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A comprehensive review of micro/nano enhanced phase change materials

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Abstract
Enhancement in properties of thermal storage materials improves their performance and contributes to reducing the greenhouse gas emissions. The enhancement can be made in a passive way, which is cost-effective and hardly requires management. For decades, phase change materials (PCMs) have been used in many applications for thermal storage, thermal control and thermal insulation purposes. PCM can store a huge amount of energy with low or no temperature swing. However, the major drawback of PCM is the low thermal conductivity. Techniques of different scales (macroscopic, microscopic and nanoscopic) have been adopted in thermal engineering to enhance the thermal conductivity of PCM. This paper presents a comprehensive review of the literature dealing with micro/nano enhancement techniques of PCMs. Enhancement effects as well as limitations of each technique are discussed in detail. Moreover, direction for future research and possible challenges are pointed out along with conclusions drawn from the studies.

Keywords Enhancement techniques · Microscale · Nanoscale · Latent heat · Phase change materials · PCM

Introduction

Almost all nations are obliged to advance in the direction of efficiency with their available energy potential due to the global scenario dominated by depletion of petroleum-based fuels, continuous global warming, drastic environmental changes, increasing global population and the associated demands of energy and products. To achieve this, it is necessary to invest in new local fronts for energy production and utilization, and adopt technologies for energy conservation without creating any additional negative impacts on the environment. Energy efficiency integrates energy conservation as the vital base. On the contrary, energy storage is independent of the type of energy to be stored for future use and requires efficient storage systems and an ability to deliver back the stored energy with minimum losses with the same potential level. Of the renewable energy sources, solar and wind energies are more technologically dominated, yet to be more commercialized; however, some forms of energy storage must be investigated to make their use sustainable. There are many forms of energy storage, including potential, mechanical, electrical, chemical, thermal, and many others are still under development. Of the well-developed techniques, thermal energy storage occupies a leading position with a very wide range of applications in conventional and non-conventional energy systems.

Within the field of thermal energy storage, three methods are in wide use, including sensible heat storage, latent heat storage and hybrid energy storage. Sensible heat storage is

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usually used with liquids, high-temperature thermal oils, rocks, etc., covering a wide range of temperatures depending on the source of heat and end use. Some drawbacks of these systems can be exemplified as temperature swing during discharging and low storage density per unit volume. In a hybrid system, storage of thermal energy is achieved with the sensible and latent heat of the storage material. It offers more advantages than a sensible heat storage system, but is complicated in terms of design and operation. Latent heat storage offers a lot of advantages such as isothermal behavior during charging and discharging processes, high energy storage density and capsulation in many convenient ways. Due to this, latent heat storage encompassed a wide range of application of these materials, including thermal control, protection of electronic equipment and PV panels in addition to application in many components in buildings such as roofs, walls, internal divisions and windows. Besides, other fields of applications include thermal energy storage systems for concentrating solar power (CSP) plants as well as cooling and refrigeration systems. Irrespective of the diverse applications of phase change material (PCM), it has some serious drawbacks impeding the domination it could have achieved in the thermal market. A deep understanding of the thermal behavior of PCM and the variation of its thermal characteristics during phase change helps its better use and hence adequate implementation. PCMs have some demerits such as poor thermal conductivity, possibility of phase segregation and subcooling. Latent heat storage is based on the exchanged heat of a PCM while undergoing solid–liquid phase change. Indeed, there are a variety of PCMs such as paraffin wax [1], hydrated salts [2], metallic PCM [3], metal alloys [4] and PCM mixtures [5].

Phase change seems to have a long history. In fact, historical periods are named after natural processes such as the Ice Age or discovery of casting of some metals such as the Iron Age and the Bronze Age. Metal casting dates back to thousands of years. Similarly, lost-wax casting which is used for molding is a very ancient technique that dates back to thousands of years. Studies on the phase change phenomenon commenced in the eighteenth century and still continue in the research area for both domestic and industrial sectors. In addition, noticeable research studies on heat transfer with solid–liquid phase change include the works of Jožef Stefan (1835–1893), who studied the polar cap during 1889–1891 [6] while theoretical works had been done beforehand by many other scientists. In fact, it is Joseph Black (1728–1799) who first discovered the concept of latent heat in his studies on ice (1758–1762). Gabriel Lamé (1795–1870) and Emile Clapeyron (1799–1864) incorporated for the first time the latent heat term (1831) in the heat balance equation to mathematically model the phase change, in a series of works initiated previously by Fourier on heat conduction [7]. Franz Neumann (1798–1895) proposed an analytical solution to the phase change problem, which was later published in 1912 [8]. These are pioneer scientists who first dealt with phase change problems, and their works are the basis for all the subsequent research investigations.

In the last century, remarkable works on phase change problems date back to 1949. Agyenim et al. [9] reported the key research studies on PCM performed since then. However, the 1970s energy crises boosted up the research works related to energy sources and their management.

As pointed out previously, the application field for energy storage is wide and PCMs showed a high potential for a variety of important applications. Unfortunately, most of PCMs suffer from serious problems, which impede their wide use and impair their thermal performance such as poor thermal conductivity, possibility of phase segregation and subcooling. To overcome these limitations and widen the application potential, extensive efforts worldwide are dedicated to improve the thermal performance of PCMs. Many studies were focused on to improve the thermal conductivity of the PCMs and consequently the heat transfer rate between the bulk PCM and the heat transfer surfaces in the system.

The effective thermal conductivity can be greatly improved by embedding highly conductive metallic wire meshes or dispersing metallic powders as in Siegel [10]. Hoogendoorn and Bart [11] studied a metal matrix embedded in an organic PCM used in a solar thermal storage. According to Charunyakorn et al. [12], microencapsulation of PCM was introduced as an enhancement technique in a research report presented by Hart and Thornton in 1982. The insertion of microparticles in PCM was used later in textile applications (e. g. diver's suit) [13, 14]. In recent years, the enhancement techniques have been developed from macroscopic scale to microscopic scale like microemulsions and more recently to nanoscopic scale by dispersion of metallic nanoparticles in PCM. An alternative approach for the enhancement of PCM thermal performance is the increase in the heat transfer area, which increases the heat transfer to or from the PCM as was initially done by Sparrow et al. [15] to enhance solidification of PCM.

Another major problem encountered in some PCM types is the subcoling effect, defined as the temperature difference between crystallization triggering and melting point. Subcooling deteriorates the thermal performance of PCM. Solutions proposed to eliminate or alleviate the negative impacts of subcooling include the addition of nucleating agents bubble agitation and ultrasonic vibration. Besides, segregation is another drawback of some salt hydrate-type PCMs. The active and passive ways to improve this characteristic are mechanical stirring, encapsulation of PCM and thickening agents.

Micro/nano-PCMs have been successfully incorporated in various thermal applications throughout the literature. The role of micro/nano enhanced PCM was extensively

investigated by researchers by experimental and numerical means. In this context, this paper reviews the micro/nano enhancement techniques and their impact on PCM characteristics. Different thermal applications as well as numerical and experimental investigations found in the literature have been examined, and the outcomes of the studies are presented critically. Furthermore, conclusions are drawn; possible challenges are highlighted, and future research direction is addressed.

Phase change materials

A good number of PCMs is available in both natural and synthetic forms suitable for a wide variety of thermal applications. PCMs can be subdivided, according to their nature, into organic [16], inorganic [17] and eutectic PCMs [18]. Organic PCMs include hydrocarbon-based PCMs that in turn can be classified as paraffin and non-paraffin. Paraffin is a mixture of hydrocarbon molecules (straight-chain n-alkanes). Their melting temperature is proportional to the chain length [19]. Non-paraffin organic PCMs such as esters, fatty acids, alcohols and glycols are more available than paraffin, and they exist over a wide range of melting temperatures. Inorganic PCM category includes mainly salt hydrates and metallic PCMs [19]. Salt hydrates are ionic compounds that can fix water molecule through hydration/crystallization processes. This reversible thermodynamic process enables the exchange of a considerable amount of heat. Therefore, salt hydrates are good candidates for energy storage. Finally, eutectics are PCMs consisting of mixture of two components or more, which have lower melting temperature than that of each of the components. In general, the choice of a PCM must satisfy certain thermal criteria, depending mainly on the application in which it is incorporated. Other physical requirements include high latent heat capacity, melting temperature suitable for the application temperature level, non-segregating behavior, low subcooling effect and small volume changes (expansion/shrinkage) during the phase change process. Moreover, PCMs should have chemical stability during charging/discharging cycles and should be compatible with their container, safe and available at relatively low costs. As it can be seen that the choice is complex, it is therefore necessary to have an engineering compromise (Fig. 1).

PCM characteristics

Because of their high latent heat, PCMs are used for thermal energy storage. On the other hand, small or no variation of temperature during charging and discharging processes is a

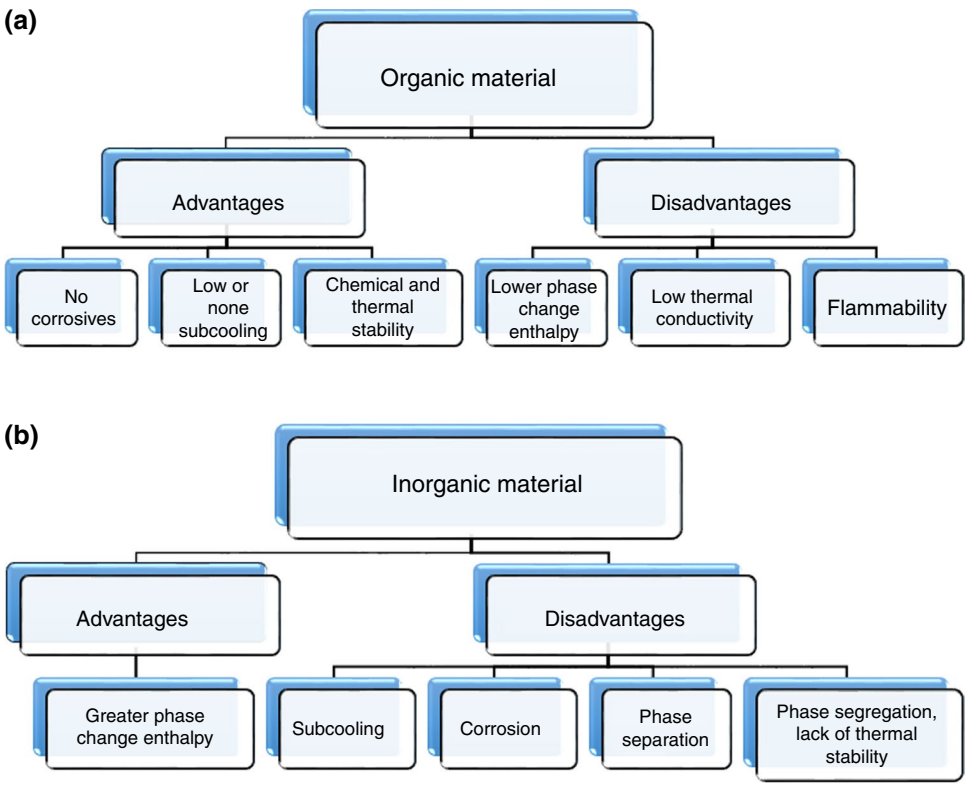

Fig. 1 Advantages and disadvantages of **a** organic PCMs and **b** inorganic PCMs

significant advantage as the system can deal with a limited range of temperatures.

Potential PCM/PCM composite should have desirable thermophysical properties. Therefore, many measurement techniques are being employed to evaluate these properties; the most commonly used is the differential scanning calorimeter (DSC) and thermogravimetric (TG) analysis. In general, there is no ideal PCM that has all the desired thermal and physical characteristics; consequently, it can be said that each PCM has its own merits and drawbacks. In the following subsections, essential PCM properties are presented and discussed.

Latent heat

During melting, a specific quantity of a solid absorbs an amount of heat. This heat is commonly known as latent heat of fusion and is used as a sufficient energy to overcome the binding forces that maintain the molecules of the solid. The latent heat of fusion is then the change in enthalpy between solid and liquid phases. PCMs have a latent heat storage capacity about 5–14-fold of that of conventional sensible heat storage materials (water, sand, concrete, rock, etc.) [19]. Consequently, latent heat storage systems have the great advantage of being compact in size. PCM hence offers higher thermal energy storage density, which explains why it is extensively being used in thermal energy storage systems. For instance, the latent heat of fusion of paraffin is in the range of 200–300 kJ kg^{-1}. The latent heat increases with the increasing number of carbon atoms.

Melting temperature

As discussed above, the liquid–solid phase change occurs isothermally or within a limited temperature range. For pure materials, phase change occurs isothermally, but for mixtures, melting/solidification takes place within a given temperature range. Thus, these mixtures are characterized by having a mushy zone in addition to the two phases, i.e., liquid and solid. The mushy zone is, however, composed of a mix of the two phases, for which temperature limits correspond to the phase change temperature range. Thickness of the mushy zone of PCM is usually in the range of Angstrom to a few centimeters [20]. Melting point of a given PCM should be selected within the operating temperature range of the thermal application. There is indeed a huge number of PCMs in the market, whose melting temperature can practically match a variety of thermal systems. Furthermore, a simple mixing of different PCMs may offer further melting temperature points. For instance, the melting temperature of paraffin mixtures changes with the mixture composition [21]. Consequently, a wide variety of PCMs of different melting temperatures can be obtained by simply adjusting the mixture proportions, which widens the respective application area.

Segregation

Selection of a PCM candidate for thermal application requires careful attention to all their merits and demerits. For instance, salt hydrates are known for a serious problem that limits their engineering integration, i.e., the fact that they melt incongruently, which results in a phenomenon called segregation, i.e., non-uniform distribution of atoms in solid phase. This drawback makes their incorporation in thermal systems a serious engineering challenge. Solid salt has the tendency to settle down at the bottom; therefore, its recombination with liquid becomes difficult. Attempts to address this problem have been made by both active and passive techniques such as mechanical stirring, encapsulating the PCM and thickening agents in the suspension [19]. Despite salt hydrates, neither organic PCMs nor eutectics suffer from phase segregation. Usually, these two PCM categories melt and solidify congruently.

Density change during phase change

Though the liquid density change during melting is well addressed in several numerical studies, the density change due to phase change was often neglected in computational works on PCMs for decades. Expansion/shrinkage of PCM during phase change may be in fact supposed to be negligible compared to other underlying parameters such as heat transfer and stored energy. However, in some research areas, the thermomechanical effect is fundamental or at least cannot be neglected.

Because of molecule organization, materials are usually denser once solidified except in some cases, e.g., water. This is why ice floats instead of sinking to the bottom in water. Generally, the volume change during melting/solidification of materials is in the range of 5–30% [20]. As a result, confined PCM might collapse the container, because of the pressure exerted if no air gap is left for expansion. In a study on freezing of water in a spherical capsule [21], the pressure exerted by expanding ice in an air gap was examined. Fundamental studies considering the PCM expansion during melting were conducted. Assis et al. [22] studied melting in a spherical capsule. An air gap was modeled allowing for the expansion of the PCM. Ho and Wang [23] presented an investigation on the melting of PCM in a rectangular enclosure, where the top wall is kept free to move as an effect of expanding PCM. Keeping an air gap is not the sole solution, another technical solution that was applied consists of an elastic envelop to allow the PCM to expand/shrink during phase change. However, the increasing pressure in the melt influences the melting characteristics such as melting point,

heat transfer and evolution of phase change front. Kowalczyk et al. [24] studied the solid–liquid phase change at high pressures. They showed that different mechanisms affect natural convection at high pressures. Pham [25] showed that the freezing point and latent heat are affected by the pressure variation.

Thermomechanical effect is considered in phase change problems. In a study on the planar solidification of a finite slab, Conti [26] proposed a thermomechanical model for the planar solidification of a slab. Dallaire and Gosselin [27] compared the results of two models: in the first model, thermomechanical effect using an elastic wall is considered, and in the second model, a compressible air gap is left in the container, which provides room for PCM expansion. Numerical results pointed out that the melting process is significantly influenced by volume change. Moreover, Hassab et al. [28] compared two models on the melting of wax. The first model does not consider volumetric expansion during melting, while the second takes it into consideration. According to the study, results indicated a significant difference between the two models.

Although regarded as a drawback, the PCM volumetric change is the basis of some engineering applications. In fact, various techniques have been used in industry to command a moving wall called actuator or thermal switch. PCM undergoing phase change expands/contracts to command a movable wall in the PCM containment. This interesting subject attracted attention of many investigators [29, 30].

Subcooling

Nucleation is the first step in the solidification process. Formation of initial crystals (nucleus) is not always possible by the simple decrease in the temperature below the PCM melting temperature. Sometimes the liquid phase exists even at temperatures lower than the melting point. This natural phenomenon is known as subcooling. Temperature difference between crystallization triggering and melting point is called the degree of subcooling. This temperature difference may be a few to tens of degrees. Some PCMs are known for their subcooling behavior during solidification such as water. In fact, water does not solidify practically at 0 °C but at a lower temperature. On the other hand, when nucleation is triggered, the phase change undergoes at 0 °C, as stated theoretically.

Subcooling is actually a major demerit and an undesirable property in PCM-based latent heat storage systems as there is a possibility of releasing only a certain amount of latent heat. In extreme subcooling cases, only sensible heat is released [31]. Also, due to subcooling, the charging and discharging cycles of the latent heat storage system are not symmetrical [32]. This increases, however, the complexity in the design and development of latent heat storage systems. Therefore, various solutions were proposed to eliminate or at least alleviate its impact. Some of the traditional methods include the addition of nucleating agents [33], maintaining cold fingers that act as a nucleus [34] and possessing a rough surface [35]. Moreover, a few unconventional techniques are getting more attention to combat subcooling issues such as bubble agitation [36], shock waves [37] and ultrasonic vibration [38]. Safari et al. [39] and Zahir et al. [40] reviewed in detail in the literature that dealt with subcooling, their influencing factors and various control techniques of possible use in heat storage.

However, subcooling in small volumes is more pronounced than in large volumes [41, 42]. The main reason for this is the dominance of homogenous nucleation particularly in small PCM volumes. In the case of microencapsulated PCMs, the curvature effect is attributed to the difference in the extent of subcooling phenomenon, which is depicted in Fig. 2. In large droplets, with their lower curvature, the surfactant molecules align with the PCM molecules result in easier crystallization. On the contrary, small droplets with higher curvature do not favor crystallization due to the misalignment between the surfactant and PCM molecules. Hence, it is highly recommended to predict the minimum size of storage capsules with the chosen PCM for which the subcooling effect is almost negligible or less.

Repeatability of a timed phenomenon with identical samples of a material is of high importance in any application. However, in the case of subcooling, repeatability is not favored. Bédécarrats et al. [43] showed that the stochastic

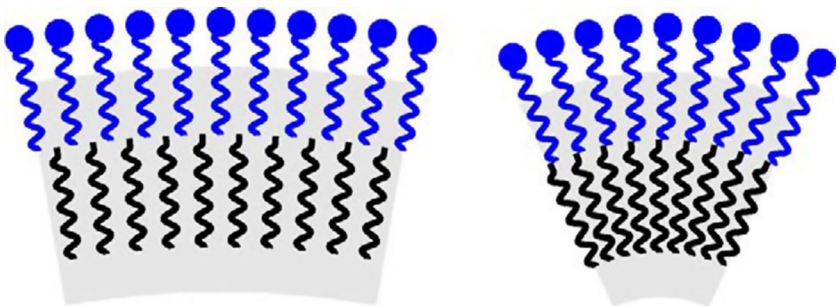

Fig. 2 Curvature effect of PCM droplets on nucleation activity

character of subcooling exists in water, and it is applicable to other PCMs also. It means that identical samples do not show the same subcooling behavior. Furthermore, the same sample shows different subcooling degrees from one experiment to another.

Each type of PCM has its own advantages and disadvantages. In terms of subcooling, organic PCMs such as paraffin and fatty acids exhibit little or no subcooling, but it is observed for inorganic PCMs particularly for salt hydrates [44]. When there is a requirement of combination of properties favoring both organic and inorganic PCMs with respect to a particular application, eutectic PCMs are preferred.

Numerical modeling of latent heat storage systems is gaining much attention due to its flexibility to model different types of systems. It also facilitates optimizing the geometric parameters and operating conditions of complex prototypes [45]. But majority of the reported numerical models do not consider the subcooling phenomenon. Accounting for subcooling in a numerical model increases both the accuracy and reliability of the model. Of the several methods available to model phase change in PCMs, enthalpy and apparent heat capacity methods are predominantly used. Günther et al. [46] developed a modified enthalpy model incorporating the subcooling effects in the enthalpy of the PCM. Similarly, Davin et al. [47] formulated a novel model modifying the specific heat of PCMs to include the subcooling phenomenon. The enthalpy and specific heat parameters used are not the idealized properties in the model, and calorimetric studies of the corresponding PCMs are taken into account to improve the accuracy of the model. It is observed that the deviation in the numerical results when compared with the experimental data is lower than that of the models not accounting the subcooling phenomenon.

Thermal conductivity

Considering the operation of a phase change material in any thermal system, it is obvious that the stored or released heat amount per unit time for the system is an important aspect since it determines the cumulative stored or released thermal energy over the running period. Heat transfer rate in a PCM thermal system is dependent on geometric parameters as well as material properties, and numerous researches have been dedicated to this topic in recent years [48, 49]. Configuration of geometric parameters such as using extended surfaces and enhancing material properties such as increasing the thermal conductivity of materials involving heat transfer are widely used methods. Integrating heat pipes and utilizing multiple PCMs with different melting/solidification temperatures are other approaches to increase the heat transfer rate in thermal systems [49].

Using extended surfaces, i.e., fins, in PCM thermal systems is based on increasing the heat transfer area and several researches can be found in the literature concerning different geometric shapes or configurations for fins [50, 51]. In general, fins are preferred due to their simplicity, effectiveness and considerable effect on the heat storage capacity of the system leading to an increased heat transfer rate as well as an advanced thermal performance consequently. Despite that, some studies in the literature can be easily found where using only fins is not sufficiently enough to reach a desirable heat transfer rate, underlying a combination of methods [52].

PCMs are known for their low thermal conductivity which highly degrades heat charging/discharging rates affecting the thermal performance of the thermal system in which they are used [9]. As previously stated, the charging and discharging times for a phase change material are crucial in almost all applications such as electronics cooling, building thermal management, battery cooling and PV panels [19]. Since the heat conduction is the only heat transfer mechanism during the solid state, low thermal conductivity affects the solidification process more than the melting process.

In this context, increasing the thermal conductivity of a phase change material can be a more reasonable solution at the first attempt since it is an intrinsic property of the material. There are several thermal conductivity enhancement techniques for PCMs in the current literature, and the topic is still a hot spot with recent advancements published by researchers [53]. Enhancement of the effective thermal conductivity of PCM is a very concurrent research area with continuous new achievements and developments. A typical way consists of insertion of metallic materials in PCM such as wires, wire mesh and metallic powders to improve the effective thermal conductivity of the PCM mixture [9]. Another effective way to enhance the PCM thermal performance is its encapsulation. Encapsulation can be made in macro- or microscale [14]; the latter is more efficient because of the higher heat transfer area. PCM encapsulation prevents also the leakage of molten PCM during charging cycle. These two enhancement techniques, microencapsulation and dispersion of nanoparticles, are intensely investigated with the objectives of improving the thermal performance of PCM and encourage its use in a variety of applications without the risk of contamination, fire hazards and possible leakage risks. In the subsequent sections, a detailed review concerning micro/nano enhancement techniques is presented and discussed thoroughly.

Microscopic enhancement techniques

Phase change materials, also acceptable as smart materials, can be prepared using a variety of techniques and need to be encapsulated in macro/micro or nanoscale in order to keep a certain volume during phase change. Effective use of the heat transferred to PCMs also depends

on the development of suitable encapsulation techniques for these materials. Microencapsulation process allows the increase in the heat transfer area, reduction in the interaction of PCMs with the external environment and control of the volume change during the phase change process. The advantages and disadvantages of encapsulation of PCMs are given in Table 1.

Comparison of encapsulation techniques

A schematic view of general encapsulation methods and the encapsulation methods used for the preparation of PCMs is demonstrated in Fig. 3. The review of literature demonstrated that microencapsulated PCMs can be obtained by using physical, physical–chemical and chemical methods. However, among the physical methods, only spray-drying was applied to prepare microencapsulated PCMs. Pan coating and air suspension coating are not suitable for the encapsulation of PCMs [54]. On the other hand, other physical methods, namely the solvent evaporation, vibrational nozzle and centrifugal extrusion, seem feasible but have not yet been implemented. Spray-drying is an economical method of preparing micro-PCMs that can be easily applied and scaled, but agglomeration can occur during the process. Sol–gel method and coacervation methods are both preferred as the physical–chemical methods in the preparation of microencapsulated PCMs. However, there is no study on ionic gelation yet while it seems as applicable [54]. The microencapsulation of PCMs with inorganic shell materials can be realized with the sol–gel method. Another way for preparing the microencapsulated PCMs is the chemical method covering interfacial, suspension and emulsion polymerization techniques. The chemical method is mostly

Table 1 Advantages and disadvantages of PCM encapsulation

Advantages	Disadvantages
Enhances chemical stability	Declines energy storage capacity
Enhances mechanical stability	Declines thermal conductivity
Increases the number of thermal cycles	Leakage problems may arise
Provides the control of volume change	Increases the cost of the PCM
Protects the PCM from environmental effects	Flammability problems
Prevents chemical reaction with other materials	Some methods are still under research
Enables improving thermal properties with the addition of some doping materials into the structure	Challenges during encapsulation processes such as agglomeration of particles, control of reaction mechanisms and scale-up problems
Allows the use of PCM mixtures	
Allows to adjust phase change temperatures by the use of PCM mixtures	

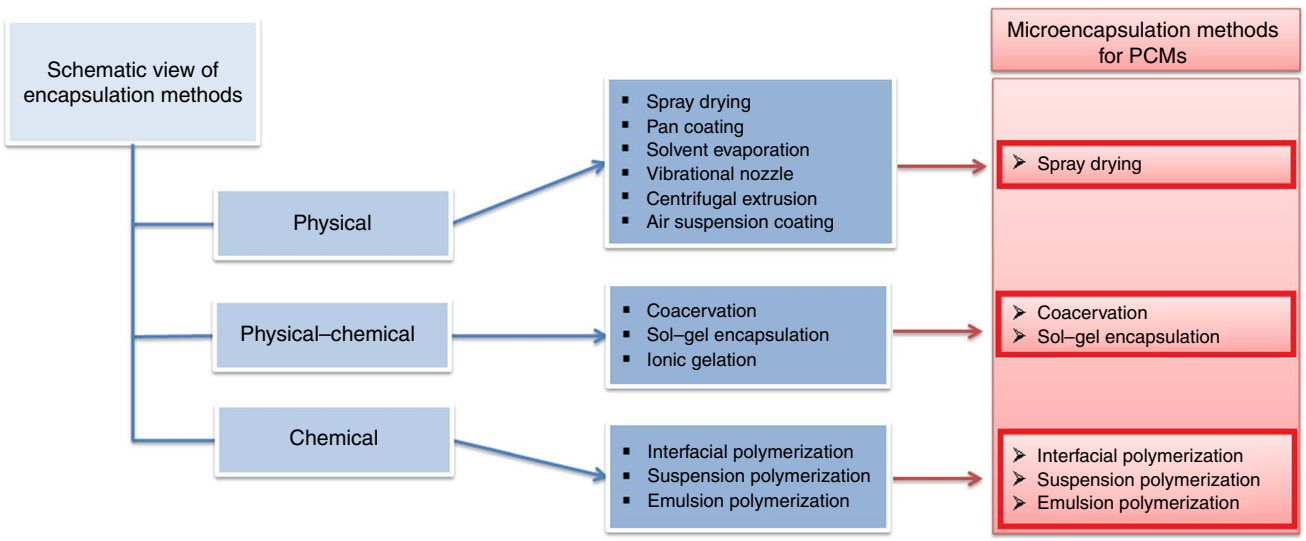

Fig. 3 A schematic view of general encapsulation methods and encapsulation methods used for obtaining PCMs

preferred for the encapsulation processes of PCMs with a wide variety of shell materials.

Evaluation of varied microencapsulated PCMs

Polymeric materials are frequently used in the microencapsulation process of PCMs [54, 55]. Microencapsulation process has so far been carried out with different shell materials comprised of urea–formaldehyde [56] melamine–formaldehyde [33], melamine and urea formaldehyde [57], methyl methacrylate [58], butyl acrylate [59], butyl methacrylate [60], lauryl methacrylate [61], styrene [62], poly(urea) [63], poly(urethane–urea) [64], methylmethacrylate-based copolymer shells [65], poly(St-co-divinylbenzene) [66], etc. by using well-known techniques such as interfacial polymerization [58, 67], emulsion polymerization [66], sol–gel [67, 68], coacervation and spray-drying [69, 70]. For instance, Sarı et al. [71] studied the encapsulation of octacosane and heneicosane as PCMs with poly(methyl methacrylate) shell via emulsion polymerization. They performed thermal cycling tests by carrying out 5000 melting/freezing process in order to investigate the chemical stability of the encapsulated PCMs. The manufactured capsules were reported as chemically stable and reliable while the latent heats of melting and melting temperatures were determined as in the range of 138–152 kJ kg^{-1} and about 39–60 °C. Additionally, thermal conductivity tests showed that the poly(methyl methacrylate) shell has no major negative effect on the thermal conductivity of the obtained PCM materials. Hawlader et al. [69] carried out the microencapsulation of paraffin wax by using spray-drying and coacervation techniques. The thermal energy storage capacity of the manufactured microcapsules was found in the range of 145.28–239.78 kJ kg^{-1} depending on the core/coating ratio. The images from the scanning electron microscope (SEM) showed microparticles with spherical and uniform size distribution. They concluded that both methods were suitable for preparing micro-PCMs and the obtained microcapsules can be used in solar energy storage applications.

PCMs have applications in many areas and their thermal stability is extremely important during latent heat storage/release processes. The thermal stability of PCMs can be determined by TG analysis. The thermogravimetric loss in TG curves demonstrates the degradation steps and amounts of mass loss during the analyses when the samples are heated to the same predicted temperature and at the constant heating rate. It is desirable that the materials to be used as latent heat storage elements are durable while the required thermal stability range differs based on the application area. Song et al. [72] encapsulated the eutectic mixture of capric and stearic acid with silica shell. They carried out the process without using a surfactant in order to prevent its reducing effect on the thermal energy storage capacity.

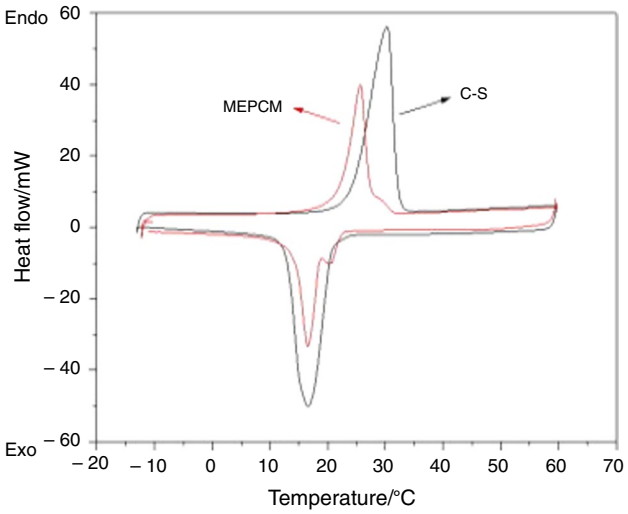

Fig. 4 DSC analysis of micro-PCMs before and after thermal cycle tests [72] (Reprinted with permission from Elsevier)

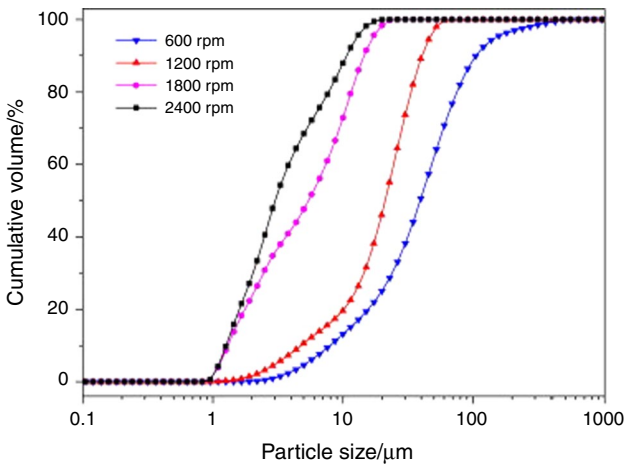

Fig. 5 Relationship between particle size of micro-PCMs and mixing rate [72] (Reprinted with permission from Elsevier)

The melting temperature and the latent heat of fusion of the obtained microcapsules were found to be 21.4 °C and 91.48 J g^{1}. The results of the thermal stability test of the produced materials were promising when considering the decomposition temperature of the micro-PCMs based on the TG analysis. According to the thermal cycling (1100 cycle) tests, the latent heat of fusion only changed by about 2.6% (Fig. 4). Furthermore, it can be said that the mixing rate significantly affects the particle size of the produced PCMs (Fig. 5), which allows some features to be acquired by influencing the microstructure of the material.

Mert et al. [73] studied the microencapsulation of n-octadecane and n-hexadecane mixture by emulsion polymerization method. The styrene and divinyl benzene were used for the preparation of the shell material. Based on their results,

the encapsulation efficiency was realized as 56.77% while latent heat of fusion and the melting temperature were 88 kJ kg^{-1} and 21.06 °C, respectively. Furthermore, thermal stability tests showed that the empty shell material degraded in the range of 382.5–450.8 °C, which ensures the protective property of the shell material. TG analysis of the microencapsulated PCM revealed that the decomposition of the microencapsulated PCM occurred in two temperature stages of 125.4–209.0 °C and 384.8–461.8 °C, demonstrating a good thermal resistance. In another study of Mert et al. [74] the investigation of the microencapsulation of a fatty acid mixture including n-hexadecane was performed. N-hexadecane was introduced into the PCM mixture based on its good thermal storage capacity and surfactant property. Emulsion polymerization technique was used for the synthesis of the microcapsules composed from oleic acid–capric acid/hexadecane as the core and polystyrene as the shell material. Figure 6 demonstrates the images obtained from the polarized optical microscopy (POM) analysis of the hollow shell material and the microencapsulated PCM. It is obvious from the POM images that the micro-PCM (Fig. 6b) seems darker when compared to the hollow shell material (Fig. 6a) due to the unbroken light. Moreover, they reported that the obtained micro-PCM is suitable for low-temperature applications due to its appropriate temperature range (14.1–24.0 °C) and latent heat of fusion (127.3 kJ kg^{-1}). Thermal stability tests indicated that a chemically stable PCM was obtained based on the TG curves demonstrating the two-step decomposition of microencapsulated PCM in the range of 150.1–214.1 °C and 377.8–455.6 °C.

Inorganic materials were also used for the microencapsulation processes. For example, Zhao et al. [67] investigated the encapsulation of n-octadecane by using sol–gel method. TiO_2 was used as the shell material, and the obtained microcapsules were 2–5-μm-sized with a spherical shape. The melting temperature and the latent heat of fusion of the microencapsulated PCM were found to be 25.68 °C and 42.57 kJ kg^{-1}, respectively. Additionally, they reported that the use of TiO_2 shell improved the thermal stability of the microencapsulated PCM. In another work, Genc et al. [68] investigated the preparation of an organic PCM as myristic acid with an inorganic shell material as TiO_2 with the same method (sol–gel). Moreover, fly ash, which is waste of the coal combustion, was introduced in the core to improve the properties of the PCM. Based on the TG analysis, it was found that the obtained myristic acid/TiO_2 microencapsulated PCM showed good thermal stability. However, the addition of fly ash in the core resulted in a significant decrease in the heat storage capacity and leakage problems.

In addition to mechanical and chemical stability of PCMs used in building applications, flame-retardant properties should also be considered. Flame retardants reduce heat transfer rate and release of carbon monoxide/carbon dioxide owing to the formation of a char coating in the course of combustion [75]. There are also studies in the literature on the preparation of phase change materials with flame-retardant properties. Chen et al. [75] designed a flame-retardant PCM composed of phosphorus-grafted hexadecanol and pentaerythritol phosphate with a latent heat of 186.9 kJ kg^{-1}. The flame-retardant characteristics were investigated by TG, FTIR and SEM analyses. They concluded that the flame intensity was limited due to the use of the grafted groups as flame retardants, which shortened the burning time by extinguishing the flame. Accordingly, they found that the burning time of hexadecanol was reduced by 96.8%, while 9.76 g remained as residual. It was stated that the flame-retardant properties obtained are due to the changes in the microstructure of the material produced. Fang et al. [76] studied the preparation of flame-retardant phase change materials for building applications. The n-hexadecane/silicon dioxide forms a stable composite material and was produced by sol–gel method. SiO_2, which is an inorganic material, was used as the support material due to its flame-retardant property. Furthermore, expandable graphite with a porous microstructure was incorporated in order to increase the flame-retardant property of the composites. For a mass percentage of 73.3% of n-hexadecane in the composites, the latent heat of fusion and the melting temperature were found as 147.58 kJ kg^{-1} and 17.97 °C, respectively. In another study of Fang et al., [77], a form stable PCM with an organic material, namely palmitic acid, was prepared. They used silicon dioxide and melamine in order to acquire and improve the flame-retardant property for

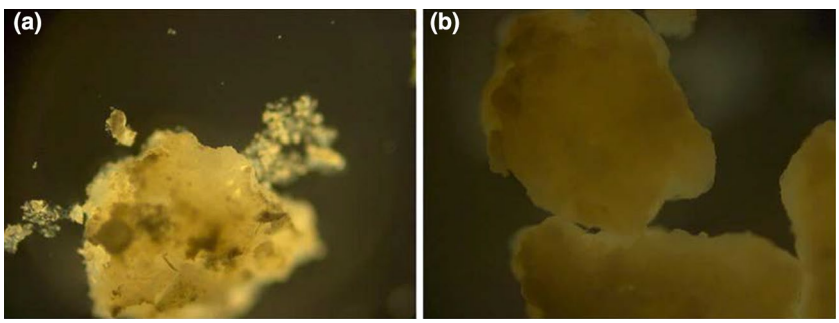

Fig. 6 Polarized optical microscopy views of **a** shell material and **b** micro-PCMs [74] (Reprinted with permission from Springer)

a palmitic acid addition of 41.1 mass%. The obtained composite material was characterized, and the melting temperature and the latent heat of fusion were found as 59.76 °C and 85.11 kJ kg^{-1}, respectively. However, increasing the proportions of the palmitic acid caused undesirable leakage from the structure. TG analysis tests indicated that the supplement of melamine enhanced thermal stability of the PCM. Additionally, flame-retardant property was verified with combustion test by using a muffle furnace. They reported that the microstructure of residual char after burning test of the material showed a decrease in the flammability of the composites.

Since most of the PCMs have low thermal conductivity, researches that are performed to increase thermal conductivity have become very important. When the literature is examined, it is seen that many materials including micro/nanosized; metals, metal oxides and carbon-based materials are generally used as additives in the preparation of latent thermal energy storage materials in order to increase thermal conductivity [78, 79]. Zhang et al. [80] designed a novel phase change material by using a rare earth-doped zirconia shell. The PCM was synthesized with *n*-dodecane as the core by in situ polycondensation method. Thermal conductivity tests revealed the improvements in thermal conductivity for the obtained zirconia microencapsulated PCMs (in the range of 0.892–0.906 W m^{-1} K^{-1}) in comparison with the pure PCM (0.152 W m^{-1} K^{-1}). On the other hand, Sm^{3+}, Er^{3+} and Yb^{3+} rare earth elements were selected for the doping of the zirconia shell in order to obtain dual function microcapsules. The effect of lanthanide series elements on the photoluminescence characteristics of shell material was obtained as $Er3^{+} > Sm^{3+} > Yb^{3+}$ while it was found to be $Sm^{3+} > Er^{3+} > Yb^{3}$ depending on increasing amount of additives (Figs. 7, 8). Furthermore, the latent heat of the obtained materials was found as 139.1, 142.4, 152.6 and 163.9 kJ kg^{-1} for Er^{3+}-, Sm^{3+}- and Yb^{3}-doped ZrO_2 shells, respectively, while the melting temperature was found to be approximately 45 °C for all materials.

Mert et al. [81] conducted a study related to the preparation of modified gamma alumina (M-γ-Al_2O_3)/fatty acid composite phase change materials (PCMs). They performed the microencapsulation of the oleic acid and capric acid besides to n-hexadecane with poly(St-co-DVB) shell by phase inversion emulsification method. They reported that the addition of 2% M-γ-Al_2O_3 into microencapsulated PCM (MEPCM) enhanced the heat storage rate from 0.0337 to 0.0358 °C s^{-1} or by 6.23% when compared to the MEPCM. Chen et al. [82] fabricated microencapsulated phase change materials by in situ polymerization. The n-octadecane and octadecylamine-grafted graphene oxide (GO-ODA) were used as the core materials while the melamine–formaldehyde (MF) resin was used as the shell material. The added GO-ODA were 0.1 mass%, 0.2 mass% and 0.5 mass% relative to n-octadecane into the composite PCMs. They obtained spherical and uniformly spread microcapsules having about 317 nm wall thickness (Fig. 9). Based on their results, the additive amount significantly improved the thermal conductivity of the PCMs when compared to the obtained micro-PCM without GO-ODA. It was found that the latent heat of fusion of the microencapsulated PCM is about 207.2 kJ kg^{-1} and the melting temperature is 32.93 °C while the thermal conductivity improvement rate of 38.52% was achieved due to 0.5 mass% GO-ODA. Table 2 illustrates the studies

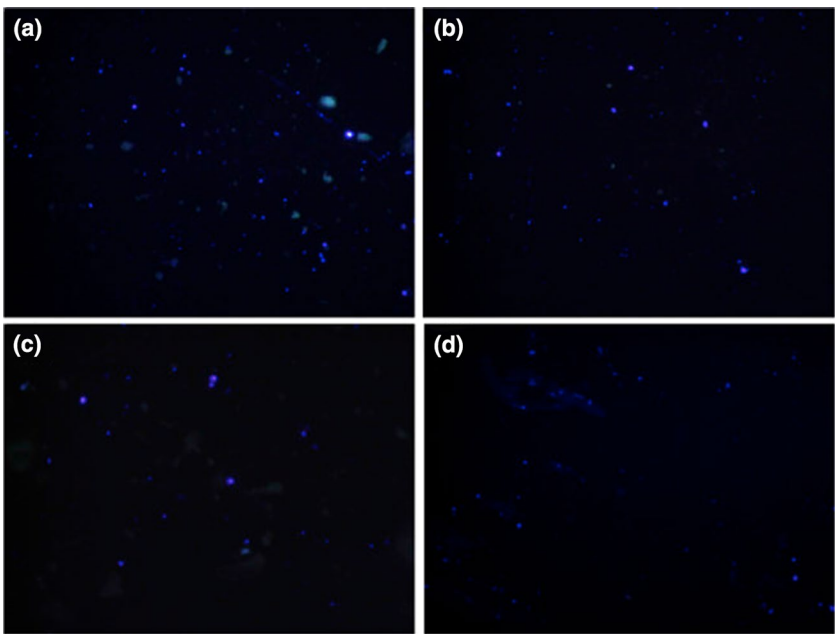

Fig. 7 Fluorescence microscope views of the **a** Sm^{3+}-doped zirconia, **b** Er^{3+}-doped zirconia, **c** Yb^{3+}-doped zirconia and **d** non-doped zirconia [80] (Reprinted with permission from Elsevier)

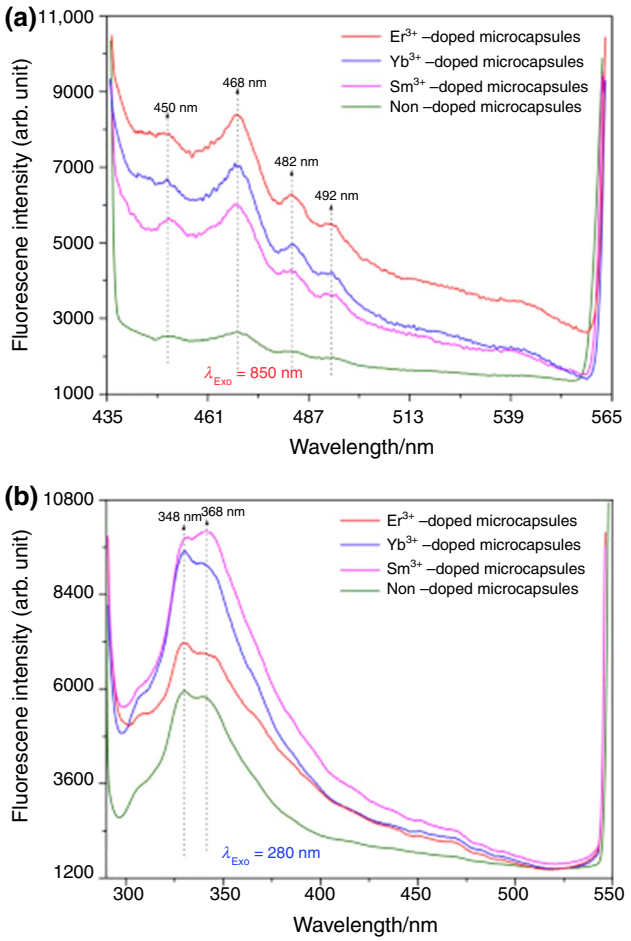

Fig. 8 Photoluminescence spectroscopy analysis of the obtained capsules at a wavelength of **a** 280 nm and **b** 850 nm [80] (Reprinted with permission from Elsevier)

related to the enhancement of thermal properties for various PCMs.

Evaluation of varied composite PCMs

In recent years, the composite PCMs have attracted attention due to notable reliable superior properties. They are also called as form-stabilized and/or shape-stabilized PCMs. A carrier material provides support for PCM integration. Direct impregnation, vacuum impregnation, templating, centrifugal spinning and intercalation are the methods reported for the preparation of the shape-stabilized PCMs [83]. Among these methods, impregnation is a simple and effective method. The enhancement can be achieved with the addition of materials, which improve the mechanical strength, chemical stability and thermal conductivity of the composites.

A significant part of carbon materials (Fig. 10) can be used as additives and/or support materials for energy storage applications [84, 85]. Badenhorst [85] reviewed the carbon materials for solar thermal energy storage applications and proposed a model for the behavior of carbon composites. It was found that the expanded natural graphite is the best option from the economic point of view due to its thermal properties and enhancement capability.

In another research study, the preparation of myristic acid–palmitic acid–stearic acid/ expanded graphite composite PCM was performed by Yang et al. [86]. The mass fraction of used fatty acid mixture was 92.86 mass%. The properties and the microstructure of the composite PCM were obtained by differential scanning calorimetry, Fourier transformation infrared spectroscopy (FTIR), thermogravimetric analysis (TG) and scanning electron microscope (SEM). They found the melting temperature and latent heat of the composite PCM as 41.64 °C and 153.5 kJ kg^{-1}, respectively. The thermal conductivity of the composite PCM was enhanced by the addition of expanded graphite and the measured value observed was 2.51 W m^{-1} K^{-1} while the ternary mixture without expanded graphite was only 0.25 W m^{-1} K^{-1}. Tian et al. [87] performed the preparation of ($NaCl–CaCl_2$)/expanded graphite using impregnation method. The binary eutectic mixture of $NaCl–CaCl_2$ was obtained with a molar ratio of 52:48. They used microsized expanded graphite (0.5–20 mass%) as the support material and impregnated the eutectic mixture into it. The melting temperature and the latent heat of $NaCl–CaCl_2$ eutectic mixture are 779.35 K and 164.2 kJ kg^{-1}, respectively. The latent heat of the composite PCMs based on the expanded graphite content ranged from 132.6 to 159.3 kJ kg^{-1}. Liu et al. [88] studied the preparation of lauric–myristic–stearic acid eutectic mixture/expanded graphite (12/1, mass%) composite PCM. They reported the latent heat and melting temperature of the composite PCM as 137.1 kJ kg^{-1} and 29.05 °C, respectively. They measured the thermal conductivity of the fatty acid mixture and the composite PCM as 0.26 W m^{-1} K^{-1} and 2.51 W m^{-1} K^{-1}, and also verified by using an experimental test considering storage and release rates.

Pielichowska et al. [89] studied the synthesis of polyurethane-based composite PCMs (PUPEG) containing poly(ethylene glycol) (PEG), 1,4-butanediol (BDO) and 4,4′-diphenylmethanediisocyanate (MDI). They prepared the composite PCMs with and without BDO. BDO was used to extend the chains (Fig. 11). They found that the latent heat of fusion and the melting temperature of the composite PCMs were in the range of 118–164.5 kJ kg^{-1} and 53.1–66.6 °C without BDO and 128–148.5 kJ kg^{-1} and 50.2–63.8 °C with BDO. Furthermore, the thermal conductivity of the obtained PUPEG with BDO increased to ~ 32 W m^{-1} K^{-1} with the addition of graphite platelets (~ 3–7 microns, 4 mass%).

Karaipekli et al. [90] used the capric–lauric, capric–palmitic and capric–stearic acids eutectic mixtures in order to prepare composite PCMs by using expanded vermiculite

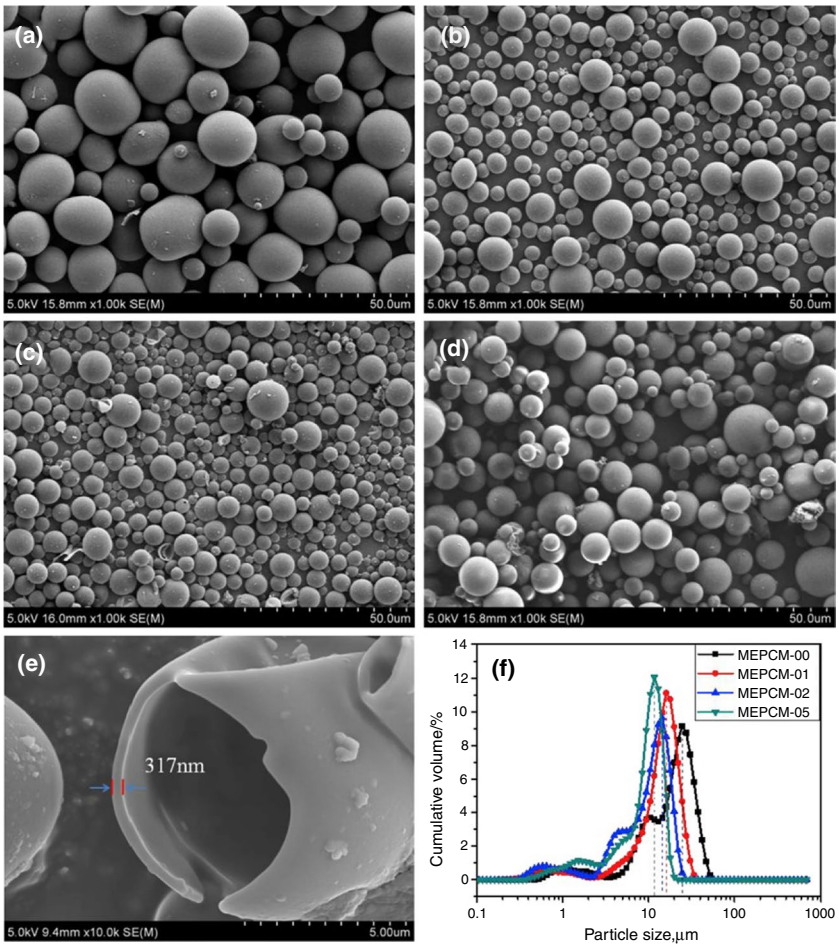

Fig. 9 SEM views (**a** 0 mass%, **b** 0.1 mass%, **c** 0.2 mass% and **d** 0.5 mass% GO-ODA, **e** wall thickness and **f** size distributions of the obtained microencapsulated PCMs [82] (Reprinted with permission from Elsevier)

via vacuum impregnation method. Vermiculite, which is natural clay mineral also named as hydrated laminar magnesium–aluminum–iron silicate, was used as the support material in order to obtain stable form PCMs. According to the results, latent heats and melting temperatures of the prepared composite PCMs were in the range of 61.03–72.05 kJ kg^{-1} and 19.09–25.64 °C, respectively, based on the DSC analyses. Moreover, they used expanded graphite to improve thermal properties of the composite PCMs. Their results showed that the addition of expanded graphite (10 mass%) changed the microstructure of the composite PCMs and therefore increased the thermal conductivity of the resulting materials. Table 3 summarizes the attempts for thermal conductivity enhancements of some composite PCMs.

Closing remarks

This part of the paper deals with the discussion of microenhancement techniques of the PCMs. PCMs can be obtained in microsized by using micro and/or nanosized materials. That is, nanosized materials can also be used to obtain microencapsulated PCMs. The enhancement techniques generally cover the thermal, chemical and mechanical development studies of PCMs besides the improvement in the thermal conductivity and storage capacity. Moreover, flame retardancy is also desired for the requirement of various application areas. On the other hand, PCMs can be obtained with desired properties via encapsulating PCM mixtures in order to adjust their melting/solidification temperatures and simultaneously aiming to reduce the cost of PCMs. Based on the literature survey, it can be concluded that the most used method in the microencapsulation of PCMs is the chemical method and the encapsulation is accomplished by using the polymer-based materials. The use of polymer-based materials in the encapsulation process as shell materials mainly affects the thermal performance of PCMs and causes the resulting materials to have relatively low thermal conductivity. On the other hand, the polymer-based shell materials provide chemical and mechanical stability and reliable PCMs. Furthermore, it has been observed that, carbon-based materials especially expanded graphite is used in order to enhance the thermal conductivity of the PCM. It has been reported that the addition of the expanded graphite

Table 2 Enhancement of thermal properties for various PCMs

PCM	Shell material	Method	Melting temperature/°C	Latent heat of fusion/J g^{-1}	Major findings	Ref
n-octadecane	Polyurethane	Interfacial polymerization	34–37	110	The microencapsulation efficiency was found as between 93.4–94.9%	[91]
n-octadecane and octadecylamine-grafted graphene oxide	Melamine–formaldehyde shell	Emulsion polymerization	32.93	207.2	Thermal conductivity enhancement was 38.52%	[82]
n-heptadecane	Poly(styrene)	Emulsion polymerization	21.5	136.9	Thermal energy storage capacity enhanced with the use of different core/shell ratios	[92]
n-octadecane	*p*(butyl methacrylate) and p(butyl acrylate)	Suspension polymerization	25.9–29.6	96–112.0	The thermal stability of the micro-PCMs was increased contrasted to the pure *n*-octadecane	[93]
Butyl stearate	Polyurea	Interfacial polymerization	28.60–29.37	76.31–85.92	Thermally stable microsized particles of approximated 25–30 µm were obtained	[94]
Octadecyl acrylate	Chitosan	Coacervation	26.4–39.9	92.9–131.4	Thermally stable microsized particles (0.29–4.05 µm) obtained. The encapsulation ratio was found to be between 49.82–68.99%	[95]
Butyl stearate	Polyurethane	Interfacial polymerization	21.7–22.3	77.1–80.6	Thermal stability of the shell material was clearly increased	[96]
n-hexadecane	Polymethyl methacrylate + poly(butyl acrylate-co-methyl methacrylate)	suspension polymerization	16.9–20.4	19.3–63.1	The flexibility and damping properties of microcapsules have been improved	[97]
Rubitherm®RT27	Polyethylene–EVA	Spray-drying	27.6–29.41	98.1	Mechanical and thermal stability enhancement was obtained with the addition of carbon nanofibers. Thermal conductivity was also improved	[98]
Eutectic *n*-tetracosane/*n*–octadecane	Poly(styrene)	Emulsion polymerization	25.96	156.39	Thermal stability and reliability were tested with 5000 thermal cycle	[99]
Rubitherm®RT31	Poly(styrene)	Suspension polymerization	31.56	75.7–135.3	The effect of different suspension stabilizers on the particle size variation was obtained	[100]
Polyethylene glycol	Silicon dioxide	Sol–gel	56.5–58.2	100.4–121.4	Thermal performance of the PCM was improved by Cu doping	[101]
Lauric acid	Silicon dioxide	Sol–gel	43.84–44.78	47.30–117.21	The highest mass percentage of PCM was obtained as 64.8% in addition to the good thermal stability	[102]
n-octadecane	Titania shells	Spray-drying	28.7	92–97	It was concluded that the obtained PCMs have ability to eliminate bacteria and reduce UV transmission	[103]

Table 2 (continued)

PCM	Shell material	Method	Melting temperature/°C	Latent heat of fusion/J g^{-1}	Major findings	Ref
n-eicosane	Titanium dioxide	Sol–gel	41.47–43.88	97.60–152.50	Thermal conductivity increased up to 5.4 times with different core/shell ratios	[104]

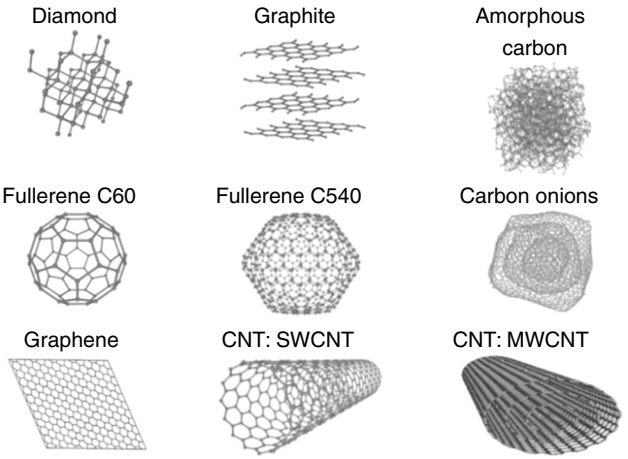

Fig. 10 Major carbon materials [85] (Reprinted with permission from Elsevier)

to the structure also strengthens the mechanical stability of the PCMs.

Nanoscopic enhancement techniques

As clearly stated in the previous sections, the primary property of PCM from a material point of view is the latent heat, which identifies the storage capacity of system. However, the efficiency of system strictly depends on the thermal conductivity, particularly for the applications, where charging and discharging rates are important. Development in nanotechnology has enabled offering a prospective technique to enhance the thermophysical properties of PCM, mainly focusing on the thermal conductivity, as it is poor and considerably degrades the efficiency of system. In this section, the studies focused on the impact of nanoparticle loadings on the properties of the base PCM are presented.

The primary idea behind introducing nanoparticles to the base fluid such as water and ethylene glycol is to improve the effective thermal conductivity of the mixture [112]. The same concept has been applied to PCM, i.e., particles in nanoscales (1–100 nm) are dispersed in PCM. It should be noted that from the practical point of view, the studies on the nanoenhanced PCMs (NEPCMs) are significantly different than those on conventional fluids. For instance, the flow in the NEPCM systems is usually laminar and heat convection is natural convection, while in nanofluids, the flow can be laminar or turbulent, and heat convection can be natural, mixed or forced. Another significant distinction is the phase change process which requires the determination of latent heat fusion of NEPCM. Moreover, the impact of nanomaterials on the solidification (discharging) and melting (charging) processes is considerably different since in the former the heat

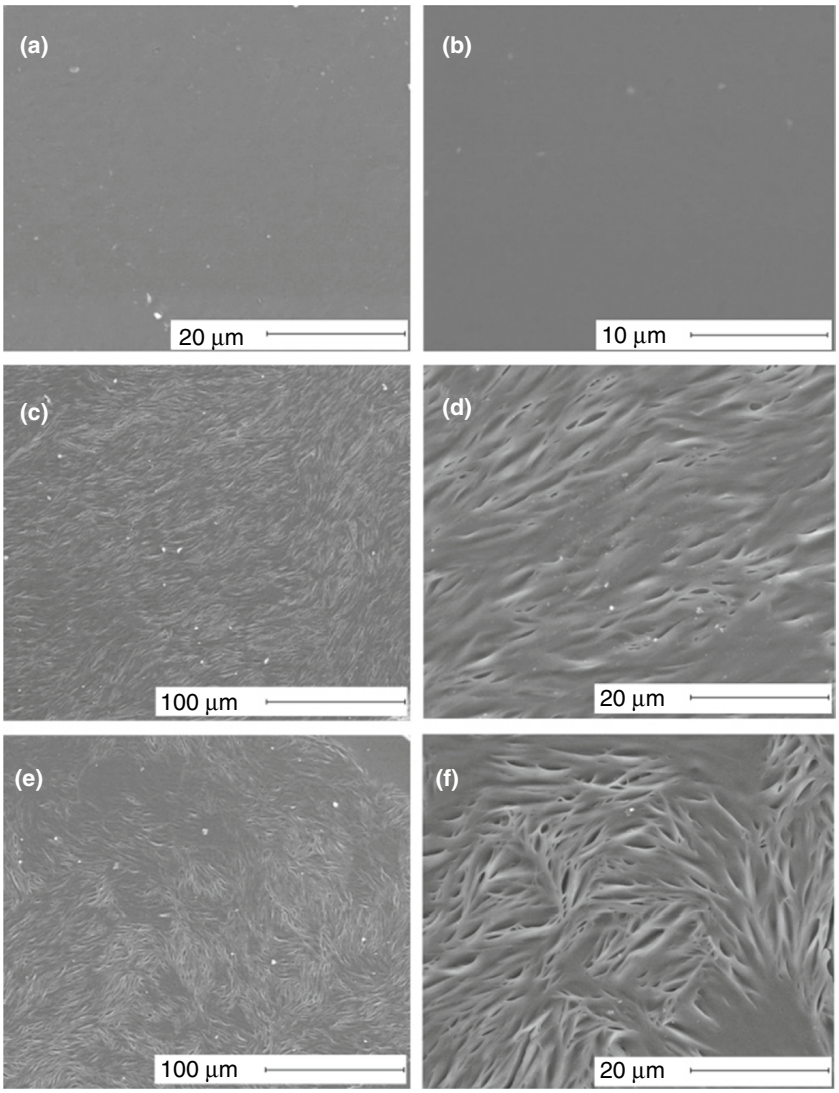

Fig. 11 Effect of graphite platelets addition on the microstructure of the polyurethane-based composite PCMs (PUPEG) in the absence and presence of BDO [89] (Reprinted with permission from Elsevier)

transfer is dominated by conduction, where the key parameter is thermal conductivity while in the latter, the increase in the viscosity should also be taken into consideration, which may offset the improvement in the conductivity or even may impede the heat transfer.

The nanoparticles are not directly introduced into base PCM; instead, they are prepared either by (1) one-step technique where synthesize and dispersion of nanoparticles are done simultaneously or (2) two-step technique where nanoparticles are produced in a dry powder form by various mechanical and chemical methods and then mix with the base PCM by ultrasonic bath, high shear mixing or magnetic stirring [113]. The primary challenge for evenly dispersion of nanoparticles is the utilization of proper mixing and stabilization techniques. If nanoparticles are not well distributed in the base PCM material, they tend to agglomerate and sediment, particularly during the solidification due to strong attraction forces (Van der Waals force) [113]. To overcome this problem, time required for solidification can be shortened, and both the mechanical mixing of the initial heterogeneous sample and ultrasonic process can be extended [114]. During this process, a cooling system should be adopted to control the temperature. More research could on the impact of surfactants, which are employed to improve stability of nanoparticles, on the key parameters of the nanoparticle. Another aspect in the preparation of nanoparticle which is usually disregarded by the researchers is their toxicity effect. The preparing procedure of the nano-PCM as well as their working safety can be found in detail in [114].

As shown in Fig. 12, different materials in nanoscale have been studied by researchers. These materials can be categorized into nanometals such as Ag [115], CuO [116], Al_2O_3 [117, 118], MgO [119], ZnO [120] and TiO_2 [121], and carbon-based additives such as graphite [122], graphite nanoplatelets [123], expanded graphite [124], graphene [125], graphene nanoplatelets [126], graphene oxide [127]

Table 3 Thermal conductivity enhancements of some composite PCMs

PCM	Support material	Additive/additive amount	Melting temperature/°C	Latent heat of fusion/J g^{-1}	Thermal conductivity enhancement	Ref
Capric acid–lauric acid	Vermiculite	Expanded graphite (10 mass%)	19.01	60.70	Increased by 150%	[90]
Capric acid–palmitic acid	Vermiculite	Expanded graphite (10 mass%)	23.13	70.03	Increased by 110%	[90]
Capric acid–stearic acid	Vermiculite	Expanded graphite (10 mass%)	25.12	71.46	Increased by 104%	[90]
Lauric–myristic–stearic acid	Expanded graphite	Expanded graphite (12/1 mass%)	29.05	137.1	Increased from 0.26 W to 2.51 W m^{-1} K^{-1}	[88]
Myristic–palmitic–stearic acid	Expanded graphite	Expanded graphite (7,14 mass%)	41.64	153.5	Increased from 0.25 W to 2.51 W m^{-1} K^{-1}	[86]
Palmitic acid	Expanded graphite	–	60.88	148.36	Increased by 2.5 times	[105]
Stearic acid	Expanded graphite	–	53.12	155.50	Thermal conductivity and the stability the composite were increased	[106]
Capric acid	Expanded perlite	Expanded graphite, 10 mass%	31.80	98.12	Increased by 64%	[107]
Lauric acid	Expanded perlite	Expanded graphite, 10 mass%	44.13	93.36	Increased about 86%	[108]
n-eicosane	Expanded perlite	Carbon nanotubes	36.12	157.43	Increased about 113.3%	[109]
Heptadecane	Bentonite clay	Expanded graphite	4–30 °C	38- 74	Increased 3.0 times	[110]
Palmitic acid–stearic acid	Bentonite clay	Expanded graphite, 5 mass%	54	89.12–163.72	Increased to 1.66 W m^{-1} K^{-1}	[111]

and carbon nanofiber [128]. The improvement in the thermal conductivity depends on numerous parameters such as PCM material, type, shape, size and concentration of nanomaterial, additives and operating temperature. The effect of these nanostructures on the thermophysical properties of pure PCM and on the improvement of various systems is presented hereafter.

Nourani et al. [129] showed that thermal conductivity of paraffin can be increased by 1–43% depending on nanoparticle fraction and operating temperature. Higher enhancement in the solid state (31%) was registered compared to liquid state (13%). This behavior was attributed to the ordered structure of solid state. Sharma et al. [130] noted 80% improvement in NEPCM (palmitic acid + TiO_2) with insignificant change in melting temperature and a slight variation in latent heat.

Wang et al. [131] measured the thermal conductivity of palmitic acid dispersed with multi-walled carbon nanotubes (MWCNTs) with 0.2, 0.5 and 1 mass%, and reported that thermal conductivity at room temperature can be enhanced by about 52% with the addition of 1% of MWCNT. Experimental study by Cui et al. [132] showed that optimal loading of Cu nanoparticles (0.5 mass%) improves the thermal conductivity of PCM (sodium acetate trihydrate) by 20% as well

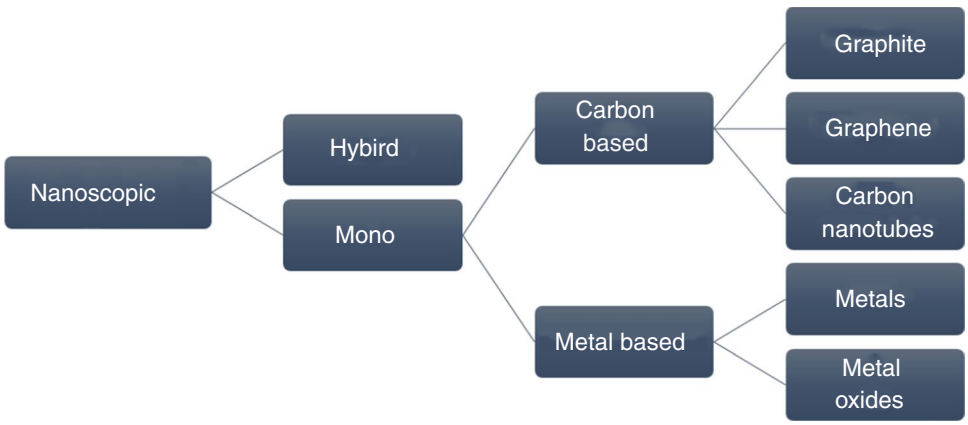

Fig.12 Nanoscopic enhancement for thermal conductivity

as reduces subcooling by around 0.5 °C. Soni et al. [133] measured the thermal conductivity of erythritol enriched with various nanomaterials (namely Al, Cu, SiO_2 and TiO_2) with 2.5 and 5 vol%. They found that Cu nanoparticles at 2.5 vol% lead to largest enhancement in thermal conductivity (8%) and largest reduction in specific heat (2.2%). Ebadi et al. [134] showed that thermal conductivity of PCM (coconut oil) can be improved considerably (7.5%) with loading of Cu with 1 mass% and melting fraction of PCM in a cylindrical tank was increased by 15% with Cu at 0.0218 mass%. The nanoparticle (Cu) was used by Lin et al. [135] where it was shown that thermal conductivity can be augmented up to 46.3% with 2 mass% loading. Also, it was stated that Cu reduced the subcooling effect as it acts as nucleation agent.

Owolabi et al. [136] compared the thermal conductivity, specific heat and thermal diffusivity of paraffin wax enriched with copper, aluminum, iron and zinc nanoparticles (0.5, 1.0 and 1.5 mass%) (Fig. 13). Experimental results showed that Zn provides the largest enhancement in thermal conductivity, varying from 46.4% at 0.5 mass% to 61.5% at 1.5 mass%, while Cu results in lowest enhancement (around 20% for all three solid fractions, Fig. 13a). Thermal diffusivity also increases with dispersion of nanoparticles in paraffin, and the trend of thermal diffusivity curves (Fig. 13b) is, in general, similar to those of thermal conductivity. However, with nanoparticle loading, specific heat value of NEPCM decreases with a different behavior depending on the nanomaterial type.

A similar study was conducted by Babapoor and Karimi [137] where SiO_2, Al_2O_3, Fe_2O_3 and ZnO nanoparticles dispersed in paraffin with different concentrations (2, 4, 6 and 8%). They found that adding nanoparticles causes a drop in latent heat while thermal conductivity and thermal diffusivity increase with increasing nanoparticle concentration, where highest enhancement in thermal conductivity was attained by Al_2O_3 (about 120% at 4 mass%), and the greatest enhancement in thermal diffusivity was observed in Fe_2O_3-composite (221.56% at 8 mass%). Dsilva et al. [138] experimentally examined the thermophysical properties of paraffin enriched with TiO_2, CuO and GO (graphene oxide) nanoparticles (0.3 mass%). Their results showed that thermal conductivity increased for all nanoparticle types, whereas the largest enhancement (101.2%) was attained by using GO. They found that specific heat capacity of all the mixtures was reduced due to lower heat capacity value of nanoparticles. However, the impact of nanoparticles on the latent heat was different, enhanced with TiO_2 (15.7%), CuO (64.7%) and degraded with GO (39.7%). The increase in the latent heat was explained by surface charge states of nanoparticles, layering in the solid–liquid phase and movement of phonons.

Aslfattahi et al. [139] demonstrated that the thermal conductivity of paraffin wax (PW70) can be augmented by 16% with the addition of a novel inorganic nanomaterial (MXene) at 0.3 mass%. It was noted that with this kind of nanoparticle loading, apart from improvement in thermal conductivity, specific heat also increases up to 43%, depending on the nanoparticle concentration and temperature.

It is noteworthy to mention that not all studies found improvement in thermal conductivity with dispersion of nanoparticles. For example, Colla et al. [140] tested the variation in thermal conductivity and latent heat of two different PCMs (Rubitherm, RT20 and RT25) with the addition of Al_2O_3 and carbon nanotubes, and found that addition of the Al_2O_3 nanoparticles causes a degradation in the thermal conductivity of both RT20 and RT25 while the carbon nanotubes remarkably enhanced the thermal conductivity of the pure paraffin waxes, with improvement reaching 35%. Their results regarding the latent heat showed that the latent heat of RT20 increases when Al_2O_3 and carbon black at 1 mass% is added. Conversely, the Al_2O_3 nanoparticles have no influence on the latent heat of RT25 whereas when adding carbon black nanoparticles, the latent heat reduces.

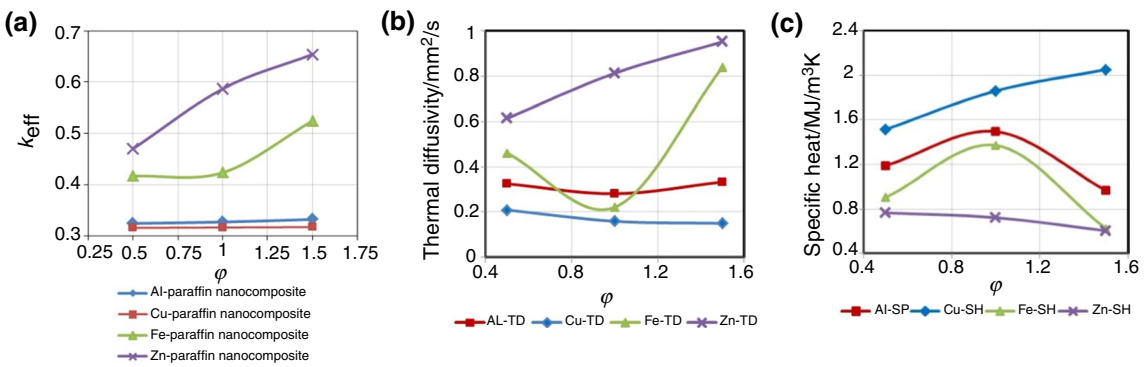

Fig. 13 Thermophysical properties of NEPCM with various loadings: (a) thermal conductivity, (b) thermal diffusivity, (c) specific heat [136] (Reprinted with permission from Elsevier)

During charging process (melting), viscosity is another key parameter as it also increases with nanoparticle loading, which suppresses convection currents and finally results in slowdown of melting process. Figure 14 shows the increase in thermal conductivity and viscosity with addition of CuO nanoparticles to paraffin. Srinivasan et al. [141] showed that inclusion of graphite at 3.5 vol% concentration to PCM (eicosane) increased the thermal conductivity by 4.5 times and viscosity by 12.5 times.

Weigand et al. [143] found that addition of nanoparticles did not change the Newtonian nature of the paraffin (IGI-1230A) but viscosity of NEPCM is highly dependent on the nanoparticle type. They did not find a significant effect of graphite nanoparticles (HGNF and xGNP) on viscosity, while the addition of MWCNT increased the viscosity by as much as 75% seen at low loading concentrations. Even higher increment was registered by Zeng et al. [144] where the measured viscosities with 1 mass% and 2 mass% MWCNT loadings were, respectively, of one and two orders of magnitude higher than that of pure PCM (1-dodecanol).

It might be expected that, compared to pure PCM, the latent heat of NEPCM will be lower, since no phase change takes places in nanoparticles. However, as already mentioned above in the study by Dsilva et al. [138], the latent heat may be increased with nanoadditives. A similar observation was reported in [145] where latent heat of paraffin wax dispersed with α-Al_2O_3 nanoparticles. The DSC measurement of Şahan et al. [146] also showed that apart from remarkable enhancement of thermal conductivity (up to 60%), latent heat storage capacity of paraffin Fe_3O_4 increased by 8% compared to pure PCM.

Recently, hybrid nanofluids (suspending at least two different nanoparticle types in the PCM) have been focused by researchers as they compromise the favorable properties of nanoparticles [147]. Kumar and Krishna [148] conducted experiments on the thermophysical properties of hybrid NEPCM (paraffin wax, RT35, enriched with CuO and Al_2O_3 nanoparticles) at different concentrations (Fig. 15). They attained the highest improvement in thermal conductivity by the combination of Al_2O_3 and CuO (75:25%) at 2 mass% (Fig. 15a), where the improvement in the thermal conductivity was doubled, compared to pure paraffin. Melting point decreased with increment of particle concentration, where the largest decrease was observed with the same aforementioned combination (75% Al_2O_3 + 25% CuO).

Arshad et al. [149] examined a detailed study on the thermophysical properties of PCM (paraffin wax, RT-28HC) containing mono- (MWCNT, GNPs, CuO and Al_2O_3) or hybrid nanoparticles with different mass percentage ratios, keeping the solid fraction at 1 mass%. Their results showed that the degree of subcooling decreases with nanoparticle loadings, and the hybrid NEPCM of paraffin/GNPs + MWCNTs at 1 mass% has the optimal value for latent heat. They found that carbon-based hybrid NEPCM had higher dispersion stability and provided higher thermal conductivity enhancement (96%) at mass percentage ratio of 0.75:0.25 than metallic oxide-based NEPCM (49%). The maximum reduction in latent heat was reported to be 3.75%.

In another study, Faraji et al. [150] investigated the potential effect of using mono- and hybrid NEPCM on the operating temperature of a heat sink (an electronic component) by an experimentally validated numerical model. Different volume fractions of nanoparticles were studied and found that the hybrid nanoparticles (1 vol% Al_2O_3 and 3 vol% Cu) had a better performance in reducing the operating temperature of electronic component with a decrease rate of 5.77% while only 4.69% was observed for the mono-nanoparticles (4 vol% Cu) with respect to pure PCM. Solidification process of an Al_2O_3-GO hybrid nanoparticles dispersed NEPCM was studied by Hosseinzadeh et al. [151] to enhance the thermal performance of a latent heat storage system. According to the findings of the study, the required time for the solidification process was about 1.7 and 2.7 times quicker than that of pure PCM for 2.5 and 5 vol% Al_2O_3-Go hybrid nanoparticles, respectively.

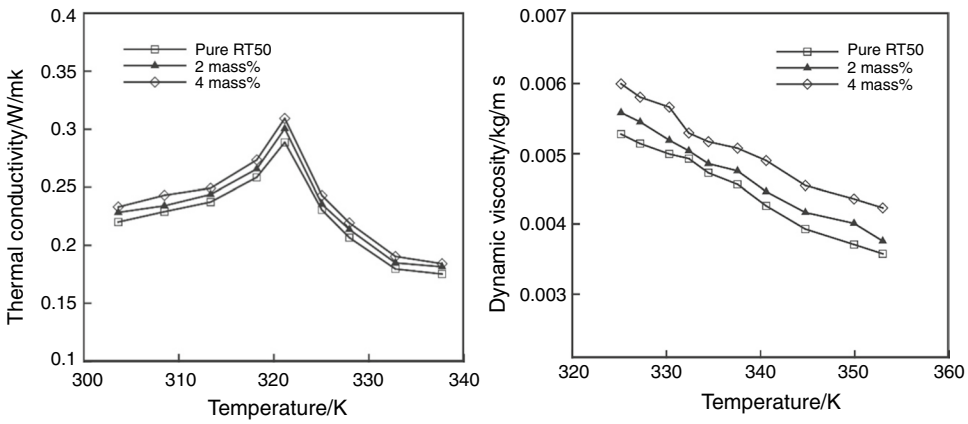

Fig. 14 Change in thermal conductivity and viscosity of RT50 for different mass fractions of CuO nanoparticles [142] (Reprinted with permission from Elsevier)

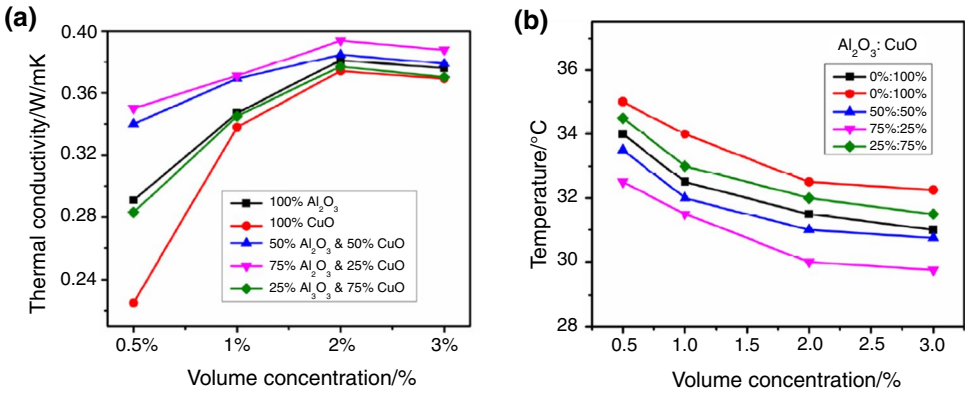

Fig. 15 Hybrid NEPCM. **a** Thermal conductivity and **b** melting temperature [148] (Reprinted with permission from Elsevier)

An extensive review of the studies in the literature regarding nanoenhanced PCM was carried out and presented with observed advantages, common drawbacks as well as faced challenges. Considering the obvious advantages of nanoenhanced PCMs reported by the researchers, it is clear that this technology is promising in the development of sustainable and thus emission-free systems. Despite its theoretically and experimentally proven advantages, it is also clear that the dispersion of nanoparticles could provide several disadvantages which need further attention and investigation. For instance, in most of the studies insertion of nanoparticles into PCM increased the thermal conductivity whereas heat transfer characteristics was also observed to be degraded due to increase in viscosity which restrains convection currents in the molten PCM. Besides, some controversial results regarding latent heat storage capacity of NEPCM were noted in the published studies needing to be addressed more clearly by the researchers. It is noted that the improved performance from NEPCM is highly dependent on the optimal nanoparticle concentration; therefore, it should be further investigated for maximum performance while keeping the balance between the thermal conductivity and latent heat storage capacity. Suitable nanoparticle selection is another important parameter to gain maximum benefit from NEPCM. As the stability of NEPCMs depends on both the used nanoparticles and base PCM, the mixture should be compatible. The selection of NEPCM also depends on the specific application. For instance, metallic nanoparticles have very large thermal conductivity which is a desirable property; however, they are not very suitable for medium–high-temperature applications of PCM since they have active chemical nature which causes them to be very reactive in high temperatures [152]. Moreover, the high density is one of the drawbacks of metal and metal oxide nanoparticles which can lead to agglomeration and sedimentation. Furthermore, as discussed above, most studies reported that introducing nanoparticles may cause an undesirable reduction in the latent heat. The latent heat of salt ($MgCl_2$–KCl–NaCl) decreased by 7.6%, 6.4% and 2.4% by the dispersion of ZnO, CuO and Al_2O_3 [153]. On the other hand, carbon-based nanoparticles possess favorable characteristics such as very large thermal conductivity, low density and stable chemical property. Apart from thermophysical properties and compatibility with the base PCM, the unit cost of nanoparticles is another factor which should be considered when selecting a nanoparticle type [154]. Therefore, thermoeconomic analysis of the nanoparticles accounting the application field is a necessity in terms of usability especially considering the fact that the cost of the nanomaterials can be much higher than that of PCMs.

Summary of the nanoscopic enhancement is provided in Table 4 with comments on the thermophysical properties of nanoenhanced PCM and nanoparticle as well as base PCM properties.

Applications of NEPCM

Nanoenhanced PCMs are utilized by researchers in numerous applications especially where charging and discharging capacity as well as required time for storage is important. They are mainly employed for thermal energy storage, electronic battery cooling, heat recovery and photovoltaic (PV) component cooling [155]. Some examples of usage of NEPCM in these fields are given below.

Buildings are one of the major application areas for thermal energy storage systems where nanoenhanced PCMs are considered by means of storing the excessive heat for later usage [156]. For instance, Dastmalchi and Boyaghchi investigated the performance of a heat exchanger by using SiO_2-based RT25 PCM to advance free cooling potential of a TES system [157]. Different volume fraction rates were studied and found 9.4% enhancement in provided cooling power with 5 vol%. They can be integrated with active cooling systems such as air conditioners to increase overall efficiency of the setup by exploiting the latent heat storage capacity and rapid phase change process properties. Said and Hassan [158] studied the potential enhancement in an AC when NEPCM is utilized. Nanoparticles of aluminum

Table 4 Summary of the nanoscopic enhancements

Reference	PCM	Nanoparticle	Remarks on thermophysical properties
Nourani et al. [129]	Paraffin	Spherical 10–20 nm Al_2O_3	Thermal conductivity shows a nonlinear increase with mass% and highest value was obtained for 10 mass% Slight changes were observed in latent heat storage capacity after 120 cycles
Sharma et al. [130]	Palmitic acid	Spherical 21 nm TiO_2	Nanoparticles improved the chemical and thermal stability for 1500 cycles Increase in thermal conductivity up to 80% was reported by using 5 mass% TiO_2 Significant increase in melting temperature and reduction in latent heat storage capacity obtained in case of 2 mass% of TiO_2
Wang et al. [131]	Palmitic acid	30 nm MWCNTs	Thermal conductivity of the composite was enhanced significantly Pretreatment of MWCNT was important for the increased thermal properties
Cui et al. [132]	Sodium acetate trihydrate	10–30 nm Cu	Thermal conductivity was increased by 20% with 0.5 mass% Cu Subcooling degree of the composite decreased to around 0.5 °C
Soni et al. [133]	Erythritol	Al, Cu, SiO2, TiO2	Significant increase in thermal conductivity (8%) was obtained with 2.5 vol% Cu Lowest reduction in specific heat was achieved with Al nanoparticle
Ebadi et al. [134]	Coconut oil	< 50 nm CuO	7.5% increase and 8.25% decrease was observed for thermal conductivity and latent heat storage capacity with 1 mass%, respectively
Lin et al. [135]	Paraffin	Hexagon 15–125 nm Cu	Thermal conductivity was increased considerably with 2 mass% Cu Subcooling effect was reduced Thermal diffusivity was increased up to 0.3446/mm^2s^{-1}
Owolabi et al. [136]	Paraffin	Cu, Al, Zn, Fe	Adding 1.5 mass% Zn nanoparticles enhanced thermal conductivity by 61.5% Cu nanoparticles resulted in lowest thermal conductivity
Babapoor and Karimi [137]	Paraffin	Amorphous 11–14 nm SiO_2, spherical 20 nm Al_2O_3 and Fe_2O_3, 50 nm cubic ZnO	Thermal diffusivity was observed to be increased with concentration for all nanoparticles and highest rate (221.56%) was obtained with 8 mass% Fe_2O_3 Latent heat reduction was seen for nanoparticle addition Thermal conductivity can be enhanced up to 0.919/Wm^{-1} K^{-1} with 4 mass% Al_2O_3
Dsilva et al. [138]	Paraffin	Spherical 160 nm TiO_2, cylindrical 190 nm CuO, folded foil ∽450 nm GO	0.3 mass% graphene oxide (GO) provided 101.2% increase in thermal conductivity Latent heat storage capacity was increased for TiO (15.7%) and CuO (64.7%), whereas it decreased for GO (39.7%) All nanoparticle additives resulted in reduced specific heat
Aslfattahi et al. [139]	Paraffin	MXene (Ti_3C_2)	16% enhancement in thermal conductivity was obtained for 0.3 mass% Specific heat was also increased by 43%

Table 4 (continued)

Reference	PCM	Nanoparticle	Remarks on thermophysical properties
Colla et al. [140]	RT20, RT25	10 nm Al_2O_3, spherical 15–20 nm CB	The addition of Al_2O_3 degraded thermal conductivity of both PCMs Up to 35% enhancement can be obtained in thermal conductivity for CB CB additive leads to significant reduction in latent heat when RT25 used as base PCM
Srinivasan et al. [141]	Eicosane	Graphite	The composition showed 4.5 times higher thermal conductivity and 12.5 times higher viscosity with 3.5 vol%
Pahamli et al. [142]	RT50	CuO	Adding nanoparticles increases thermal conductivity and dynamic viscosity Melting time was reduced by 11.16% with 4 mass%
Weigand et al. [143]	Paraffin (IGI-1230A)	HGNF, xGNP, MWCNT	HGNF and xGNP did not result in any viscosity change while MWCNT increased viscosity up to 75% Newtonian nature of the fluid remained the same
Zeng et al. [144]	1-dodecanol	8–15 nm CNT	Significant increases were observed in viscosity
Mohamed et al. [145]	Paraffin	Spherical 1.4–2 nm α-Al_2O_3	Thermal conductivity increases with increasing concentration
Şahan et al. [146]	Paraffin	40–75 nm Fe_3O_4	48% and 67% enhancements in thermal conductivity were observed for 10 mass% and 20 mass% nanomagnetite dispersion, respectively Slight increase in latent heat storage capacity was attained
Kumar and Krishna [148]	RT35	CuO, Al_2O_3	Thermal conductivity was doubled by using combination of Al_2O_3 and CuO 75:25% Melting temperature was decreased considerably

oxide (Al_2O_3), copper (Cu) and copper oxide (CuO) were considered as additives while PCM SP24 E was utilized as base fluid. The authors stated that the coefficient of performance of the cooling system was increased and up to 7.41% reduction in power consumption was observed for 5 vol%. Considering the accelerating pace of the electronics and battery technologies, the cooling requirement of these systems become a research hot spot among the researchers, and therefore, NEPCMs are also employed for this purpose. In this context, mono- and hybrid NEPCMs are utilized for cooling of heat sink by Arshad et al. [149], and found that the highest increase in thermal conductivity was achieved with hybrid NEPCMs of which are GNPs and MWCNTs. NEPCMs are also utilized for PV applications to reduce operating temperature to improve the electricity conversion efficiency and life span of PV cells. Al_2O_3 was dispersed into RT55 PCM and integrated with a PV panel by Nada et al. [159]. As the authors reported, 13.2% increase in the efficiency of PV module was observed for NEPCM while only 5.7% increase was achieved for pure PCM with respect to the case without PCM. Summary of the review studies and common applications of the NEPCM in the literature is presented in Table 5 with major findings.

Closing remarks

So far, characteristics of PCMs were defined and nanoscopic enhancement methods of PCMs were discussed with advantages and disadvantages, and also, faced challenges were pointed out. Common applications of enhanced PCMs were provided with major findings. In this section of the paper, final comments on the methods were provided.

In this context, utilizing nanomaterial in pure PCM is an effective solution to augment the poor heat transfer characteristics of PCM since nanomaterials have a much higher thermal conductivity comparing with the base PCM and surface-to-volume ratio compared to microparticles, enabling higher heat transfer rate. Besides, nanomaterial enhancement is a more stable method compared to microscale ones. However, adding additives in the pure PCM has some drawbacks also. For instance, it is not easy to guarantee that the distribution of additives in PCM is uniform which can

Table 5 Some applications of NEPCM

Reference	PCM	Nanoparticle	Application	Major findings
Dastmalchi and Boyaghchi [157]	RT25	SiO_2	Free cooling potential in buildings	Increase in cooling power by 9.4, 8.3 and 7.4% with 5, 3 and 1 vol% SiO_2, respectively
Said and Hassan [158]	PCM SP24 E	Al_2O_3, CuO, Cu	Air conditioning performance improvement	7.41% saving in power consumption with 5 vol% Cu
Pahamli et al. [142]	RT50	CuO	Shell and tube heat exchanger	11.16% reduction in melting time with 4 mass% CuO
Arshad et al. [149]	RT28-HC	Al_2O_3, CuO, MWCNT, GNP	Microelectronic thermal management	Hybrid NEPCMs (MWCNT and GNP) showed higher thermal conductivity
Soni et al. [160]	Erythritol	Cu, Al, TiO_2, SiO_2	Waste heat recovery technology	9.7% faster discharging by using Cu/ Erythritol composite with 2 mass% Cu
Sharma et al. [161]	RT42	CuO	Photovoltaic operating temperature management (integrated in building)	Significant increase in electrical power output by using CuO 0.5 mass%
Krishna et al. [162]	Tricosane	Al_2O_3	Electronic cooling, heat pipe	53% reduction in fan power consumption with 2 vol% nanoparticle
Jilte et al. [163]	Eicosane, PureTemp37, PureTemp44	Al_2O_3	Li-ion battery thermal management for electric vehicles	Restricts cell temperature below 46 °C even in hot ambient
Narayanan et al. [164]	Paraffin	Nanographite (NG)	Solar water heating	Melting time was obtained as 3 min with 93% reduction rate with respect to pure PCM Overall efficiency of the system was increased
Venkitaraj et al. [165]	Pentaerythritol	Al_2O_3	Internal combustion engine heat recovery	18.3% energy saving by adding 0.5 mass% nanoparticle
Ma et al. [166]	RT24	Cu	PVT integrated ceiling ventilation system	Higher melting and solidification rate was seen 25.1% higher heat rejection was achieved
Bayat et al. [167]	RT44	CuO, Al_2O_3	Electronic device cooling	At low concentrations, efficiency of heat sink was increased; however, increasing the fraction to 6 vol% decreased the efficiency compared to pure PCM 2 vol% Al_2O_3 provided a better performance than that of 2 vol% CuO

be a serious problem in long-term usage by aggregation as well as sedimentation of nanoparticles, leading to decrease in thermal properties. Viscosity increase is another faced deficiency as it decreases the heat transfer, and thus melting and solidification rate. However, the above-mentioned drawbacks are remarkably lower in the NEPCM compared to microencapsulated PCMs.

Conclusions

Micro/nano-PCM was successfully incorporated in various thermal applications. The role of micro/nano enhanced PCM was extensively investigated by researchers. The micro/nano enhancement techniques of phase change materials (PCMs) have been reviewed in this paper. The following conclusions have been drawn:

- Polymeric shell materials including methacrylate, styrene are mostly preferred in the encapsulation process, inorganic metal oxide shells such as SiO_2 and TiO_2 are also used.
- Heat storage capacity of the PCM varies depending on the core-to-shell ratio. As the amount of shell increases, the heat storage capacity decreases, which increases the application cost.
- Carbon materials including graphene and expanded graphite are used as both additive and framework in order to obtain enhanced thermal properties. Also, they strengthen the mechanical stability of the PCMs.
- Graphite nanoplatelets in general provide higher improvement compared to metallic nanoparticles.
- Despite reported reductions in latent heat storage capacity of PCM by nanoenhancement, some researchers also observed improvements.
- Finally, nanomaterial enhancement is a more stable method compared to microscale methods.

For future research, more experimental works are needed with focus on the melting and solidification rate considering sedimentation and agglomeration issues in long term.

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