

Review

Towards Phase Change Materials for Thermal Energy Storage: Classification, Improvements and Applications in the Building Sector

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Abstract: The management of energy consumption in the building sector is of crucial concern for modern societies. Fossil fuels' reduced availability, along with the environmental implications they cause, emphasize the necessity for the development of new technologies using renewable energy resources. Taking into account the growing resource shortages, as well as the ongoing deterioration of the environment, the building energy performance improvement using phase change materials (PCMs) is considered as a solution that could balance the energy supply together with the corresponding demand. Thermal energy storage systems with PCMs have been investigated for several building applications as they constitute a promising and sustainable method for reduction of fuel and electrical energy consumption, while maintaining a comfortable environment in the building envelope. These compounds can be incorporated into building construction materials and provide passive thermal sufficiency, or they can be used in heating, ventilation, and air conditioning systems, domestic hot water applications, etc. This study presents the principles of latent heat thermal energy storage systems with PCMs. Furthermore, the materials that can be used as PCMs, together with the most effective methods for improving their thermal performance, as well as various passive applications in the building sector, are also highlighted. Finally, special attention is given to the encapsulated PCMs that are composed of the core material, which is the PCM, and the shell material, which can be inorganic or organic, and their utilization inside constructional materials.

Keywords: phase change materials; thermal energy storage; energy efficiency; building applications; construction materials



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1. Introduction

The contemporary societies have enhanced energy needs, leading to an increasingly intensive research for the development of energy storage technologies. Global energy consumption, along with CO₂ and greenhouse gasses emissions, is accelerating at a very fast pace due to global population growth, rapid global economic growth, and the ever-increasing human dependence on energy-consuming appliances. This rapid increase in global energy consumption has particular environmental implications that pose serious challenges to human health and the environment. Another consequence of the increment of global energy consumption is the reduction in the availability of traditional energy resources, such as oil, coal, and natural gas. This outcome has created a growing need for the development of new systems for the conversion and storage of clean and sustainable energy [1,2].

The building sector has a very large impact on the overall global energy consumption, and, furthermore, to the environment, by high emissions of greenhouse gasses, CO₂, and the acidification of the oceans. The increased energy consumption does not occur only during the production of structural materials and the building construction, but mostly for

the operation of the premises [3]. It has been proven that buildings' operation energy consumption for providing indoor comfort accounts for 30% of total energy consumption [4]. Thermal energy storage (TES) is a promising and sustainable method for decreasing the energy consumptions in the building sector. Systems of TES using phase change materials (PCMs) find numerous applications for providing and maintaining a comfortable environment of the building envelope, without consumption of electrical energy or fuel [5].

Phase change materials are substances that are able to absorb and store large amounts of thermal energy. The mechanism of PCMs for energy storage relies on the increased energy need of some materials to undergo phase transition. They are able to absorb sensible heat as their temperature rise, and, at the phase change temperature, absorb a large amount of heat, which is called latent heat of fusion, in order to change phase. The energy stays stored in the PCM until the temperature decreases and the material undergoes phase transition again, which also signifies the energy release [1].

The materials used as PCMs can be classified based on the type of phase change to solid-liquid, liquid-gas, and solid-solid compounds. The latent heat in solid-solid PCMs, such as polyurethanes, cross-linked polyethylene, and other polymers, is relatively low compared to the latent heat of those that are in the solid-liquid form [6]. As an outcome, the PCMs used for building applications are mostly solid-liquid type. These can be organic, such as paraffin, fatty acids, etc., inorganic, such as hydrate salts and metals, or their eutectic mixtures. Organic PCMs are the best candidates for multiple building applications, though their low thermal conductivity requires the fabrication of composite materials with enhanced thermal conductivity. The most investigated approach is the encapsulation of PCMs with thermal conductive materials. The encapsulation method presents many advantages, such as the leakage of liquid phase management and the protection of the PCM from corrosion. Another approach is the formation of form-stable composite PCMs, which consist of the PCM dispersed inside a cross-linked polymer matrix, a porous mineral material or expanded graphite or perlite [3,5].

There has been a lot of research for the utilization of these materials in active and passive building applications for the reduction of electrical energy and fuel consumption. Phase change materials are used in active applications for heating, ventilation, and air conditioning systems, domestic hot water applications, suspended ceilings, external solar facades, etc. [4]. Furthermore, PCMs are used in passive applications in buildings that aim for the improvement of the thermal performance of the construction systems such as the ceiling, the walls, and the floor. These applications include the incorporation of the PCMs inside constructional materials [7].

2. Thermal Energy Storage (TES)

Energy storage systems aim for the conversion of energy into a form that can be stored in order to be used when there is necessity. Thermal energy storage system is a type of a sustainable energy storage system that is based on the utilization of materials that can store thermal energy when increasing their temperature and release it when the temperature is reduced. There are three types of TES systems: sensible heat, latent heat, and chemical storage system (Figure 1). The present work presents latent heat storage systems using PCMs [8,9].

2.1. Sensible Heat Storage (SHS)

In TES systems, thermal energy can be stored either as sensible heat or as latent heat (Figure 2). In case of sensible heat storage (SHS) systems, storing of energy is induced by utilization of the heat capacity gained by temperature increment of the material. The energy storage capacity of SHS systems depends on the specific heat capacity of the material, the quantity of the material and the temperature change gradient. Radiation, convection, or conduction are the parameters that affect and can raise the corresponding temperature [9,10].

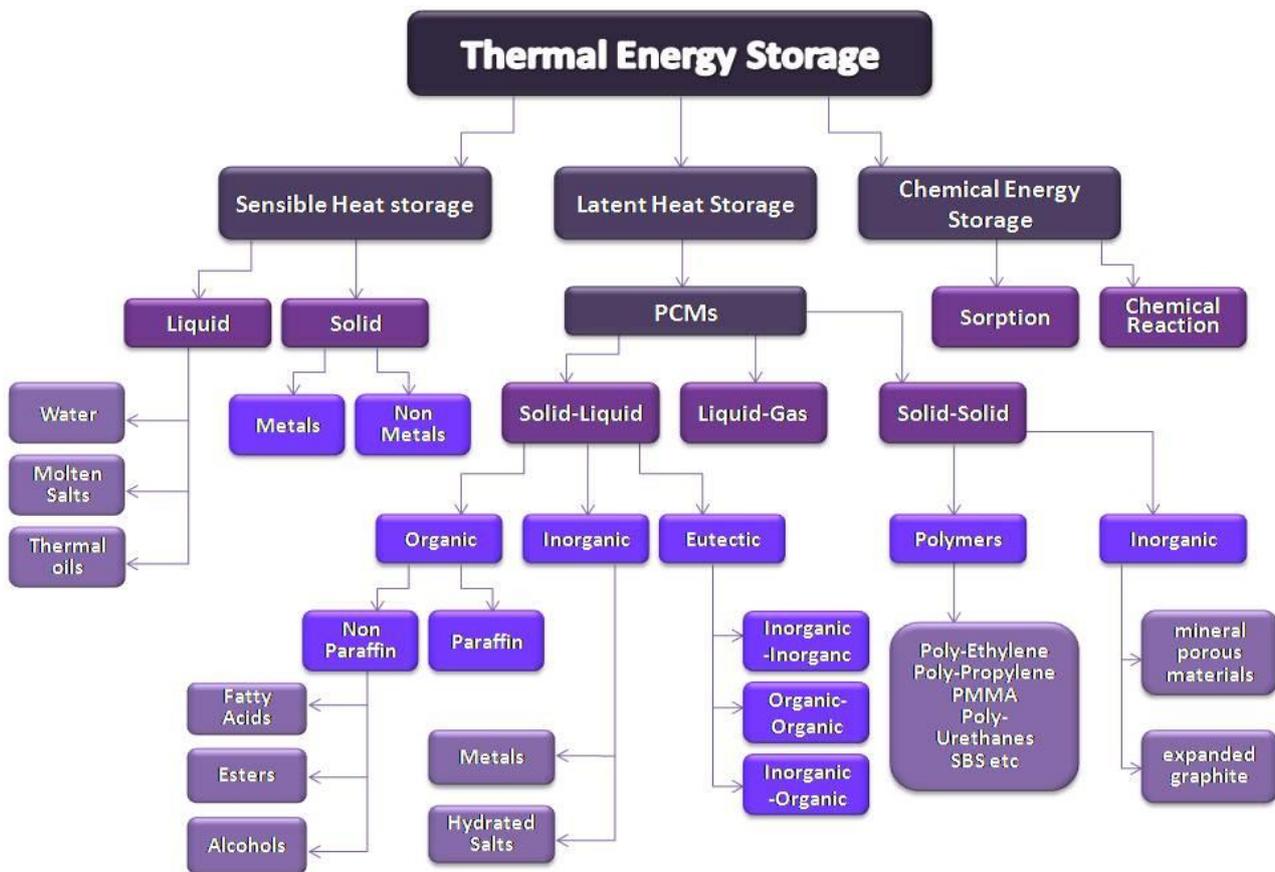


Figure 1. Classification of thermal energy storage types and materials.

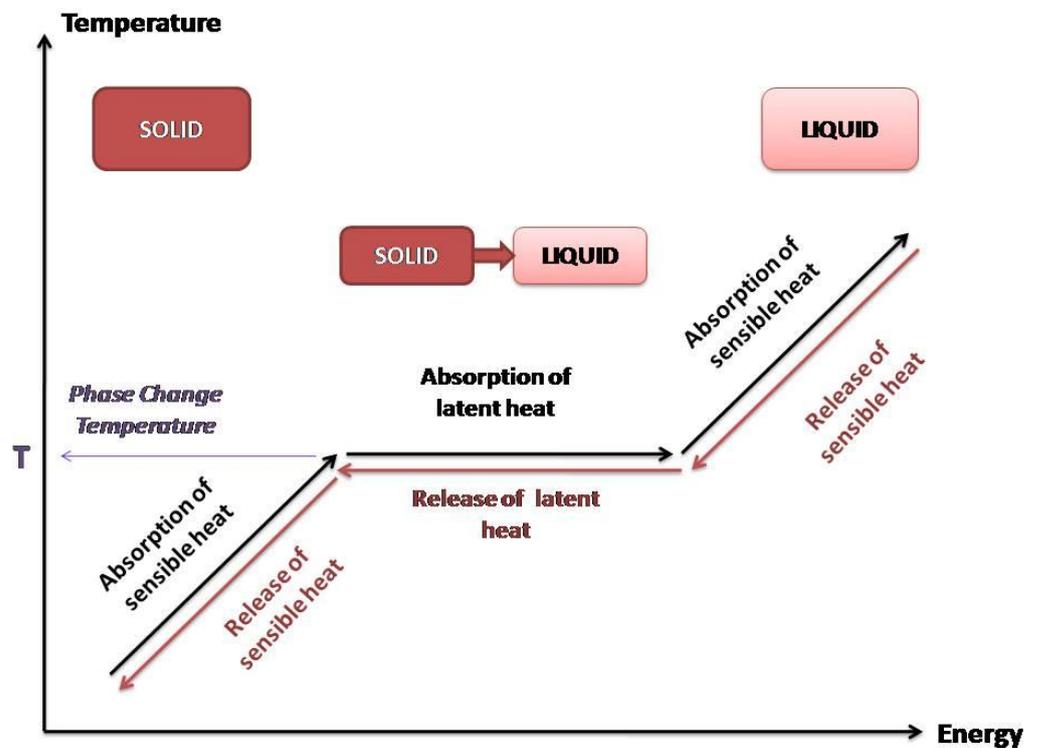


Figure 2. Sensible and latent heat.

The materials used for SHS are either in the liquid phase or the solid phase. The utilized liquid phase materials are water, molten salts, and oils. Water as an SHS material is very efficient for applications in temperatures below 100 °C, due to its high specific heat capacity, abundance, and low cost. Molten salts also have desired properties, and they are suitable for application above 100 °C. On the other hand, oils have low specific heat capacity and thermal conductivity, thus their performance is limited. Solid-phase materials used for SHS can be metals or nonmetals. Metals such as aluminum, copper, iron, and metal alloys have high thermal conductivity and specific heat capacity, though their high cost limits their application. Nonmetallic materials that can be used for SHS are rocks, concrete, marbles, bricks, granite, etc., but the disadvantage of all of these materials lies in their low thermal conductivity and specific heat capacity [6,8].

2.2. Latent Heat Storage

Latent heat storage (LHS) systems are based on the absorption or release of heat that takes place during the phase transition of a material (gas to liquid, liquid to solid, and vice versa). The amount of energy being stored depends on the mass of the material used and the latent heat of fusion, which is characteristic for every material, and it is related to its molecular structure. The materials used for LHS are also PCMs due to the fact that they store energy through phase transition. The energy storage consists of both sensible and latent heat, as presented in Figure 2. The increase of temperature to the phase change temperature results in the absorption of sensible heat from the PCM. At phase change temperature, the PCM absorbs latent heat at a molecular level for the phase transition. This amount of heat is called latent heat of fusion or evaporation, depending on the kind of phase change. The systems of LHS that use PCMs are considered as a promising thermal storage technology and they have been investigated in a large range for many applications [6,8,9].

2.3. Thermal Energy Storage in Buildings

There is urgent necessity for the development of new technologies for energy conservation in the building sector. The application of TES systems is a promising technology with many advantages, including the increasing of energy and economic efficiency in buildings, as well as the reduction of electrical energy consumption and, furthermore, the reduction of environmental pollution and CO₂ emissions [11].

The systems of TES that are applied in buildings can be either active or passive. Active TES systems are characterized by forced convection heat transfer and, in some cases, also mass transfer, such as a heat exchanger. Active systems mainly aim to control the indoor conditions of a building, for example providing free cooling. Additionally, an active TES system can be applied for peak shaving purposes in heating, ventilation, and air conditioning systems [7].

On the other hand, passive TES systems aim to create or maintain comfort conditions in the building, exploiting naturally available energy sources such as the solar energy or the wind, along with architectural design of building components, such as shading effect using blinds, etc. Passive TES systems minimize the use of mechanically-assisted heating or cooling systems. The main idea is to maximize the comfort conditions of the building envelope without using external energy sources. Some examples of passive TES systems are the use of ventilation facades and the PCM wallboards [12,13].

3. Phase Change Materials

3.1. Classification of PCMs

There is a wide variety of compounds that are used as phase change materials for numerous different applications due to their different physical and chemical properties. For building applications, solid-liquid PCMs are preferred because of their ability to absorb and release large amounts of energy within a narrow range of temperature. Solid-liquid

PCMs used in buildings can be classified into three major groups: organic compounds, inorganic compounds, and eutectics of organic and/or inorganic compounds.

3.1.1. Organic Materials

Organic PCMs can be paraffinic, such as paraffin wax, which is the most commercially used organic PCM for building applications, or they can be nonparaffinic, such as fatty acids, fatty acid esters, glycolic acids, alcohols, etc. Paraffinic PCMs consist of hydrocarbon chains, while nonparaffinic also contain electronegative atoms in their chains [8,9]. Paraffin waxes consist of hydrocarbon chains ranging from 8 to 15 carbon atoms, and pure paraffin of hydrocarbon chains range from 14 to 40 carbon atoms. Thermal properties of some paraffin waxes and pure paraffins are presented in Table 1.

Table 1. Thermal properties of some paraffins.

Material	Chemical formula	Melting Temperature (°C)	Melting Enthalpy (J/g)	Thermal Conductivity (W/(m.K))	Density (kg/m ³)	Ref
n-Tetradecane	C ₁₄ H ₃₀	5.5	228	-	-	[8]
n-Pentadecane	C ₁₅ H ₃₂	10	205	-	-	[8]
n-Hexadecane	C ₁₆ H ₃₄	18.0	210.0–238.0	0.2 (solid)	760.0 (liquid, 20.0 °C)	[10]
n-Heptadecane	C ₁₇ H ₃₆	19.0	240.0	0.2	776.0 (liquid, 20.0 °C)	[10]
n-Octadecane	C ₁₈ H ₃₈	28.0	200.0–245.0	0.15 (liquid, 40.0 °C)	774.0 (liquid, 70.0 °C)	[10]
				0.36 (solid, 25.0 °C)	814.0 (solid, 20.0 °C)	
n-Nonadecane	C ₁₉ H ₄₀	28.0	179	0.2	750.0 (liquid)	[4]
					870.0 (solid)	
n-Eicosane	C ₂₀ H ₄₂	32.0–33.0	222.0	0.18 (liquid, 60.0 °C)	780.0	[10]
				0.26 (solid, 19.0 °C)		
n-Heneicosane	C ₂₁ H ₄₄	36.0–37.0	247	0.15 (liquid)	-	[10]
				0.42 (solid)		
n-Docosane	C ₂₂ H ₄₆	39.0–41.0	201.0	-	-	[10]
n-Tricosane	C ₂₃ H ₄₈	44.0	249	-	-	[8]
n-Tetracosane	C ₂₄ H ₅₀	47.5	232	-	-	[8]
		50.6	255	-	-	[8]

Nonparaffinic PCMs can be fabricated from biosourced raw materials, such as animal fats, and vegetable oils, such as beef tallow, margarine, coconut oil, castor oil, etc. These materials are sustainable, biodegradable, nontoxic, and less flammable. On the other hand, their major drawbacks are that they are more corrosive than paraffin and more expensive [14,15]. Some nonparaffinic PCMs are presented in Table 2.

Table 2. Thermal properties of nonparaffins.

	Material	Melting Temperature (°C)	Melting Enthalpy (J/g)	Ref
Fatty acids	Capric Acid	30.2	142.7	[4]
	Capric Acid	32	152.7	[5]
	Lauric acid	43.05	172.3	[5]
	Myristic acid	51.80	178.14	[13]
	Palmitic acid	60.42	233.24	[13]
	Stearic acid	54.29	188.28	[5]
Fatty acids esters	Butyl stearate	19	140	[16]
	Propyl palmitate	19	186	[17]
	Methyl palmitate	29	205	[8]
	Methyl eicosanate	45	230	[8]
	Methyl behenate	52	234	[8]
Alcohols	1-dodecanol	26	200	[17]
	Phenol	41	120	[8]
	Cetyl alcohol	49.3	141	[8]
Polyethylene glycol (PEG)	PEG 400	3.2	91.4	[13]
	PEG 600	22.2	108.4	[13]
	PEG800	25.39	133.6	[5]
	PEG 1000	34.89	143.62	[13]
	PEG 2000	52.63	180.70	[13]
	PEG 4000	48.95	183.10	[13]

Organic PCMs exhibit a great number of advantages. First of all, the phase change temperature rises in proportion to the number of carbon atoms in the chain, providing availability in a broad range of temperatures for different applications. Another advantage of this type of PCMs is that they are noncorrosive, chemically inert, and thermally stable in the temperature range needed, therefore, no degradation problems occur during their use. Additionally, they demonstrate a congruent melting process which means that the phase change happens repeatedly without phase segregation. Furthermore, they have high latent heat, good nucleation properties, low liquid phase sub-cooling capability, and minimal volume variation. Finally, they are compatible with most of the construction materials, they can be recycled, and their cost is relatively low. On the other hand, organic PCMs also exhibit some disadvantages based on their low energy storage capacity, low density, low thermal conductivity, and high flammability [8,9,14,15].

3.1.2. Inorganic Materials

There are two kinds of inorganic compounds that can be used as PCMs: hydrated salts and metals. Hydrated salts have been immensely studied for their use as PCMs. Their general formula is $AB \cdot nH_2O$, and the phase change is in fact the dehydration reaction of the hydrated salt. Regarding metal category, they include low melting metals (eutectics) but these materials have not yet been seriously studied as PCMs [8]. The greatest properties of inorganic PCMs are the high thermal conductivity and the high energy efficiency (high enthalpy). In addition, other advantages are the low volume change during phase transition and that they are inflammable [14].

The main drawback of inorganic PCMs is the incongruent melting which leads to phase segregation and, furthermore, to decreased performance after every charge-discharge circle. Another disadvantage is the poor nucleating properties that resulting in supercooling of the liquid phase before crystallization. Additionally, inorganic PCMs are widely corrosive, in some cases toxic, show limited compatibility with construction materials, and they are rather expensive [14,15]. The advantages and disadvantages for both organic and inorganic PCMs are summarized in Table 3.

Table 3. Advantages and disadvantages of organic and inorganic phase change materials (PCMs).

	Advantages	Disadvantages
Organic PCMs	Wide phase change temperature range. Thermally stable—no degradation. Chemically inert. Noncorrosive. Congruent melting process—no phase segregation. High latent heat. Good nucleation properties. Low liquid phase sub-cooling capability. Minimal volume variation. Compatible with most of the construction materials. Recyclable. Low cost.	Low thermal conductivity. Low density. High flammability.
Inorganic PCMs	High thermal conductivity. High energy efficiency (high enthalpy). Low volume change during phase transition. Non-flammable.	Incongruent melting—phase segregation. Poor nucleating. Supercooling of the liquid phase. Corrosiveness. Toxicity. Limited compatibility with construction materials. Higher cost.

3.1.3. Eutectic Mixtures

The eutectic accrues from the mixture of two or more compounds of organic, inorganic, or both PCMs. In this way, an immeasurable number of eutectic mixtures can be fabricated. This gives the opportunity to produce a material with the desiring thermal properties, such as phase change temperature and latent heat. So, the most important advantage of eutectic mixtures is the ability of producing a material with the suitable phase change temperature for an application. The organic eutectic mixtures show some extra advantages in comparison with inorganic or inorganic/organic mixtures. These are the long-term stability, high phase change enthalpy, and facility of impregnating into porous support material due to their high chemical compatibility and surface tension. The main disadvantage is their high cost [14,18]. Thermal properties of some hydrated salts and eutectic mixtures are presented in Table 4.

Table 4. Thermal properties of inorganic materials and eutectic mixtures used as PCMs.

Inorganic Material	Melting Temperature (°C)	Melting Enthalpy (J/g)	Ref	Eutectic Mixtures	Melting Temperature (°C)	Melting Enthalpy (J/g)	Ref
CaCl ₂ ·12H ₂ O	29.8	174	[8]	Capric Acid-Palmitic Acid	26.2	177	[4]
LiNO ₃ ·H ₂ O	30.0	296	[8]	Capric Acid-Myristic Acid	21.7	155	[4]
LiNO ₃ ·3H ₂ O	30	189	[8]	Capric Acid-Stearic Acid	24.7	179	[4]
LiNO ₃ ·3H ₂ O	30	296	[13]	Capric Acid-Lauric Acid	19.2–20.3	144–150	[4]
KF·4H ₂ O	18.5	231	[13]	Capric Acid-Lauric Acid	19.09	141.5	[5]
CaCl ₂ ·H ₂ O	29	190.8	[13]	Butyl stearate-palmitate	17–20	137.8	[4]
Na ₂ SO ₄ ·10H ₂ O	32	251	[13]	Palmitic Acid-Stearic Acid	32.1	151.6	[5]
Mn(NO ₃) ₂ ·6H ₂ O	25.8	125.9	[13]	Capric Acid-Palmitic Acid-Stearic Acid	19.93	129.4	[4]
Mn(NO ₃) ₂ ·6H ₂ O	25.5	148	[17]	Lauric Acid-Myristic Acid-Stearic acid	29.29	140.9	[5]
K ₂ HPO ₄ ·4H ₂ O	18.5	231	[17]	Capric Acid-1-dodecanol	27	126.9	[4]
FeBr ₃ ·6H ₂ O	21	105	[17]	Ca(NO ₃) ₂ ·4H ₂ O-Mg(NO ₃) ₂ ·6H ₂ O	30	136	[17]
LiNO ₃ ·2H ₂ O	30	296	[17]	CH ₃ COONa·3H ₂ O + NH ₂ CONH ₂	30	200.5	[17]
LiBO ₂ ·8H ₂ O	25.7	289	[17]	CaCl ₂ + NaCl + KCl + H ₂ O	26–28	188	[17]
CaCl ₂ ·6H ₂ O	29	191	[17]	Na ₂ SO ₄ ·10H ₂ O-Na ₂ HPO ₄ ·12H ₂ O	32.52	226.9	[5]

3.2. PCM Properties

For a material to be used as PCM, there are some thermal, physical, chemical, and kinetic properties that have to be satisfied. In addition, the final decision for a PCM to be manufactured for thermal storage also takes into account the environmental impact and the economics. Regarding the thermal properties, firstly, the phase transition temperature has to be in the desired operating temperature range in order to aver that the absorbing and releasing of heat happens in the desired range for the application temperature. Another very important characteristic for PCMs is high thermal conductivity of both liquid and solid phases, which is required in order to support the absorbing and releasing process of thermal energy. The latent heat of fusion per unit volume also has to be high, so that the storage density is higher and sensible storage can be achieved. In addition, high specific heat offers extra sensible heat storage. Finally, and also very important, is for the melting to happen congruently, in order for the phase change to be reproducible with stable cycling and long life [11,14,19].

On the physical properties needed, an important requirement is the minimum volume change during phase transition as well as small vapor pressure at the temperature of operation. Also, it is desired that the material has high density [14,19]. The kinetics of

the charging/discharging cycle are also considerable because the insufficient nucleation rate leads to supercooling of the liquid phase, which is undesirable because the melting and solidification process take place in different temperatures. Therefore, high nucleation as well as enhanced crystal growth are required [8,14]. Apart from that, several chemical properties have to be satisfied by a PCM. Firstly, the freezing and melting cycle has to be completely reversible and the material should not degrade after a big number of cycles. Additionally, the material has to be noncorrosive to the environment used [11,14]. Finally, the materials used as PCMs have to be nontoxic, inflammable, and nonexplosive, both for safety and environmental reasons. From an economical point of view, they have to be available and abundant in nature, and cost-effective [19].

4. Improvement of Thermal Performance

4.1. Encapsulation

The practical use of solid-liquid PCMs impedes, due to some deterrents, characteristics, such as leakage of the liquid phase. To overcome these problems, new types of PCMs forms have been investigated, such as form-stable (or shape-stabilized) PCMs and encapsulated PCMs [20]. Encapsulation methods are used in order to overcome the leakage problems by keeping the material suitably contained inside a coating, a shell, or a matrix (form-stable PCMs). Encapsulation of PCMs can bring great improvement in enhancing the stability and heat transfer efficiency of the PCM, as well as facilitating its utilization, storage, and transportation.

The obstruction of material interaction with the environment not only prevents the leaking of the material, but also protects it from interacting with the environment, which could provoke degradation or corrosion during the melting-freezing cycles [2,21]. Furthermore, encapsulation increases the surface area of the PCM, which enhances the heat transfer efficiency. Moreover, the capsule form gives the capability of controlling the volume changes during melting, as well as the possibility of increasing thermal conductivity by inserting additives such as nanoparticles or C-based materials. Another great capability of manufacturing composite PCMs is that they can be applied directly in applications without any extra devices. For example, the fabrication of a PCM can be in forms such as powders or pastes, and they can be used directly as additives in constructional materials [21,22].

The encapsulated PCMs are composed of the core material, which is the PCM, and the shell material, which can be inorganic or organic. Their shape can be spherical, tubular, oval, or irregular, depending on the materials and the fabrication process. Additionally, a core-shell composite can have single or several cores within the capsule and multiple shells. A classification of encapsulated PCMs is related to their size. The PCMs can be characterized as macroencapsulated when their size is bigger than 1000 μm , microencapsulated when their size is between 1 and 1000 μm , and, finally, nanoencapsulated when their size is less than 1 μm [21]. The most interesting encapsulated PCMs to investigate are microencapsulated and nanoencapsulated PCMs because of the higher surface area per volume unit, which seems to facilitate thermal transfer and lead to better thermal performance. Another reason is that small particle sizes are more durable to mechanical stress [22].

4.1.1. Microencapsulation

Microencapsulated PCMs emerge from a coating process of the pure PCM. Droplets or individual particles of the PCM are coated with another material to form capsules of 1–1000 μm size. The core material can be any solid-liquid PCM, and the shell (container) material can be an inorganic or a polymer material. The most studied inorganic shells are SiO_2 and TiO_2 [23], while the organic shells used are poly(methyl methacrylate) (PMMA) [24], polystyrene [25], melamine-formaldehyde [26], and other, more complicated, structures [27]. There are numerous microencapsulation methods that can be used (Figure 3). The selection of the suitable microencapsulation method depends on the physical and chemical proper-

ties of both core and shell materials [22] and on the chemical environment for which they are intended to be used, for example in building [28].

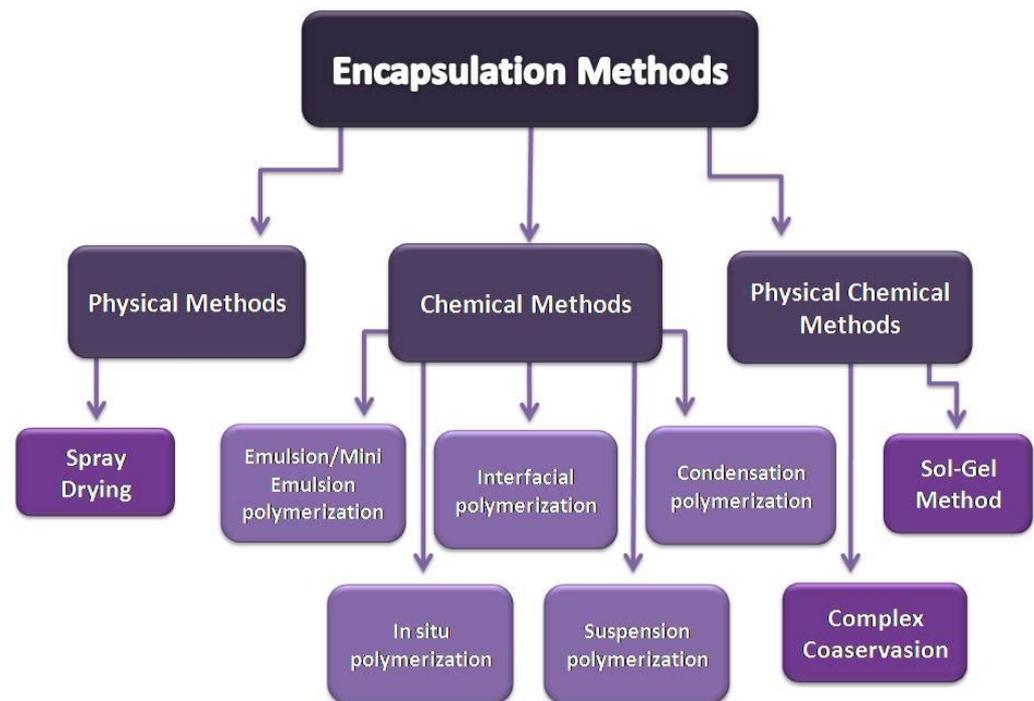


Figure 3. Physical, chemical, and physicochemical methods of encapsulation.

4.1.2. Methods of Microencapsulation

In physical methods, the material that creates the shell does not take part in any chemical reactions. The shell is mechanically applied on the core material by physical processes such as binding due to adhesion, drying, etc. There are a lot of physical methods, such as spray drying, vibrational nozzle, centrifugal extrusion, solvent evaporation, etc., although the method that is most used for microencapsulating PCMs is spray drying. The equipment and knowledge in this method is widely available. Additionally, the method can be easily scaled up, with average microcapsule size around some micrometers and efficient thermal performance; although, the high operating temperature, the agglomeration of microcapsules in the drying chamber, and the remaining uncoated particles are some its disadvantages [22,29].

In physicochemical synthesis methods, the capsule emerges through a physicochemical process. A physicochemical process is a combination of physical and chemical methods. The physical methods include processes such as cooling, heating, phase separation, etc., while the chemical methods include chemical processes such as condensation, hydrolysis, cross-linking, etc. Those methods combined result in microencapsulation. The most widely-used physicochemical methods are complex coacervation and sol-gel technique.

The complex coacervation method is suitable for fabrication of microcapsules with shell of organic materials such as chitosan, gum Arabic, gelatin, etc. This method is based on phase separation. The shell polymer is dissolved in an emulsion with the PCM (core material). The shell is formed around the droplet of the core material by evaporation of the solvent. In another way, the formation of the microcapsule can be managed by electrostatic coalescing of two different organic polymers around the droplet, and then decreasing the temperature and pH of the emulsion to initiate phase separation [30]. On the other hand, the sol-gel technique is used for the fabrication of inorganic shell microcapsules, such as SiO₂, TiO₂, etc. The sol-gel technique includes a sol solution, which is a solution of the hydrolyzed precursor compound, and an emulsion of the PCM. When the sol is added

to the emulsion, the synthesis of the shell is happening on the PCMs droplet's surface, producing a gel of the microcapsules [31].

Finally, in chemical methods, the shell results from polymerization on the surface of a droplet or a particle of the core material. The most important methods are emulsion polymerization, suspension polymerization, interfacial polymerization, condensation polymerization, and in situ polymerization [22,31]. Suspension and emulsion polymerizations are widely used for PMMA and polystyrene shells, while the interfacial polymerization is preferred when the final shell consists of two or more monomers. In in situ polymerization, no monomers are used. The precursor compound hydrolyses in situ, and it initiates the polymerization. It is used for the synthesis of organic shell materials such as polyurea-formaldehyde and melamine-formaldehyde. Finally, condensation polymerization can also be used for inorganic shells, such as SiO₂, and it is usually part of other synthesis techniques, such as sol-gel [32].

4.1.3. Nanoencapsulation

Recent developments in nanotechnology, and specifically in synthesis methods of nanoparticles, allow the encapsulation of PCMs on nanoscale. Systems on nanoscale have essentially different physical and chemical properties to their counterparts on macroscale. The size effects of nanoscale provide outstanding properties to nanoencapsulated PCMs, which can make improvements to the efficiency of existing applications as well as meeting the requirements for new ones. For example, nanoencapsulation is proved to dramatically reduce the supercooling effect. Furthermore, the nanoencapsulated PCMs, due to their size, are able to form stable dispersions in fluids, known as nanofluids, without rapidly increasing their viscosity, which opens the path for new applications. In addition, nanoencapsulated PCMs have proven to be more durable to mechanical stress than larger capsules, which in some applications is very important [22,32].

The nanocapsule diameter is expected to be less than 1 µm, while in microencapsulated PCMs it is most typically 5 to 400 µm. As a result, not all the fabrication methods of microencapsulation that are presented in the previous section can be adopted for PCM capsules on nanoscale. The methods that are suitable for producing nanocapsules are mainly chemical. Specifically, the efficient synthesis techniques are emulsion polymerization, miniemulsion polymerization, interfacial polymerization, in situ polymerization, and sol-gel technique [22,32].

4.2. Form-stable PCMs

Solid-liquid PCMs, as known, present some disadvantages related to the liquid phase, such as leakage, volume change, supercooling, etc. To overcome these obstacles, composite PCMs are being investigated. A modification approach for pure PCMs, in order to enhance their performance and stability, is the fabrication of form-stable PCMs. Form-stable, or shape-stabilized, PCMs consist of a 3D matrix, or a porous structure, where the pure PCMs are entrapped. The matrix or porous structure can be in macro, micro, or nano scale [2,33]. The advantages of this technology are the limitation of liquid phase leakage, the enhancement of the thermal conductivity, the controlling of volume change during melting/freezing cycles, the reducing of PCM interaction with the environment, the avoidance of additional device requirement, and the ability of manufacturing the thermal energy system in the desired forms and dimensions for easy application. The materials used as substrates can be polymers or inorganic porous minerals [5,34].

4.2.1. Polymer Form-stable PCMs

In polymer-based form-stable PCM composites, the PCM is entrapped inside a cross-linked polymer matrix. The synthesis of the polymer matrix can be achieved with many different methods, providing structural diversity and, as a result, the ability of fabricating a product with special specifications, properly designed for each application. Additionally,

polymeric cross-linked materials, as substrates, have shown great encapsulation rate results, which is a very important property [5].

There is a wide variety of the polymeric materials that can be used for this purpose. Materials that have been commonly used are polyethylene [35], polypropylene [36], polyurethane [37], poly methyl methacrylate [38], poly vinyl chloride [39], styrene-butadiene-styrene triblock copolymer [40], etc. Nevertheless, due to environmental concerns, there is great necessity for reducing the utilization of nonrenewable petroleum-based polymers. This has led to research for raw materials that can be received from natural sources, such as biomass, and they are renewable, biodegradable, environmentally friendly, of high abundance, and low cost. Such materials are celluloses, starches, and vegetable oils. Specifically, cellulose, agarose, chitosan [41], castor oil [42], etc. have been used for the fabrication of form-stable PCMs.

4.2.2. Inorganic Form-stable PCMs

Form-stable PCMs can also be fabricated with inorganic mineral porous materials such as kaolin, diatomite, vermiculite, sepiolite, bentonite, attapulgite, fly ash, opal, etc., as well as with expanded materials such as expanded graphite and expanded perlite. The porous structure of these materials makes them suitable for their utilization as carriers for the encapsulation of the PCM. The fabrication of inorganic porous form-stable PCMs can be performed with impregnation method, melting intercalation technology, and melting adsorption method [43].

There is chemical compatibility between PCMs and the porous materials. The interactions developing between them are mainly surface tension, hydrogen bond, Van der Waals, etc. Due to these interactions, the form-stable composites show increased thermal stability and reliability. The absorbance rate, which is connected with latent heat capacity, is high in the case of expanded graphite, diatomite, and expanded perlite carriers. Thermal conductivity is vital for the energy storage and release efficiency. In mineral porous materials, thermal conductivity is relatively low but it can be easily enhanced with the addition of expanded graphite as an additive [43,44].

4.3. Thermal Conductivity Enhancement Techniques

Thermal conductivity in a thermal energy storage system is a very important factor for the efficiency of energy storing and releasing. PCMs', especially organics', main disadvantage is their low thermal conductivity. Low thermal conductivity decreases the heat transfer rate which means that the stored energy cannot be used efficiently, putting limitations on plenty of applications. As a result, the enhancement of thermal conductivity of PCMs is tremendously important for the amplification of system's performance [45]. The research that has been held for the improvement of thermal conductivity is mainly based on the improvement that encapsulation offers [10,46,47], the addition of highly-thermal conductive materials, such as carbon-based nanomaterials [48,49], metallic [50], or inorganic nanoparticles [51], and in the fabrication of form-stable PCMs with highly-thermal conductive carrier materials such as metallic foams [52], expanded graphite [53], etc. Another approach is the fabrication of nanofluid PCMs, which are dispersions of thermal conductive nanoparticles, for example, TiO_2 , in the PCM liquid [54] (Table 5).

Table 5. Recent applications of micro- and nanoencapsulated PCMs with improved thermal conductivity.

Core Material	Shell Material	Encapsulation Method	Capsule Size	Thermal Conductivity of Pure PCM (W/(m.K))	Thermal Conductivity of Encapsulated PCM (W/(m.K))	Year	Ref
n-Eicosane	TiO ₂	Interfacial polycondensation	Tubular: 1–5 µm length, 50–300 nm diameter Octahedral: 2–4 µm Spherical: 0.2–4 µm	0.161	1.244 (tubular) 1.023 (octahedral) 0.724 (spherical)	2019	[23]
N-octadecane	Poly(styrene-co-divinylbenzene-co-acrylamide)	Miniemulsion polymerization	-	-	-	2019	[27]
Myristic acid-Palmitic acid Eutectic	PMMA	Emulsion polymerization	0.1–70 µm	-	-	2019	[24]
Stearic Acid	SiO ₂ /GO	Sol-gel	2 µm	0.16	0.24 (SiO ₂) 0.28 (SiO ₂ /GO)	2018	[49]
➤ n-Dodecane ➤ Nanoalumina-Reinforced n-Dodecane	CNTs reinforced Melamine–Formaldehyde resin	In situ polymerization	-	0.14	0.297 0.219	2020	[55]
n-Octadecane	Boron Nitride reinforced Melamine-Formaldehyde	In situ polymerization	5–10 µm	0.14	0.11	2020	[56]
Paraffin	Graphene Oxide /Graphene nanoplatels	Self-assembly	-	0.25	0.90	2020	[57]
Stearyl Alcohol	SiO ₂	Sol-gel	5–12 µm	0.14	0.15	2020	[58]
Methyl Laurate-based	Polyurethane	Pickering emulsion interfacial polymerization	8–10 µm	-	-	2020	[59]
n-Octadecane	SiO ₂ /graphene	Miniemulsion polymerization	256–473 nm	0.6416	1.4941	2019	[60]

Table 5. Cont.

Core Material	Shell Material	Encapsulation Method	Capsule Size	Thermal Conductivity of Pure PCM (W/(m.K))	Thermal Conductivity of Encapsulated PCM (W/(m.K))	Year	Ref
<ul style="list-style-type: none"> ➤ n-Octadecane ➤ n-Eicosane 	Crosslinked Polystyrene	Miniemulsion polymerization	136 nm 134 nm	0.22 0.18	0.12 0.11	2020	[61]
n-Octadecane	SiO ₂	Miniemulsion polymerization	335 nm	0.15	0.38	2018	[62]
<i>n</i> -Eicosane-Fe ₃ O ₄	SiO ₂ /Cu	Pickering emulsion interfacial polymerization	428–631 nm	0.4716	1.3926	2020	[63]

4.3.1. Enhancement of Thermal Conductivity by Encapsulation

According to the literature, organic PCMs have low thermal conductivity, which does not allow their efficient use in several applications. The preparation of core-shell or form-stable composite organic PCMs increases the thermal conductivity, as well as the heat transfer rate, due to increment of the surface area. A very important factor for the improvement of thermal conductivity is the size of the microcapsules. The extreme reduction of capsule size increases the thermal resistance because of the high contact rate of the capsules [47]. Another notable factor is the shell-to-core ratio. A higher shell-to-core ratio causes more increment on thermal conductivity but reduces the rate of energy storage because of the smaller amount of PCM inside the capsule [46]. The optimum shell-to-core ratio considering thermal conductivity, thermal storage, and mechanical strength is around 1:3 [64].

Inorganic shells, such as SiO₂ and CaCO₃, present better improvement on thermal conductivity than organic shells, such as PMMA, though they have decreased mechanical properties. For that reason, there has been investigation for fabricating core-shell PCMs with double shell: polymer shell for mechanical strength and inorganic for thermal conductivity enhancement [46]. Additionally, another point of view is the forming of a metallic second shell, which can improve thermal conductivity along with mechanical strength and agglomeration problems. Recent studies of micro/nanoencapsulation and form-stable composites are tabulated in Tables 5 and 6, respectively.

Table 6. Recent applications of form-stable composites PCMs.

PCM	Carrier	Preparation Method	Thermal Conductivity of Pure PCM(W/(m.K))	Thermal Conductivity of Encapsulated PCM (W/(m.K))	Year	Refs
PEG 10000	Graphene Aerogel/ Melamine Foam	Vacuum-assisted Impregnation	0.32	1.32	2020	[63]
Dodecane	Expanded graphite	Vacuum Infiltration	0.14	2.2745	2019	[65]
Lauric Acid Stearic Acid Eutectic	Carbonized Corn cob	Vacuum Impregnation	0.228	0.441	2019	[66]
PEG 1000	Halloysite NanoTube reinforced with Ag nanoparticles	Vacuum Impregnation	0.293	0.902	2019	[67]
Castor Oil	Polyurethane- Acrylate Oligomer	In situ polymerization	-	-	2019	[42]
<i>m</i> -Erythritol	Sepiolite and Exfoliated Graphite nanoplatelets	Vacuum Infiltration	0.372	0.756	2020	[68]
PEG 6000	Epoxy Resin porous Al ₂ O ₃ ceramic	High- temperature blending and curing	0.393	2.54	2020	[69]

Table 6. Cont.

PCM	Carrier	Preparation Method	Thermal Conductivity of Pure PCM(W/(m.K))	Thermal Conductivity of Encapsulated PCM (W/(m.K))	Year	Refs
Capric Acid-Palmitic Acid Eutectic eutectic	Silica Xerogel/ Exfoliated Graphite nanoplatelets	Sol-gel	0.22	0.70	2020	[70]
Lauric Acid-based	➤ Carbon black/calcium carbonate powder	Dispersion of nanoencapsulations in sonication bath	0.042	0.268	2020	[71]
	➤ MWCNTs/ calcium carbonate powder		0.033	0.024		
PEG 4000	Almond shell Biochar	Vacuum impregnation	0.251	0.402	2018	[72]

4.3.2. Enhancement of Thermal Conductivity with Nanoparticle Additives

The enhancement of thermal conductivity of PCMs can be efficiently achieved with the fabrication of composite PCMs, which consist of the PCM material and a dispersion of high-thermal-conductivity additives. The PCMs mostly enhanced are organic PCMs such as paraffin, fatty acids, fatty acid ester, alcohols, and their eutectic mixtures. The additives can be carbon-based nanostructures [73,74], metallic nanoparticles, or nonmetallic nanoparticles. Besides the nature of the additives materials, the size, the shape, and the aspect ratio are the main factors that define the thermal conductivity improvement.

Carbon-based materials, such as carbon fibers (CF), carbon nanotubes (CNTs), graphene, graphite, and their derivatives, are widely being investigated for thermal conductivity enhancement, with very promising results. Carbon-based materials can be used as additives directly in the organic PCM, or they can be added inside a composite PCM, such as a form-stable PCM or a microcapsule, for further thermal conductivity improvement. CNTs' disadvantage is agglomeration, and as a result, CNTs show limited dispersion ability inside the PCM. This problem can be overcome with treatment of the CNTs, such as oxidation or doping, which weakens the intramolecular forces. On the other hand, carbon fibers show better dispersion ability, and they can be added efficiently without further treatment. Addition of graphite particles can also achieve great enhancement, although graphene nanoparticles are the most effective due to low interfacial thermal resistance and large aspect ratio [45,74].

Metallic nanoparticles can also be used as additives for the enhancement of thermal conductivity. The metallic nanoparticles that have been used are silver, copper, nickel, and magnesium nanoparticles. All of these metallic additives enhance efficiency of the thermal conductivity, but their practical use is limited because of a number of drawbacks that they show, such as low dispersion due to high agglomeration, low thermal stability, and high density [45,50].

Nonmetallic nanoparticles that can be added for thermal conductivity improvement are alumina (Al_2O_3), magnetite (Fe_3O_4), titania (TiO_2), mesoporous SiO_2 , aluminum nitride (AlN), boron nitride (BN), etc. Nanoalumina particles improve the thermal conductivity, and the heat transfer, and they reduce the supercooling effect, although nanoalumina, along with titania, suffers from low dispersion problems [51]. Samaneh Sami and Nasrin Etesami [75] controlled the aggregation of TiO_2 nanoparticles inside paraffin PCM by adding the surfactant reagent stearyl lactylate.

4.3.3. Enhancement of Thermal Conductivity with Metallic Foams and Expanded Graphite

Another perspective for thermal conductivity enhancement is the fabrication of a composite material consisting of the PCM and metallic foam as a carrier. Metallic foams that have been used for this purpose are copper foam [76], nickel foam [77], and porous graphite foam [78]. The composites can be prepared with vacuum infiltration or vacuum impregnation. These structures have plenty of advantages, such as high thermal conductivity, high thermal and chemical stability, high porosity, low density, and high aspect ratio. Their low density and high aspect ratio are the properties that make metallic foams prevail over metallic nanoparticles. Taking into account that thermal conductivity depends on the arrangement of the two components in the composite, it is mentioned that thermal conductivity is higher when the porosity is low because there are less interfacial interactions, and, as a result, the thermal resistance is lower. Although the energy storage capacity is improved when the porosity is higher, it is highlighted that both of those effects have to be considered for the optimization of the final material. Porous graphite and copper foam composite PCMs exhibit higher thermal conductivity in comparison with nickel foam composites [45].

Expanded graphite (EG) is a structure that comes from the oxidation and desiccation of graphite that has all the desired properties to be used for enhancement of thermal conductivity: chemical stability, high thermal conductivity, low density, and aspect ratio. The fabrication of the form-stable composite PCM can be achieved by impregnation of the molten PCM in the EG. The thermal conductivity of the composite depends on mass fraction, packing density, aspect ratio, surface area, and thickness of EG. High mass fraction and packing density leads to higher thermal conductivity [45,79,80].

5. Applications of PCMs in Buildings

In the past few decades, PCM technologies and the feasibility of their incorporation for thermal energy storage in the building sector have been investigated thoroughly. Thermal energy systems using PCMs are a sustainable and environmentally friendly solution that can definitely diminish the required energy consumption for the provision of comfort conditions of the building envelope. The PCM applications for thermal energy storage in this sector are divided in two categories: active and passive systems [12,81].

Active application systems based on PCMs require mechanical equipment or a source of additional energy for their operation, for example electricity to pumps or fans [82]. These systems are more suitable for cases where there is need for more heat transfer performance or better control of the application [64]. Active thermal storage systems with PCMs include systems located inside the building envelope for heating, ventilation, and air conditioning and systems that are integrated in the building structure and operating through air or water distribution, as well as systems located outside the building envelope, such as storage containers for domestic hot water, etc. [81,83]. On the other hand, passive application systems aim to improve the thermal performance of the construction systems such as the walls, the floor, the ceiling, etc. [84]. The most noteworthy passive applications of TES systems in building are presented in this section.

5.1. PCM Passive Application Systems in Building

Passive application PCM systems exploit the naturally-available energy sources along with the architectural design of building components to minimize the energy requirements of building operations. The main characteristic of these systems is that there is no requirement for mechanical equipment or additional energy, due to the fact that the heat is charged or discharged only because of temperature fluctuations when the environment's temperature rises or falls beyond the PCM's phase change temperature (Figure 4). Passive application PCM systems in the building sector can be classified as systems that are integrated into the building materials, such as materials for the walls, the floor, the ceiling, etc., and as systems that are implemented as components to the building envelope, such as blinds, suspended ceilings, etc. [16].

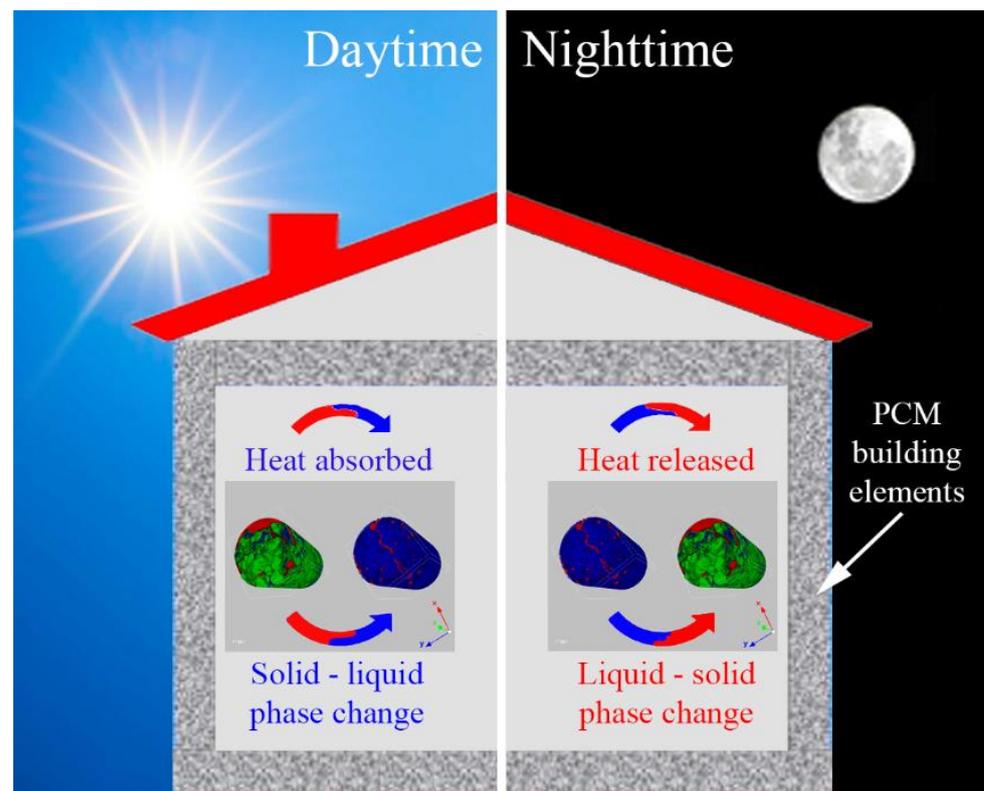


Figure 4. Charging process (working of PCM during daytime) and discharging process (working of PCM during nighttime).

5.1.1. PCMs in Wall

The most general and effective solution for building energy saving is the incorporation of PCM into constructional materials that are applied either to the internal or the external surface of the walls. PCMs can be integrated into mortars, gypsum boards, concrete blocks, bricks, and panels.

Mortars and Plasters

Mortars and plasters have been thoroughly investigated for PCM applications due to their use as coating materials for most of the building surfaces, along with their ability to have different compositions and their low cost. There are different kind of mortars, depended on the binder, such as gypsum, lime, and cement mortars [14]. The research that has been carried out about integration of PCMs in mortars and plasters is mostly about encapsulated PCMs, which involve high costs. As Cunha et al. [85] reported, nonencapsulated PCMs incorporated into mortar do not cause any significant enhancement to the mortar's properties. On the other hand, there are many studies showing that encapsulated PCMs into mortar and plaster have notable results for energy storage.

Sandra Cunha et al. [86] investigated the effects on mechanical, physical, and thermal properties of four different innovative mortars, by the direct integration of pure PCM. The physical and mechanical properties were affected, for example water absorption was reduced and mechanical strength was significantly changed above 10% of PCM. Thermal behavior amplifies in proportion with PCM amount. A total of 20% of PCM showed very efficient thermal performance and mechanical properties suitable for interior mortar application. Cynthia Guardia et al. [87] incorporated an encapsulated PCM to cement-lime mortar and studied both its thermal and mechanical properties. The addition of 10% and 20% of the PCMs remarkably increased the thermal properties for energy storage, while decreased the mechanical properties within the permissible limits. Hamed Abbasi Hattan et al. [88] studied the integration of polyethylene glycol (PEG) shape-stabilized

in silica fume PCM in cement mortar for plastering building external brick walls. The experiment included thermal performance tests on outdoor temperature walls in two different cities. The thermal performance of the mortar was high, and the demands could be fulfilled without incorporating an amount of PCM that could cause decrease in mechanical strength, density, and water absorption.

Gypsum Boards

Another constructional element that can be used for TES are gypsum boards. The implementation of PCM technology into gypsum boards has been studied since 1990 because gypsum boards are low-cost and they are used widely in plenty of constructional applications. Srinivasaraonaik et al. [89] incorporated microencapsulated PCMs into gypsum mixture for gypsum boards. The addition of PCMs caused reduction in the compressive and flexural strength, while the porosity of the gypsum composites increased. As long as it concerns the thermal properties, thermal conductivity of the gypsum composites decreased in proportion with the amount of PCM incorporation. Similar results were obtained from the integration of graphene oxide microencapsulated PCM composites [73]. Additionally, in another study, Juan Pablo Bravo et al. [90] modified gypsum boards with a paraffinic microencapsulated PCM (20 wt%) and implemented a two-month enclosure test. The results were analyzed in a computer simulation program and they showed that microencapsulated PCMs with phase change temperature from 26.5 °C to 29.2 °C allow the charge and discharge of the material and, thus, the provision of indoor thermal comfort.

Concrete Blocks and Bricks

Another technology that has been investigated is the incorporation of PCMs into building elements such as concrete blocks and bricks. Vinh Duy Cao et al. [91] incorporated microencapsulated PCMs in Portland cement and in geopolymer concrete. The results obtained from thermal and mechanical analysis show that latent heat capacity increases, while thermal conductivity and compressive strength decreases, in proportion with the conciseness of PCMs. The addition of 3.2 wt.% and 2.7 wt.% to Portland cement and geopolymer concrete, respectively, can reduce the power consumption of the building in 23 °C by 11% and 15%, respectively. PCMs can also be successfully incorporated in bricks. Rajat Saxena et al. [92] integrated eicosane and OM35 PCMs into bricks. The results show an essential reduction of temperature fluctuation (4.5 °C to 7 °C) between incorporated and conventional bricks. A recent study from Mahmudul Hasan Mizan et al. [93] investigated the enhancement of interfacial bonding between concrete and PCM. The experiment included the preparation of 36 specimens with different surface preparation techniques each. The strength improvement was achieved by using silica fume.

PCM Panels and Wallboards

There are numerous applications of panels and wallboards of incorporated PCMs with conventional construction materials. In addition, there has also been research for the manufacturing of panels and wallboards of different materials, such as polymers [94,95] and metals [96]. Hang Yu et al. [97] investigated the fabrication of diatomite-based form-stable composite PCM wallboard for external building walls. Sayilacksha Gnanachelvam et al. [98] studied the utilization of tree wallboards (gypsum plasterboard, fiber cement board, and magnesium sulphate board) and a bio-PCM mat as fire resistant wallboards for their application to light-gauge steel-framed (LSF) wall systems made of cold-formed steel studs. Gypsum plasterboards provide better fire resistance than the other wallboards, and fiber cement boards provided the lowest. Behzad Maleki et al. [99] investigated the fabrication of plaster wallboards enhanced with nanocapsules with CuO nanoparticles. The PCM plaster wallboard reduced the thermal load of building by 13.83%.

5.1.2. Floor Applications

Building floors are another area where PCM technology can be applied for energy saving by thermal regulation. The applications that have been investigated for floor solutions are very varied. The addition of PCMs in the construction can be by adding a single layer of PCM [100,101] or by adding a multilayer of different types of PCMs [102,103]. Additionally, another approach is the development of floor panels with capillary network for PCM circulation [104], or the use of PCMs along with an electrical powered system for diminishing the demanded energy consumption [105]. Finally, PCMs can also be integrated in the raw materials used for construction, such as concrete [91]. Wanchun Sun et al. [84] investigated the thermal performance of a double-layer PCM radiant floor system containing two types of inorganic composite PCMs. The composites PCMs used were $\text{Na}_2\text{HPO}_4 \bullet 12\text{H}_2\text{O}@\text{EG}$ and $\text{CaCl}_2 \bullet 6\text{H}_2\text{O}@\text{EG}$. During winter, the thermal comfort lasted 2.2 times more than the reference room, which contained pebbles in the floor. During the summer, the thermal comfort lasted 1.7 times more. In both cases, the system can achieve shifting of the peak load. Shilei Lu et al. [86] studied the manufacturing of a PCM floor heating system consisting of a double pipe with three different modules. Regardless of the module, indoor thermal comfort was achieved. The average indoor temperature fluctuation was 1.8–3.0 °C.

5.1.3. Ceiling Applications

The development of ceiling solutions based on PCM technology has also been a field of research. There are many approaches for PCM ceiling applications, such as the incorporation of PCM ceiling panels into the roof construction [106,107], the development of ceiling panels with capillary network for PCM circulation [108], and the coupling of PCM technology with other technologies [109,110]. Mariana Velasco-Carrasco et al. [106] investigated the thermal performance of three different PCM blister panels for ceiling tiles application. The PCM used was INERTEK 23. The PCM was incorporated in three blister panels, two of which were enhanced with the addition of aluminum and steel wool particles, respectively. The panels were embedded between the roof slabs. The results obtained showed that the overall thermal performance of the aluminum- and steel-wool-particle-enhanced panels was improved, especially in the case of steel wool particles. Shilei Lu et al. [109] developed an innovative building cooling system of PCM ceiling coupled with earth-air heat exchanger (EAHE). The evaluation of experimental methods and data analysis indicated that indoor room temperature with this system could reduce peak temperature by 2.1 °C under 8-h timed cold storage experiment and 2.7 °C under 12-h timed cold storage experiment. Hansol Lim et al. [110] proposed a PCM integrated thermoelectric radiant cooling panel, which consists of thermoelectric modules, heat sinks, insulation, and PCM layer between two aluminum panels. The PCM layer provides passive cooling by freezing the PCM during the operation period for shifting the electrical load to the off-peak period demand periods.

5.1.4. Windows and Glazed Applications

Modern building designs contain large, glazed areas such as windows, glazed façade, and, sometimes, glazed roof, as they allow natural room lighting and vision, although glazing materials have very poor thermal performance which leads to increased energy consumption of the building. This indicates the necessity of expanding the PCM technologies for thermal energy storage to glazed materials also. Applications of PCM technology in glazed materials has been investigated. Changyu Liu et al. [82] studied the optical and thermal performance of a PCM-filled glazed unit in comparison with an air-filled glazed unit. The thermal performance of the PCM filled unit was highly improved, although the optical properties were degraded as the transparency was very low, especially when the PCM was at the liquid phase. An important factor to this matter is the thickness of the PCM in the glazed unit. Increased thickness improves the thermal performance but decreases the transparency. In this study it was found that the thickness should not be more than 16

mm in order to satisfy both thermal and optical demands. Corresponding study was held in reference [111–113].

6. Conclusions

A thermal energy storage system is a type of a sustainable energy storage system that is based on the utilization of materials that can store thermal energy when increasing their temperature and release it when the temperature is reduced. Latent heat storage systems using PCM are based on the absorption or release of heat that takes place during the material's phase transition (latent heat of fusion). There is a wide variety of compounds that are used as phase PCMs. For building applications, solid-liquid PCMs are preferred because of their ability to absorb and release large amounts of energy within a narrow range of temperature. Solid-liquid PCMs utilized in buildings can be classified into three major groups: organic compounds, inorganic compounds, and eutectics of organic and/or inorganic compounds. Organic PCMs gather the most advantageous properties.

The fabrication of composite PCMs enhances the thermal conductivity, thermal stability, and heat transfer rate, as well as impedes the leakage of the liquid phase. The encapsulated PCMs are composed of the core material (PCM) and the shell material, which can be inorganic or organic. A core-shell composite can have single or several cores within the capsule and multiple shells. The PCMs can be characterized by their size. The most interesting encapsulated PCMs are microencapsulated and nanoencapsulated PCMs, as the higher surface area per volume unit facilitates the thermal transfer and leads to better thermal performance. Encapsulation can be achieved with physical, chemical, or physico-chemical methods. The most widely-used methods for micro- and nanoencapsulation are chemical methods, such as emulsion, interfacial, and suspension polymerization, and by the physicochemical sol-gel technique.

Form-stable, or shape-stabilized, PCMs consist of a 3D matrix, or a porous structure, where the pure PCMs are entrapped. In polymer-based form-stable PCM composites, the PCM is entrapped inside a cross-linked polymer matrix. The synthesis of the polymer matrix can be achieved with many different methods, providing structural diversity and, as a result, the ability of fabricating a product with special specifications. Form-stable PCMs can also be fabricated with inorganic mineral porous materials, as well as with expanded graphite and perlite.

Thermal conductivity in a TES system is a very important factor for the efficiency of energy storing and releasing. As a result, the enhancement of thermal conductivity of PCMs is requisite. The improvement of thermal conductivity can be achieved with encapsulation, addition of highly-thermal-conductive materials such as carbon-based nanomaterials, metallic or inorganic nanoparticles, and the fabrication of form-stable PCM.

The application of TES systems in the building sector is a promising technology with many advantages. TES systems applied in buildings can be either active or passive. Active TES systems are characterized by forced convection heat transfer and, in some cases, also mass transfer. On the other hand, passive TES systems aim to create or maintain comfort conditions in the building, exploiting naturally-available energy sources, such as the solar energy or the wind, along with architectural design of building components. The main characteristic of these systems is that there is no requirement for mechanical equipment or additional energy due to the fact that the heat is charged or discharged only because of temperature fluctuations when the environment's temperature rises or falls beyond the PCM's phase change temperature.

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