should have van der Waals-type interactions that require sufficiently small particles.

The formed amorphous "gel" is characterized by a large number of pores (<1 μm) containing liquids (solvents and non-reacting monomers) and smaller polymer chains [152]. As the reaction progresses, the smaller polymer chains are consumed, and solvents and monomers diffuse less in the pores. The material densifies and stabilizes when some parts depolymerize and polymerize again, resulting in well-compact gel and releasing some solvent that needs to be eliminated by drying. The formation of long macromolecular chains can induce their aggregation. As a result, the viscosity increases, and the solution undergoes a transition to a gel characterized by an infinite three-dimensional network structure (Figure 11).

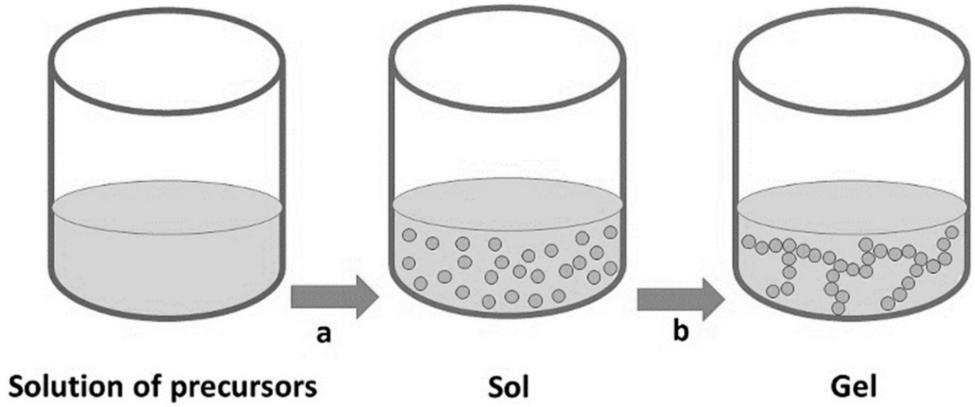


Figure 11. The condensation of precursor and gelation step [37].

Various physicochemical parameters such as the phases (solvents, precursors), temperature, pH, or drying, influence the sol-gel transition process (gelling). These parameters determine the reaction mechanisms and kinetics and thus the final properties of the material. Parameters must be studied and adapted to specific applications.

Different studies used the sol-gel method to encapsulate PCM materials by inorganic shells. Therefore, inorganic materials have attracted significant attention thanks to their excellent properties, such as high thermal conductivity, non-flammability, and durability.

- Silica shell

Many studies have reported synthesizing encapsulated PCMs with an inorganic shell (SiO_2) using the sol-gel process. Most of the resulting capsules with SiO_2 shells showed a well-defined core/shell structure with excellent shape stability. It was indicated that PCM/SiO_2 microcapsules revealed a high thermal energy storage capacity and an improved thermal conductivity.

Zhang et al. used silica as a shell material to encapsulate *n*-octadecane [153]. They indicated that the microcapsules exhibited a spherical shape of 7 to 16 μm in diameter, with a smooth and compact shell structure. An enhancement of *n*-octadecane thermal conductivity was observed after encapsulation with the silica shell. Moreover, it was also mentioned that some low-cost silicon sources such as sodium silicate and oil shale ash could be used to synthesize encapsulated PCMs, making them more cost-effective [154,155]. He et al. developed *n*-alkanes microcapsules using sodium silicate as a silica source [156]. They investigated the influence of pH values, and they obtained microcapsules having a regular spherical shape with a mean diameter of 8 μm by adjusting pH values between 2.95 and 3.05 (Figure 12). The synthesis of paraffin/SiO_2 was also carried out in acidic conditions by Fang et al. [157]. The pH adjustment in the 2–3 pH range led to the formation of the particles with a PCM content of 87.5%.

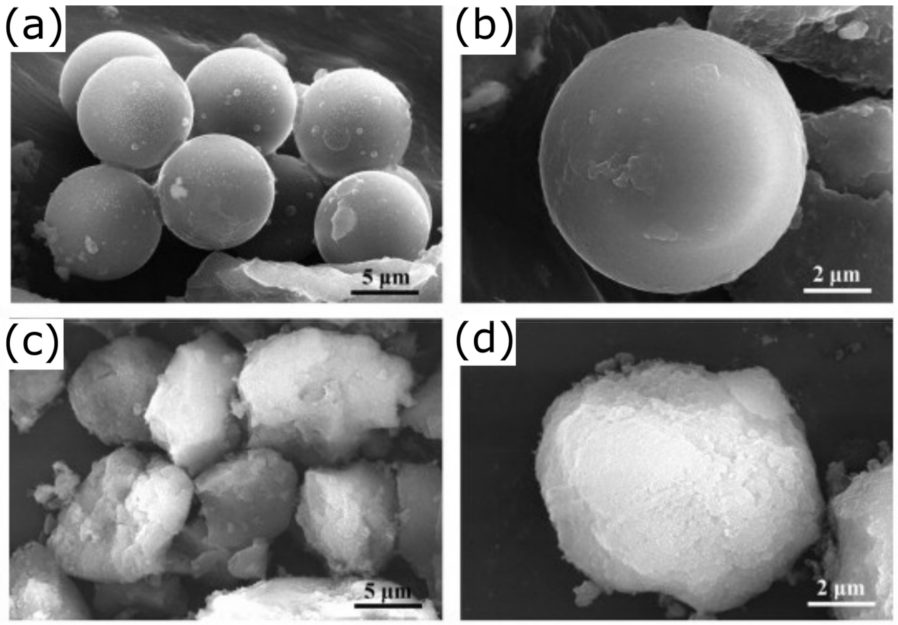


Figure 12. SEM micrographs of *n*-octadecane/sodium silicate mass ratios and pH values: (**a**,**b**) 50/50 and pH between 2.95 and 3.05; (**c**,**d**) 50/50 and pH between 7 and 8 [156].

The weight ratio precursor to PCM in the formulation influences the morphology of the microcapsules and the landing capacity and, therefore, heat storage properties [158]. An increase in silica precursors, such as methyltriethoxysilane (MTES), led to increased surface particle roughness due to the silica aggregates deposition onto it. Thus, the core to shell ratio decreased, decreasing the phase change enthalpy of the mPCMs. On the other hand, Chen et al. have shown the increase in emulsifier and dispersed to continue phases volume ratio allowed to enhance the encapsulation efficiency [159].

Sol-gel processes also allow the designing of PCM submicromic capsules. In this way, the emulsion step and the hydrolysis and condensation reactions conditions played a key role in the particle properties. Thus, the formulation parameters such as the concentration of silica precursor, the effect of ethanol, and the ammonia to TEOS ratio were investigated to determine their impact on the particle size. According to Yuan et al., the mean diameter of the submicromic particles increases with the increase in TEOS or ammonia in the system [160]. Li et al. have realized their emulsion from an ultrasonic dispersion with a high surfactant content to ensure the formation of submicromic droplets in an alcohol medium [161]. The condensation of the silica species was initiated by dripping ammonia. The obtained rough particles with a mean diameter of 200 to 500 nm exhibited a latent heat of about 45.5 $J \cdot g^{-1}$, corresponding to a loading content of 31.7%. The pH of the condensation step has a strong influence on the particle size and, therefore, on the heat storage capacity related to the PCM loading content [162].

- Titania shell

Improving the structural and thermal performance of encapsulated PCMs is a challenge that researchers are exploring. In this context, many works have been directed toward the synthesis of the titanium oxide (TiO_2)-based membrane to avoid leakage problems and protect the PCM after many heating/cooling cycles. TiO_2 is mainly chosen because of its thermal and mechanical properties and as a chemically inert material. The formation of TiO_2 shell consists of the hydrolysis of titania organic precursors (titanium (IV) isopropoxide, titanium (IV) butoxide (TNBT), titanium (IV) ethoxide, etc.) before the polycondensation of the TiO_2 sol on the PCM droplets (Figure 13). Particle size is controlled by formulation parameters such as weight ratios of surfactant to PCM, PCM to solvent, and PCM to precursor, and by process parameters such as stirring time and speed.

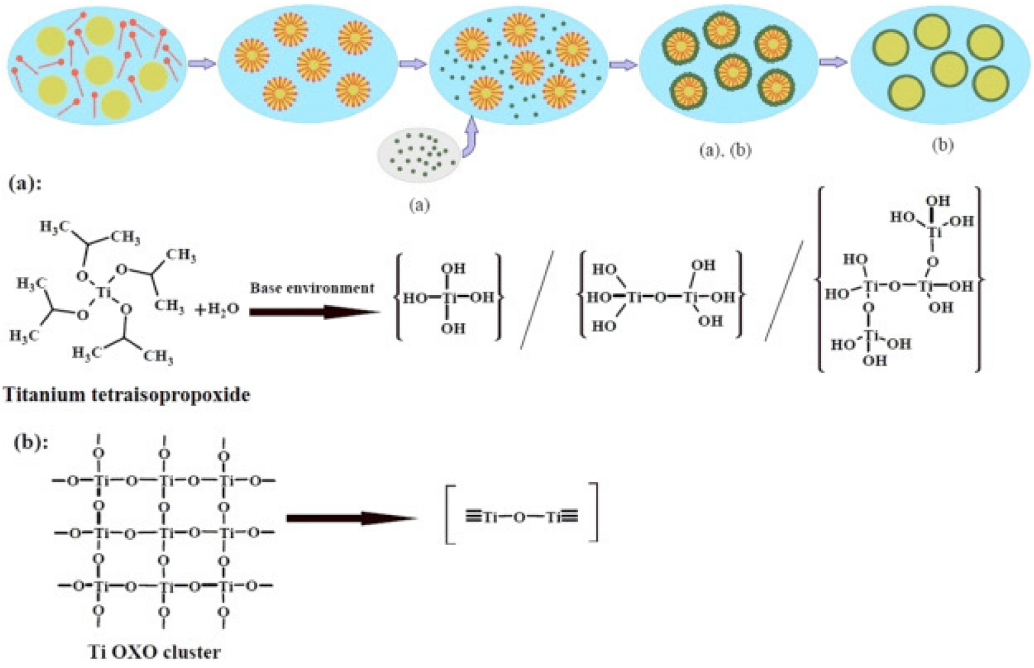


Figure 13. The hydrolysis and condensation steps of titania precursor [163].

Latibari et al. encapsulated SA using TiO_2 as a shell material through the sol-gel method under alkaline pH conditions [163]. Titanium tetraisopropoxide was used as a TiO_2 precursor. They obtained particles with a nano spherical shape with a size distribution between 583 and 946 nm and showed suitable chemical stability and thermal reliability. The influence of the SA/TiO_2 weight ratio and pH values were investigated. They noticed that the encapsulation efficiency of the microcapsules increased by increasing the SA/TiO_2 weight ratio, and the most suitable pH for the formation of nanocapsules was about 10.

However, Li et al. encapsulated stearic acid with amorphous TiO_2 composites, and they indicated that acidic pH was more effective in preparing the composite PCMs than under alkaline pH conditions [164]. Yanghua et al. prepared LA/TiO_2 microcapsules. They established that encapsulation efficiency depended on the amount of anhydrous ethanol used to prepare the precursors mixture. It influenced the kinetics of the hydrolysis and condensation reactions of tetrabutyl titanate [165].

Cao et al. reported the encapsulation of PA using the same method [166]. Diluting the precursor in ethanol solution decreases the hydrolysis pull kinetics, which promotes the formation of a denser and more even membrane upon condensation of the hydrolyzed precursors. On the other hand, an excess of ethanol also limits polymerization. Thus, control of membrane formation is achieved by adjusting the amount of ethanol. The encapsulation efficiency is controlled by the choice of precursor. Furthermore, the surfaces of the microcapsules become more homogeneous and smoother in decreasing the mass ratio of the TNBT to ethanol [167].

Other studies have focused on replacing the continuous medium to limit the reaction kinetics of the titanium-based precursors. Thus, Chai et al. chose to use formamide [168], while Zhao et al. preferred to use anhydrous ethanol to realize an oil-in-water emulsion [169]. This choice, restricted to PCMs not reacting with ethanol, allowed to obtain spherical particles with an average diameter between 2 and 5 µm, presenting suitable physical and thermal properties for the targeted application. Furthermore, they showed that the sizes of the microcapsules were not affected by *n*-octadecane/TNBT weight ratio. They also indicated that a few scattered particles were distinguished on the surface of the microcapsules. The precipitation of TiO_2 particles on the microcapsules was related to the increase in deionized water amount during the synthesis.

- Other inorganic shells

PCMs were also encapsulated by other inorganic materials or metal oxides such as $CaCO_3$ and Al_2O_3 to enhance the thermal properties such as thermal conductivity and thermal stability [170–172]. Pan et al. have successfully developed a new type of mPCMs through the sol-gel process using AlOOH as the shell precursor [173]. They de-noted that the thermal conductivity of the mPCMs was higher than that of PA one.

The examination of various studies dealing with different encapsulation techniques of PCMs permitted us to realize a comparative approach that allows identifying the advantages and the disadvantages of each route (Table 4).

Table 4. Comparison of different encapsulation methods.

Process	Advantages	Drawbacks
Suspension polymerization	Uniform spherical particles; suitable heat control of the reaction; cost-effectiveness.	Process adapted only for water-insoluble monomers; coalescence of particles during polymerization.
Emulsion/miniemulsion polymerization	The possibility of employment of high molecular weight polymer; kinetics of polymerization.	Adjuvants and surfactants remain in the polymer; difficult control of polymerization step.
Dispersion polymerization	Encapsulation in a single-step process.	
In situ polymerization	Uniform coating.	The release of free formaldehyde.
Interfacial polymerization	High mechanical resistance.	Aggregation of particles.
Spray drying	Reproducible; cost-effectiveness; homogeneous particles; suitable controlling of particle size [139].	High temperature; agglomeration of particles; remaining uncoated particles [174]; low thermal transfer efficiency; not adapted for inorganic PCMs [175].
Electrospraying	One-step green process; high encapsulation efficiency; easy handling; non-toxic chemical additives nor surfactants.	Frequent clogging of the nozzle tip; the nozzle tips are more easily plugged by the used fluid or particulates; very low flow rate for smaller droplets [176].
Coacervation	Efficient control of particles size and shell thickness [174].	Employment of toxic chemical agents; residual solvents and coacervating agents on the capsules surfaces.
Sol-Gel	High thermal conductivity; suitable mechanical resistance; thermal stability; chemical inertness; non-toxicity.	Long reaction time; expensive row material [87].

5. Multifunctional mPCMs

In the last few years, continuous improvements have been made to the mPCMs performance in terms of thermal conductivity, thermal and chemical stability, and durability. However, the challenge of recent researches was to develop innovative mPCMs by adding new functionalities to the PCMs microcapsules.

Rodríguez-Cumplido et al. reported in their work different nanocapsules and microcapsules developed recently, and they discussed different encapsulation possibilities to integrate new functionalities to the encapsulated PCMs or to enhance their thermal properties [177]. In Figure 14, it was summarized three ways to reach this purpose, i.e., (i) the addition of additives within the core materials, (ii) the development of encapsulated PCMs with hybrid shells, and (iii) the development of encapsulated PCMs with multiple shells.

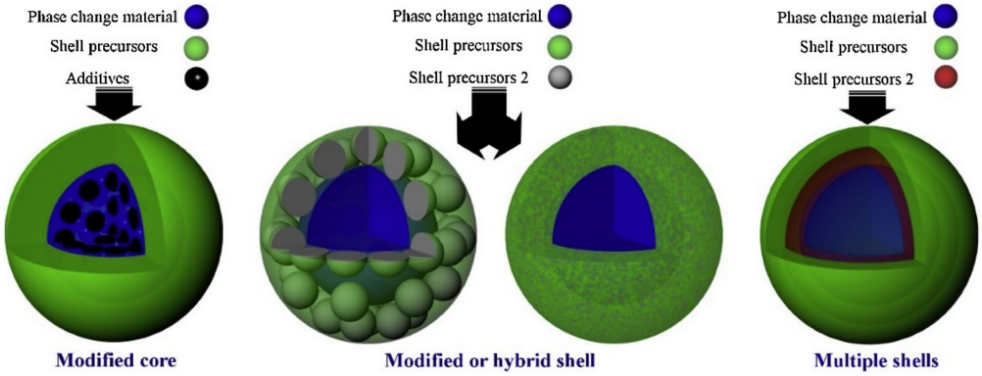


Figure 14. Different shape of multifunctional mPCMs [177].

5.1. Multifunctional mPCMs

5.1.1. Photocatalytic and Antibacterial Activity

The design of mPCMs exhibiting various functions and latent heat storage using an inorganic shell has gained growing interest. Due to the functional properties of inorganic materials, it was possible to give other functionalities to mPCMs. Several photocatalytic materials, such as metal oxides (TiO_2, ZnO, SnO_2, Fe_2O_3, WO_3, In_2O_3), sulfides (ZnS), precious metal semiconductors (AgI, Bi_2O_3, Bi_2WO_6), and nonmetallic semiconductors, were employed in the encapsulation of PCMs.

Double layers shells were designed by combining functional materials and silica for antibacterial and solar photocatalytic properties. Liu et al. encapsulated *n*-eicosane with silica/Cadmium sulfide (CdS) as a double-layered shell through the sol-gel method, followed by in situ precipitation [178]. They indicated that the thermal conductivity of *n*-eicosane was significantly improved from 0.15 to 1.02 $W \cdot m^{-1} \cdot K^{-1}$ due to the shell materials. In addition, they noted that the CdS is a promising semiconductor material activated by visible light. They denoted that *n*-eicosane/silica-CdS microcapsules presented an excellent photocatalytic activity to decompose pollutants, which is confirmed by the photo-degradation of about 90 wt% of methylene blue (MB) after 4 h of sunlight illumination. Microcapsules composed of the *n*-eicosane and SiO_2/Ag double-layered shell were de-signed by Zhang et al. via interfacial polycondensation process followed by silver reduction [179]. They indicated that the antibacterial test showed that the microcapsules have suitable reactivity against *Bacillus subtilis* and *Staphylococcus aureus*.

Fei et al. prepared *n*-octadecane/titania microcapsules through the aerosol process with a hydrothermal post-treatment [180]. They demonstrated that the obtained mPCMs have an enthalpy of 92–97 $J \cdot g^{-1}$ with photocatalytic, antibacterial activities, and reacting with mercaptans. Chai et al. developed *n*-eicosane/TiO_2 (crystalline form) [168]. Due to the crystalline TiO_2 shell materials, the mPCMs presented a better photocatalytic effect, which could also be an antimicrobial for some Gram-negative bacteria. They indicated that the developed microcapsules have great potential for food preservation and sterilization, medical protective clothing, solar energy storage, etc. Several studies have suggested doping TiO_2 with nitrogen, carbon material, or by combining it with another metal oxide to improve its photocatalytic activity in visible light.

Liu et al. used ZnO-doped TiO_2 to develop dual-responsive mPCMs with solar photocatalytic activity and enhanced solar energy storage [181]. On the other hand, antibacterial activity was obtained due to the presence of ZnO. Therefore, the developed dual-responsive mPCMs presented significant properties for heat energy storage, medical and photocatalytic applications.

ZnO was used as a shell material to develop *n*-eicosane microcapsules for thermal energy storage, antibiosis photocatalytic, and antibacterial activities [182]. The bifunctional microcapsules were synthesized via in situ precipitation method in an O/W emulsion system. The mPCMs exhibited excellent phase change performances with a latent heat of about 140 $J \cdot g^{-1}$ and high encapsulation efficiency. Furthermore, they depicted that the microcap-

sules revealed a high photocatalytic activity. The antibacterial experiments showed that the developed materials have a high antibacterial response against *Staphylococcus aureus.*

5.1.2. Photothermal Conversion Activity

The choice of inorganic materials for shell materials for photothermal conversion property is a suitable alternative to polymeric materials due to their better durability, flame retardancy, and thermal and chemical stability. These materials of various species can be used alone or coupled with other additives to improve the thermal properties. Jiang et al. used calcium carbonate ($CaCO_3$) to improve the solar thermal conversion of paraffin [183]. They established that paraffin/$CaCO_3$ microcapsules have an excellent light to heat energy conversion property. PCMs double-layered microcapsules were used as photothermal materials that convert solar light to heat in heat transfer fluids for direct adsorption in solar collectors. Ma et al. encapsulated paraffin with SnO_2/CNTs composite shell for the same dual application through in situ precipitation [184]. Graphene oxide (GO) was recognized as an excellent material to increase light absorption in the visible region of mPCMs. Yuan et al. [185] developed paraffin/SiO_2/graphene oxide (GO) bifunctional microcapsules. The developed microcapsules showed suitable thermal characteristics with melting point and melting enthalpy of 57.5 °C and ~80 $J \cdot g^{-1}$, respectively.

Paraffin/graphene-melamine-formaldehyde mPCMs were synthesized via in situ polymerization [186]. Graphene was not only used to improve the thermal properties but also to stabilize the Pickering emulsion. Two of the main interests of the presence of graphene were relied on to the suppression of the leakage problem and the increased of the light-to-thermal conversion efficiency up to 90.7%.

Copper (I) oxide was also used to convert sunlight into thermal energy. The self-assembly process synthesized paraffin/Cu_2O-Cu microparticles. The thermal conductivity of the microcapsules was about 0.92 $W \cdot m^{-1} \cdot K^{-1}$, while that of PCM was only 0.25 $W \cdot m^{-1} \cdot K^{-1}$, which allows for a high photothermal conversion efficiency [187]. Adding CNTs in this PCM formulation allowed increasing the thermal conductivity by 1.6% and 1.8% at 30 and 80 °C, respectively, and has improved the photothermal conversion performance of the microcapsule slurry [188].

5.1.3. Photoluminescence Activity

Zhang et al. encapsulated *n*-eicosane with zirconium oxide (ZrO_2) shell using a sol-gel method for photoluminescence property [189]. The melting temperature and latent heat of *n*-eicosane/ZrO_2 with a mass ratio of 50/50 wt% were 43.75 °C and 123.4 $J \cdot g^{-1}$, respectively. They showed that after being excited by UV radiation, the photoluminescence test indicated that the developed mPCMs have significant fluorescent characteristics, which can be used for thermosensitive and photosensitive sensors, intelligent textiles, electronic devices, etc. These different properties can be improved by adding rare earth in the mixture, allowing notably excellent thermal reliability over several freeze/melt cycles, with a latent heat of phase change about 139–163 $J \cdot g^{-1}$ [190]. The rare earth element Ce^{3+} was also used to dope the $CaCO_3$ shell obtained by self-assembly precipitation and improve the photoluminescence activity of the microcapsules [191].

5.1.4. Miscellaneous Properties

The use of MnO_2/SiO_2 hybrid shell to entrap *n*-docosane exhibited suitable thermal properties and high electrochemical effectiveness for Li-ions battery cells application and thermoregulatory electrode systems in supercapacitors [192]. Kalaiselvam et al. encapsulated a binary mixture of oleic acid and polyethylene glycol SiO_2/TiO_2 double shell via a sol-gel process followed by the consecutive adsorption of the ionic layer for suitable electrode materials for electrochemical energy storage and cold thermal energy storage [193].

The superparamagnetic properties of membranes can be provided by the presence of Fe_3O_4 for applications in biotechnology and bio-engineering. In this case, these particles can also stabilize Pickering emulsions. The work of Li et al. has led to the encapsulation of

n-eicosane or *n*-docosane by TiO_2/Fe_3O_4 [194] and SiO_2/Fe_3O_4 [195,196]-based membranes, respectively. The resulting microcapsules have shown great potential in intelligent textiles, stealth aircraft, and other military systems, etc.

n-eicosane/CuO-doped polyuria and *n*-octadecane/TiO_2 doped PMMA microcapsules were developed through interfacial polymerization [197] and suspension-like polymerization [134], respectively. Both shells spared damage caused by ultraviolet light in textiles applications. The thermochromic function was achieved by Wang et al. by the employment of thermochroic pigment-PMMA composite shell in the encapsulation of *n*-octadecane via suspension-like polymerization method [198]. Guo et al. used poly(MMA-co-MAA) to encapsulate *n*-eicosane via an in situ polymerization process that led to obtaining pH-responsive microcapsules to be used as drugs or chemicals sensitive to temperature during thermal energy storage [199].

6. Conclusions

This paper reports research carried out on the encapsulation of phase change materials for energy storage applications. Several requirements must be considered for selecting PCMs, such as the temperature of phase change transitions, density, and their associated enthalpies. The TES applications can be classified as high-, medium-, and low-temperature areas. In high-temperature applications, inorganic materials are the most used, while on the lower and medium side, organic materials such as commercial paraffin and fatty acids are employed. For practical use, microencapsulation techniques were employed to enhance the thermal properties of materials and limit leakage and contamination during application. The PCM microencapsulation methods were classified into three categories, i.e., (i) chemical, (ii) physical, and (iii) physicochemical ones. The choice of one of these microencapsulation techniques is not only based on the desired characteristics of the microcapsules, such as their size, core and shell materials, and thermal and mechanical properties, but also by taking into account the advantages and the drawbacks of the different processes. In recent years, research has focused not only on the development of more environmentally friendly processes and the choice of new materials for membrane synthesis but also on new functionalities. Thus, mPCMs have become multifunctional, where the membrane protects the active from the external environment, improves heat transfer, or provides a complementary activity to that of energy storage. These new functionalities are either brought by a modification of the PCMs formulation with notably the incorporation of additives or by new membranes, whether hybrid or multilayer. Thus, the development of multifunctional microcapsules extends application areas (e.g., pollutants degradation by photocatalytic activity, antibacterial for medical application, photoluminescent for thermosensitive and photosensitive sensors, etc.).

The efficiency of thermal energy storage technology is strongly dependent on the cost-effectiveness of the technology and the selected raw materials. In the large-scale application of thermal energy storage, the essential areas are reducing the cost of storage materials and maintaining high energy storage efficiency. Thus, improving the thermal conductivity of thermal energy storage materials is a significant priority. Therefore, our future study will focus on optimizing the thermophysical properties of PCMs and investigating conductor materials that improve the heat transfer and stabilize the shape of PCMs. In addition, exploring the cost-effectiveness of microencapsulated PCMs manufacturing technologies will be beneficial and contribute significantly to the future direction of phase change materials research.

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Abbreviations

TES: thermal energy storage; PCMs, phase change materials; mPCMs, microencapsulated phase change materials; SHTES, sensible heat thermal energy storage; LHTES, latent heat thermal energy storage; TCS, thermochemical; Cp, specific heat; SA, stearic acid; PA, palmitic acid; MA, myristic acid; LA, lauric acid; CA, capric acid; MF, melamine-formaldehyde resin, UF urea-formaldehyde resin, PU polyuria; PS, polystyrene; St, styrene; MMA, methyl methacrylate; PMMA polymethyl methacrylate; SMA, styrene-maleic copolymer; MMF, methanol-modified MF; MMF, methylated melamine-formaldehyde; BMF, butylated melamine-formaldehyd; Fe_2O_3, iron(III) oxide; ZnO, zinc oxide; TiO_2, titanium dioxide, CNFs, cellulose nanofibers; MDI, methylene diphenyl diisocyanate; TDI, toluene diisocyanate, IPDI, isophoronediisocyanate; TEOS, tetraethylorthosilicate; SiO_2, silicon dioxide; PLA, polylactic acid; PCL, polycaprolactone; MTES, methyltriethoxysilane; TNBT, titanium (IV) butoxide; $CaCO_3$, calcium carbonate; CdS, cadmium sulfide; SnO_2, stannic oxide, GO, graphene oxide; Cu_2O, copper (I) oxide; ZrO_2, zirconium oxide.

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