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Review article

Role of nanostructured coatings on composite phase change materials for thermal durability enhancement: A review



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ABSTRACT

With the rapid growth in energy demand and the increasing need for stable thermal storage, the use of phase change materials (PCMs), particularly in the form of phase change composite materials, has received widespread attention. Despite the high advantages of composite phase change materials (CPCMs) in latent heat storage, problems such as leakage, low thermal conductivity, and performance degradation in successive thermal cycles have still limited their use. One of the novel solutions to increase the thermal durability of these materials is the application of nanostructured coatings on their surfaces. By creating physical and chemical barriers, these coatings not only prevent leakage and oxidation but also improve heat transfer and increase structural stability under operational conditions. In this review article, we first introduce the basic principles of PCMs and the structure of CPCMs. Then we investigate the key role of nanostructured coatings in improving thermal stability, reducing supercooling, and increasing thermal cycling. Also, industrial applications of this technology in various fields such as solar energy storage, thermal control of buildings, thermal management of lithium-ion batteries, and electronic systems are reviewed.

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KEYWORDS

Composite PCMs
Nanostructured coatings
Thermal energy storage
Thermal durability
Latent heat storage



1. Introduction

In recent decades, the rapid growth of energy demand, supply fluctuations, and environmental pressures caused by the consumption of fossil fuels have created a strong impetus for the development of energy storage technologies, especially thermal energy [1]. Among the various options, latent heat energy storage (LHTES) using phase change materials (PCMs) has attracted widespread attention from researchers due to their high energy density, good heat transfer efficiency, and long-term cyclability. However, the direct application of PCMs is associated with challenges such as leakage into the liquid

phase, low thermal conductivity, and instability during freeze-thaw cycles [2].

To overcome the inherent disadvantages of PCMs, their incorporation into porous matrices, nanomaterials, or coating materials has led to the development of composite phase change materials (CPCMs). CPCMs not only overcome the leakage problem by physically or chemically immobilizing the active material in a stable structure, but also improve the thermal conductivity and storage capacity by appropriately selecting the matrix phase (such as inorganic oxides, porous carbon, or polymer nanocomposites) [3, 4]. However, even CPCMs suffer from structural degradation, recrystallization, and performance degradation

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during repeated thermal cycling, making their thermal durability a key limitation. One of the novel approaches to enhance the thermal and mechanical durability of CPCMs is the application of nanostructured coatings on their surfaces. Nanostructured coatings can not only act as a thermomechanical barrier against leakage, oxidation, and unwanted chemical reactions, but also increase the cyclic stability of the material by improving heat transfer at the contact surface and reducing thermal stresses. These coatings are generally made of advanced materials such as reduced graphene oxide (rGO), TiO₂ or SiO₂ nanoparticles, bimetallic oxides, and even 3D carbon structures [5, 6].

From a mechanistic perspective, nanostructured coatings play a key role in phase stability and heat transfer by increasing the effective contact area, reducing the interfacial thermal resistance, and inhibiting recrystallization or supercooling. For example, the use of multi-walled carbon nanotubes (MWCNTs) and graphene can increase the thermal conductivity of CPCMs by several times. Also, oxide coatings can prevent structural degradation under extreme temperature conditions through their dielectric properties and chemical resistance. In some studies, these coatings have even prevented the penetration of UV radiation and corrosive gases into the CPCM matrix, which is of critical importance for outdoor applications [7, 8]. The applications of nanostructured coatings on CPCMs span a wide range of industries: from solar energy storage in thermal power plants to thermal control in electronic systems, smart wall design in green buildings, and even temperature management of lithium batteries in electric vehicles. However, industrial implementation of these coatings requires overcoming challenges such as coating continuity, manufacturing cost, and long-term chemical compatibility. Future research should focus on developing self-healing, recyclable, and responsive coatings that can change properties in response to temperature, light, or pressure [9].

In this review, after providing an overview of the basic concepts of PCMs and introducing the structure and physicochemical properties of CPCMs, an in-depth study of the thermal stability limitations of this class of materials will be conducted. Next, the critical role of nanostructured coatings as a novel approach to increase thermal durability and reduce the degradation of CPCMs' performance in sequential thermal cycling is analyzed. Also, the industrial applications of this technology in thermal energy storage systems, their advantages, and practical performance are reviewed. Finally, the challenges in the implementation of nanostructured coatings, along with future research directions, are presented for the development of the next generation of CPCMs with high durability and efficiency.

2. Overview of PCMs

PCMs are a special group of thermal energy storage materials that can absorb and release latent heat through phase changes, particularly between solid and liquid states. During the melting process, these materials absorb heat without an essential temperature change, and upon freezing, they release this stored energy at a nearly constant temperature. This uncommon thermal profile provides PCMs to be deactivated and temperature adjusted on a regular schedule, making them ideal for many kinds of thermal energy storage usages. The three major categories for PCMs are: mineral, organic, and eutectic. These materials can even be useful in systems that use renewable energy or in efforts to increase energy efficiency in structures and factories. Organic materials, which include paraffins and fatty acids, are examples that are recognized for their high chemical resistance and low reactivity to

freezing. Minerals such as salt hydrates store more heat but face problems such as phase separation and corrosion. Eutectic compounds, which are mixtures of several components, are designed to create a balance between desirable thermal and chemical properties. These materials are widely used, especially in renewable energy systems and in the design of low-energy buildings and facilities [10, 11]. Organic PCMs contain compounds such as paraffins, fatty acids, fatty acid esters, polyols, and polyethylene glycols, each of which has its unique thermal properties. Paraffins are widely used due to their high chemical stability and suitable melting point for latent heat storage. Fatty acids, which are often of biological origin, have a high capacity for heat storage and therefore have a special place in many bio-based applications. Fatty acid esters, with their favorable thermal properties, are used in specific and specialized applications. Polyols, including sugar alcohol compounds, are used in applications requiring high temperatures due to their higher melting points and suitable heat capacities. Polyethylene glycols also cover a wide range of melting points and latent heat capacities, depending on their molecular weight. Aside from melting temperature and latent heat, other important thermophysical parameters, like as heat transfer capacity, density, and thermal conductivity, impact efficiency. In general, these characteristics are critical for choosing and building efficient latent heat storage devices [12, 13].

In the clean energy field, PCMs are used in solar water heating systems, solar heating and cooling of buildings, and concentrated solar thermal power plants (CSP). Due to their ability to precisely regulate temperature, their application in various industries is rapidly increasing. By storing excess solar energy during the day and gradually releasing it when needed, PCMs can improve the efficiency and sustainability of systems, even during periods of inactivity. In the building industry, these materials are incorporated into the structure of floors and walls to intelligently regulate indoor temperatures without the need for active equipment and reduce dependence on heating and cooling systems. In heating, ventilation, and air Conditioning (HVAC) systems, PCMs help reduce peak loads, save energy, and improve indoor temperature control by storing excess heat or cold during off-peak hours and releasing it during peak hours. Additionally, PCMs are used in cooling appliances, clothing, food cold chains, and pharmaceutical products, including vaccine containers. These materials can actively regulate the temperature of the surrounding environment, providing solutions with minimal heat loss, and their low maintenance requirements make them an efficient option for applications requiring precise temperature regulation and energy efficiency [14].

As mentioned earlier, organic PCMs are divided into two categories: paraffinic and non-paraffinic. Paraffins, which are widely used in construction projects, are composed of hydrocarbon chains and have attracted attention due to their thermal stability, non-corrosive properties, and repeatable ability to undergo phase change. Non-paraffinic PCMs such as fatty acids and esters, although biodegradable and biocompatible, are usually more corrosive and have a higher production cost. Both organic groups can be combined with building materials and provide high heat capacity, but are poor in thermal conductivity and may have limitations in terms of flammability. Inorganic PCMs, which mainly consist of hydrous salts, perform better in terms of energy density and thermal conductivity, but face problems such as phase separation, supercooling, and abrasive nature. Meanwhile, eutectic materials, which are obtained by combining organic and inorganic materials, offer precise melting points and long-

term thermal stability, but their production is costly and their manufacturing process is complex [15]. Cold energy storage systems (CTES) using PCMs have attracted increasing attention due to their high energy storage density and excellent temperature control capabilities. In these systems, the PCMs absorb and release heat during the phase change process, thereby maintaining the environmental conditions or equipment performance within a desired temperature range. This technology is particularly useful in HVAC systems, where cooling energy can be stored during off-peak hours and used during peak periods [16]. CTES is also used in cold storage, food storage, and the transportation of temperature-sensitive goods to ensure thermal stability. To improve the thermal conductivity of PCMs in CTES systems, strategies such as the addition of nanoparticles, microencapsulation, and the use of composite materials are being applied. However, challenges such as supercooling, phase separation, and performance degradation over time remain and require ongoing research to overcome them [17]. Microcapsules with dimensions from 1 to 30 micrometers are commonly utilized to encapsulate PCMs in building supplies, including cement and plasterboard. They contain barrier materials that avoid leaks throughout phase shifts, and they have to endure extreme pressure, temperatures, and chemical contamination. Their very small size allows them to be easily incorporated into permeable building materials without compromising the mechanical strength of the materials. The technology is relatively simple to implement, but its production costs are high. In comparison, macroencapsulation (larger capsules) provides only a small increase in thermal performance. Another encapsulation method is based on polymers that act as durable shells; these coatings allow for expansion and contraction of the PCM volume and prevent moisture loss. Polypropylene and polyethylene are widely used in this field due to their high mechanical durability and controlled vapor permeability. In general, the use of various encapsulation methods plays an important role in improving the stability of PCMs, reducing leakage, and increasing their performance in construction projects, and is an effective solution to overcome technical challenges [18]. Encapsulation of PCMs leads to increased efficiency of energy storage tanks, especially the use of small capsules that provide better thermal performance. Microcapsules perform well at low temperatures, but pose manufacturing challenges in high-temperature applications. The development of cost-effective and high-temperature-resistant encapsulation technologies is critical. Optimization studies should focus on the design of the tanks, operating conditions, type of PCMs, and materials of construction. Heat transfer is mainly by conduction before melting and then by convective heat transfer; increasing the role of convection is considered a major challenge. The use of dimensionless numbers such as Rayleigh and Nusselt can be useful in optimizing the tank shape to improve heat transfer [19]. The amount of PCM affects system performance; insufficient volume reduces efficiency, and too much volume causes excessive temperature rise. Further research is needed to determine the optimal amount of PCM, especially in applications such as solar cooking. Also, PCMs typically cause a delay in heat release, which requires more effective thermal management [20, 21].

3. CPCMs: Structure and limitations

Organic PCMs are widely used due to their thermal stability and low corrosion, but liquid leakage during the phase change process is one of

their main challenges. To solve this problem, form-stable CPCMs have been developed by adding preservatives, such as polymers and porous materials. Although polymers are common, the use of porous materials such as silica, bentonite, and carbon foams has attracted more attention due to their cost reduction and improved thermal performance. The low thermal conductivity of PCMs has led to research focusing on enhancing this property. For example, thin graphite foams, aluminum nitride, carbon fibers, and silver nanoparticles have been shown to improve the thermal conductivity of PCMs [22]. On the other hand, in thermal insulation applications, low conductivity is still desirable. Delignified wood with its porous structure and suitable mechanical properties is considered an efficient, non-toxic, and biocompatible thermal insulation. Still, it has not been used as a support substrate in CPCMs so far. Also, 1-tetradecanol (TD) with a phase change temperature of about 37 °C is a suitable option for ambient temperature applications. To enable visual monitoring of the phase change, it has been proposed to add thermochromic materials, including dye, developer, and co-solvent, to the CPCMs' compositions [23]. The use of TD as a co-solvent adjusts the color change temperature and provides thermal observability. Combining thermochromic materials with delignified wood produces materials with optimal thermal performance, high stability, and visual monitoring capabilities that are widely used in thermal insulation, decoration, furniture, and energy optimization of buildings [24].

In recent years, a significant effort has been made to improve CPCM manufacturing methods to improve their thermal storage performance. One of the most common methods is absorption in a molten state; in this process, porous materials such as expanded graphite or diatomite are immersed in molten paraffin to allow PCM to penetrate holes. After that, the composite is dried using compressed air or a combination of air and a suitable dryer to remove the surface paraffin. Another method is vacuum impregnation, which, by creating a vacuum, allows penetration of PCM, become deeper and more uniform, and the encapsulation ratio increases significantly. Also, the pre-treatment of porous carriers is done to increase the absorption, purity, and expansion of the inter-layer distance to increase the storage capacity. To improve thermal conductivity and prevent PCM leakage, the final surface of the material is coated with a combination of epoxy, graphite powder, and silica vapor. These advances have led to higher durable materials, better thermal efficiency, and wider applications in thermal storage [25, 26].

In the process of making CPCMs, the primary goal is to increase storage capacity, enhance thermal conductivity, and prevent leakage of the PCM. A simpler method, called self-absorption, is also used, in which penetration is only carried out through capillary force; however, it is less efficient. Metal foams such as copper and nickel are a good substrate for PCM maintenance due to their high porosity and good thermal conductivity. Also, graphite and carbon foams are well combined with PCM due to their low density and good thermal performance. New methods, such as the use of graphene aerogels, have also been introduced. These aerogels with a three-dimensional porous structure allow for effective maintenance of PCM, such as fatty acids. In some examples, nickel foam with graphene coating and surface modification has made possible the spontaneous absorption property of PCM [27]. Also, the cold compression technique creates a strong and stable structure by combining PCM powder and conductive materials such as graphite. In another method, PCM is first dissolved in solvents such as toluene to improve permeability and more effectively enter the

structure by applying a vacuum. In order to improve performance, in some samples, nanostructured materials such as nano-silica or carbon nanotubes have been added to the structure [28]. These additives prevent PCM leakage during thermal cycles by creating stronger bonds and a more stable structure. The efficiency and thermal stability of PCM composites depend on the type of porous structure, surface characteristics, and operating conditions such as melting temperature, phase type, and impregnation. For example, in copper foams, the penetration of PCM is fast but superficial, while nickel foams create deeper and more uniform penetration. These factors directly affect the final performance of composite material in thermal storage [29].

The support matrices in PCM composites are typically composed of porous materials with high specific surface area and a structure containing numerous micropores, which allow for uniform distribution and effective retention of the PCM within the structure. However, there are key limitations in the performance of these composite materials that require special attention. One of the most important challenges is to increase thermal conductivity; adding conductive fillers to the PCM matrix usually yields limited results and may reduce the stored energy density, especially when using non-carbon fillers. Furthermore, paraffin, which is one of the common PCMs, exhibits significant volume expansion during phase change, which can affect the long-term stability of the system. On the other hand, traditional methods of loading PCM into porous substrates, such as direct impregnation and immersion, suffer from leakage problems, especially after enduring successive heating and cooling cycles [30]. Although the encapsulation technique alleviates this problem to some extent, protecting the encapsulated particles during and after the fabrication process involves significant complexities and costs. In addition, PCM leakage may be caused by the presence of moisture during mixing, which is usually controlled by protective coatings such as epoxy; however, these coatings, in addition to increasing costs, require special care during the construction and maintenance stages. Finally, vacuum impregnation processes used to improve PCM adsorption in porous structures are often energy- and time-consuming, and in some cases are not practical. All of these limitations are major challenges in the development and effective utilization of composite PCMs and require further research and technological improvements [31, 32].

Low thermal conductivity is one of the main challenges in the application of polymer CPCMs, which can significantly limit the

thermal efficiency of these materials in energy storage systems. In order to improve thermal performance, the use of high-conductivity additives such as expanded graphite, natural graphite, and carbon fibers in the structure of these composites has been considered. On the other hand, due to the flammable nature of some polymer bases used in CPCMs, the addition of flame retardants such as organophilic-modified montmorillonite and melamine phosphate is necessary to improve thermal stability and increase safety under operational conditions [33].

4. Thermal stability and durability challenges of PCMs

Thermal energy plays an important role in life and industry, but there is always a time and space gap between production and consumption. PCMs store and release latent heat, making them an excellent energy storage method. Lauric acid is a common organic PCM with high storage capacity and stability; nevertheless, leakage, poor thermal conductivity, and inherent stiffness at ambient temperature limit its use. Carbon nanotubes and thermoplastic elastomers have helped to address some of these difficulties, although flexibility at ambient temperature remains a challenge [34]. Cenospheres are used as a resistant and conductive shell to cover PCMs and reduce material leakage. The bio-silica coating on these shells improves adhesion to building materials and increases their durability. The combination of lauric acid, thermoplastic polyester elastomer, and modified carbon nanotubes creates a flexible composite material with high thermal conductivity that has wide applications in the thermal management of lithium-ion batteries and energy storage in buildings. The use of CPCM with a bio-silica coating also contributes to better performance and longevity of these materials [35, 36].

Thermal energy can be stored in three main ways: sensible heat storage, latent heat storage, and thermochemical storage. The common classification of thermal energy storage methods and materials is shown in Fig. 1. PCMs, which absorb and release energy when changing state, are one of the effective methods of storing latent heat. These materials are found in different states, such as solid-to-liquid, solid-to-gas, solid-to-solid, and liquid-to-gas. PCMs have wide applications in areas such as building construction, solar energy storage, and electronic cooling. However, the complexity of the phase change process and their low thermal conductivity have limited their use. To improve performance, the addition of conductive materials and

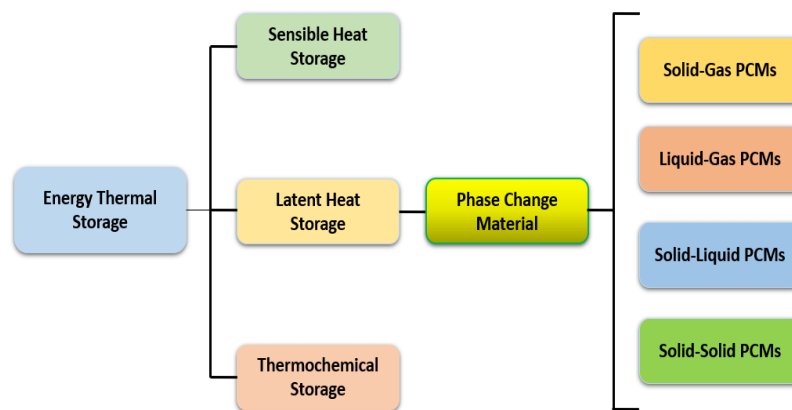


Fig. 1. Common thermal storage methods and materials. Modified with permission from Ref. [37].

the use of porous structures with high conductivity are employed. Despite the advances, more research is needed to develop this technology fully [37, 38].

Thermal energy storage using phase-change materials (PCMs) has been proposed as an innovative solution in the field of renewable energy technologies, especially in solar-biomass thermal systems that require continuous operation. These materials are able to store and release thermal energy with or without temperature changes, and due to their high energy storage capacity in low volume and environmental compatibility, they have been highly regarded in heating and cooling applications [39]. The selection of the appropriate phase change material requires the evaluation of important parameters such as cost, availability, thermal conductivity, chemical stability, melting temperature, and ultra-cooling behaviors. Since intermittent melting and freezing cycles are inevitable for all PCMs, maintaining the stability of thermal properties such as latent heat storage capacity and melting temperature during these cycles is important to ensure the durability of the system's performance and economic performance [9, 40]. To evaluate these characteristics, several methods have been developed, among which T-history and differential scanning calorimetric (DSC) methods are considered to be the most common analytical techniques. The DSC method is recognized as an outstanding technique for measuring the physical and thermal properties of PCMs. In practical applications, PCMs are usually melted and frozen once a day, but in the laboratory, accelerated thermal cycling tests are performed under controlled conditions and at a higher rate to investigate their long-term stability. In recent years, a major part of research has been devoted to the development, improvement of properties and durability testing of PCMs and their composites [41]. As mentioned above, thermal energy storage (TES) is one of the key methods in the optimal utilization of energy resources, divided into three main types: tangible heat storage, latent heat storage, and

thermochemical storage. In a tangible heat storage method, heat energy is stored by changing the temperature of a substance such as water or stone [42]. This method is simple and cost-effective, but requires a significant volume of material. Latent heat storage is based on the phase change of the material, so that a large amount of energy is stored or released at a constant temperature and in a small volume. PCM plays a major role in this process and must have properties such as proper melting temperature, high latent heat, thermal conductivity, and chemical stability to ensure optimal performance and safety of the system. Thermochemical storage is the most advanced type of TES, which acts based on reversible chemical reactions between adsorbent and absorbent materials. This method allows for long-term storage with high energy density and minimum losses [43]. A typical example of this method is the absorption-desorption systems of ammonia with mineral salts that store thermal energy in the structure of ammonia. By using composite structures such as salt composition with vermiculite, thermal conductivity is improved, and problems such as volume change and mechanical degradation are reduced. Also, the addition of booster materials such as iron powder can reduce the energy release temperature and improve the efficiency of the system. Finally, the development of new materials and advanced structures has created many opportunities to increase durability, improve efficiency, and improve the performance of thermal energy storage systems, which provides a clear path for the advancement of sustainable energy technologies. The density of energy storage in latent heat is greater than that of tangible heat, but thermochemicals have the highest density [44]. The only method of tangible heat is widely commercialized, and two other methods are being developed. The durability of the heat is about 20 years, and the durability of the other two methods is less. Also, latent heat has a wider working temperature range and higher efficiency. To compare the storage power, commercial capability, and durability of PCMs, refer to Fig. 2 [10, 45, 46].

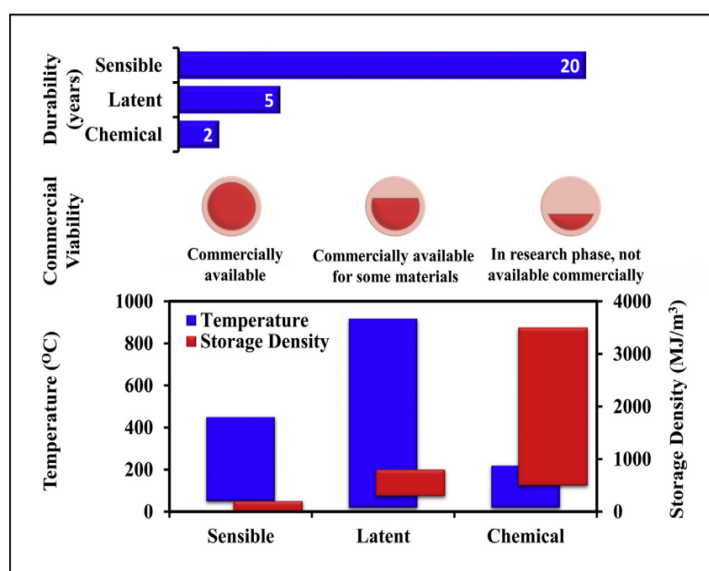


Fig. 2. Storage capabilities, commercial viabilities, and durability aspects of PCMs for thermal energy storage. Reprinted with permission from Ref. [10]. ©Copyright Elsevier.

5. Nanostructured coatings in thermal durability of PCMs

The application of nanostructured coatings on CPCMs as a novel method to enhance thermal durability is one of the main focuses of recent research in the field of thermal energy storage. These coatings can play a very important role in improving the physical, chemical, and thermal stability of CPCMs and overcoming key obstacles such as leakage, supercooling, oxidation, and structural degradation during successive thermal cycles.

Studies have shown that the application of coatings of metal oxide nanoparticles, such as TiO_2 , SiO_2 , ZnO , and Al_2O_3 on the surface of CPCMs forms a protective layer against moisture and oxygen penetration and significantly increases the resistance to thermal degradation. In a study by Deng et al. [47], a TiO_2 mud-like coating on polyethylene glycol showed that the material structure remained stable even after 100 freeze-thaw cycles, without a significant decrease in thermal storage capacity.

Also, the use of carbon nanostructures such as reduced graphene oxide (rGO) and multi-walled carbon nanotubes (MWCNTs) significantly increases the thermal conductivity and thus improves the dynamic performance of CPCMs. In a study by Chen et al. [48], graphene nanostructure coating on CPCMs significantly reduced the peak operating temperature and increased mechanical strength in thermally turbulent environments.

In addition, mineral layered structures such as alumina-modified vermiculite have also been shown to be successful in improving the thermal stability of CPCMs. According to Deng et al. [49], the combination of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ with alumina vermiculite increased thermal stability and prevented unwanted phase transitions.

In order to improve long-term reliability, some studies have used dual-layer coatings. For example, Gandhi et al. [50] suggested that a nanostructured outer layer of oxide and an inner layer of carbon can simultaneously optimize thermal properties and mechanical strength. In some cases, the use of bio-based coatings such as nanoparticle-modified cellulose has also been considered. Liu et al. [51] showed that paraffin/silica/chitosan composite coatings reduced leakage while maintaining stability for up to 100 cycles.

In general, nanostructured coatings prevent leakage and evaporation of

PCMs in the liquid phase by creating effective physical barriers, and also improve the heat transfer rate in thermal charging and discharging processes by increasing surface thermal conductivity. These coatings enhance the chemical stability of the material by preventing destructive reactions with environmental factors such as oxygen, moisture, and ultraviolet radiation, and also prevent phase separation during repeated thermal cycles by strengthening the bond between the matrix phase and the PCM. Despite these advantages, challenges such as the complexity of the manufacturing processes, possible incompatibility with different matrices, and high production costs still prevent the widespread implementation of this technology on an industrial scale and require further research to optimize the design and process [52].

Various types of nanostructured materials have been used as protective and reinforcing coatings in the structure of CPCMs, each of which helps to improve the thermal durability and performance stability of these materials with its own mechanism. In general, these nanostructures can be divided into four main categories: (1) metal nano oxides such as TiO_2 , SiO_2 , and ZnO , which play the role of physical and oxidation-resistant barriers; (2) carbon nanostructures such as graphene, carbon nanotubes (CNTs), and reduced graphene oxide (rGO), which are effective in improving heat transfer due to their high thermal conductivity; (3) polymer nanocomposites, which are often a combination of organic polymers and inorganic particles and enhance surface adhesion with high flexibility; and (4) biological and natural nanostructures such as modified cellulose nanocrystals and chitosan, which are used in sustainable and green applications. Fig. 3 presents a schematic view of this classification and the functional properties of each group of nanostructures for improving the thermal durability of CPCMs [53].

6. Applications in thermal energy storage systems

Technological advances in the field of thermal energy storage (TES) play a key role in increasing the efficiency of renewable energy systems and reducing dependence on unstable sources. One of the most effective methods of heat storage is the use of PCMs and especially their composite type (CPCMs), which can store or release a large amount of energy during the melting and freezing process. However,

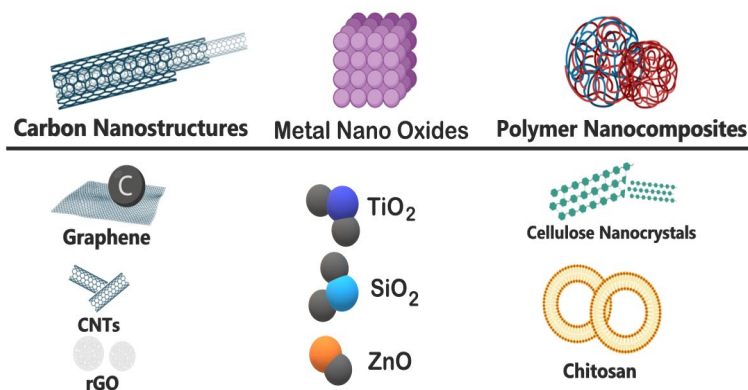


Fig. 3. Classification of nanostructures for improving the thermal durability of CPCMs.

the long-term thermal performance of CPCMs is affected by factors such as leakage, reduced structural stability, and chemical degradation. The use of nanostructured coatings on the surface of CPCMs is an effective solution to improve their durability and efficiency in TES applications, especially in conditions where repeated heating and cooling cycles occur [54].

One of the key areas of application of this technology is in solar energy storage systems, where solar radiation varies intermittently throughout the day and there is a need for stable systems to store heat during the hours of radiation and use it during the hours of no radiation. In this application, CPCMs coated with nanoparticles such as TiO₂ and graphene have found a special place due to their high resistance to temperature fluctuations and preservation of heat capacity. Research has shown that the use of nanostructured coated CPCMs in solar collectors makes a significant contribution to reducing energy losses and stabilizing the operating temperature of the system [55].

In the construction and design of passive thermal envelopes, the use of CPCMs as part of structural materials to reduce indoor temperature fluctuations has become common. By applying nanostructured coatings, not only is the thermal durability of these materials ensured in daily and seasonal cycles, but also properties such as moisture resistance, reduced supercooling, and greater adhesion to structural surfaces are achieved. Studies conducted in the field of green building design show that walls and roofs containing nanostructured CPCMs can reduce heating and cooling energy consumption by more than 30% [50, 56].

In the field of thermal management of electronic systems, especially in the semiconductor industry, servers, and lithium battery energy storage systems, maintaining optimal operating temperatures is of great importance to prevent performance degradation or critical failure. In

this field, CPCMs coated with conductive nanostructures such as CNTs or graphene act as thermal interfaces and transfer heat more efficiently. Experimental results show that the use of these materials in the design of battery cases or integrated circuit housings can reduce peak temperatures by more than 40% and prevent thermal degradation of components [57].

In industrial heat storage systems such as boilers, heat exchangers, and chemical processes with high thermal loads, the use of nanostructured coated CPCMs as an interface between the heat source and the storage medium increases the heat transfer coefficient, reduces the risk of explosion or material leakage, and extends the useful life of the system. In particular, in industries such as food processing, pharmaceuticals, and advanced materials manufacturing, which require precise control of process temperatures, this technology offers significant operational and economic benefits [58, 59].

Finally, novel applications of nanostructured coated CPCMs in the field of thermal transport are also being developed, such as temperature management systems for electric vehicles, thermal insulation in space vehicles, and even wearable thermal systems. In these areas, the characteristics of nanostructured coatings, such as lightness, stability in extreme environments, and multifunctional performance (thermal, mechanical, and biological), make them an unrivaled option.

Overall, nanostructured coatings play a crucial role in the development of stable and reliable applications of CPCMs in thermal energy storage systems by providing capabilities such as improved conductivity, leakage prevention, increased adhesion, and preservation of phase structure. The development of this technology can lead to the formation of a new generation of smart thermal systems with high efficiency, longer life, and environmental compatibility. Table 1 summarizes the research conducted in recent years on improving the properties of phase change material composites.

Table 1. Materials used, methods, and applications of CPCMs.

Nanomaterial used	PCM preparation/coating method	Applications/pros & cons	Ref.
TiO ₂ nanoparticles	Sol-gel coating on PEG matrix	<ul style="list-style-type: none"> ✓ Improved thermal reliability up to 100 cycles ✓ Prevents leakage ✗ Limited thermal conductivity gain 	[47]
Vermiculite/Al ₂ O ₃ hybrid	Vacuum encapsulation and compression molding	<ul style="list-style-type: none"> ✓ High thermal stability under cyclic loading ✓ Improved flame resistance ✗ Bulkier composite structure 	[49]
SiO ₂ aerogel	Vacuum impregnation + surface encapsulation	<ul style="list-style-type: none"> ✓ Shape-stabilization ✓ Reduced supercooling ✗ Fragility under mechanical load 	[51]
CNTs (carbon nanotubes)	Melt blending + physical dispersion in paraffin matrix	<ul style="list-style-type: none"> ✓ Excellent thermal conductivity improvement ✓ Fast response time ✗ Agglomeration issues if not functionalized properly 	[53]
Graphene oxide (GO)	In-situ reduction of the GO coating over the CPCM composite	<ul style="list-style-type: none"> ✓ Increased thermal conductivity ✓ Better structural integrity ✗ High cost of graphene-based materials 	[60]
Metal–organic frameworks (MOFs)	Microencapsulation with MOF shells	<ul style="list-style-type: none"> ✓ High surface area ✓ Maintains latent heat capacity ✗ Brittle and costly 	[61]

7. Conclusions

In this paper, the role of nanostructured coatings on composite PCMs (CPCMs) was investigated as a novel approach to improve thermal durability and increase structural stability. A review of recent studies showed that the use of nanostructured coatings not only prevents leakage, oxidation, and chemical degradation during successive thermal cycles but also enhances dynamic performance and heat storage capacity by improving thermal conductivity and reducing boundary thermal resistance. Coatings based on metal oxides, carbon structures (such as graphene and carbon nanotubes), and bio-based compounds have each been specifically effective in reducing supercooling, increasing chemical stability, and improving the mechanical strength of CPCMs. The results indicate that this technology can play a decisive role in solar energy storage systems, building temperature control, thermal management of lithium-ion batteries, and the electronics industry. Despite the significant advantages, challenges such as high production cost, complexity of the coating process, and issues related to long-term chemical compatibility have created barriers to widespread commercialization. Therefore, future research should focus on developing self-healing, recyclable, and responsive coatings to environmental stimuli (temperature, pressure, or light) to create a new generation of CPCMs with high efficiency, long-term durability, and environmental compatibility.

CRediT authorship contribution statement

Nima Sakkaki: Writing – original draft, Writing – review & editing.

Asieh Akhoondi: Writing – review & editing.

Farrokhfar Valizadeh Harzand: Writing – original draft, Supervision.

Haleh Jafarzadeh: Writing – review & editing.

Data availability

The data underlying this article will be shared on reasonable request to the corresponding author.

Declaration of competing interest

The authors declare no competing interests.

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