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Paraffin as Phase Change Material

Amir Reza Vakhshouri

Abstract

Nowadays, numerous problems, including the environmental problem caused by fossil fuels, have led to greater attention to the optimal use of energy and the development of renewable energy. One of the most important parts of using energy efficiently is storing it. Among the many ways introduced for energy storage, thermal energy storage, including latent heat, is among the most interesting. This storage is done with materials called phase change materials (PCMs). These materials store the energy in the form of latent heat at constant temperature during the phase transition, discussed in this chapter, and release the same stored energy in the crystallization process. These materials are mainly classified into three categories: organic, inorganic, and eutectics. Today, these materials are widely used with different properties in a variety of fields. Paraffin is one of the most important organic PCMs due to its numerous advantages that will be discussed in the following sections. From the methods of using paraffinic PCMs, two main methods, encapsulation and shape-stable PCMs, are discussed in detail. On the whole, this chapter of the book attempts to briefly discuss paraffins and their unique role in thermal energy storage systems as phase change materials.

Keywords: phase change materials, paraffin, encapsulations, shape-stable PCMs, thermal conductivity

1. Introduction

There may not be a precise background to the first discovery and application of phase change materials (PCMs). Perhaps, from the earliest days where human has acquired the intellect, he has realized the existence of these substances or, maybe, has used them without recognizing their nature. Throughout science and technology evolution, more precisely, since the heat capacity of materials and sensible or latent heats have been known, their ability to store and release thermal energy has also been considered. However, A. T. Waterman submitted the first report of discovery in the early 1900s. In recent years, scientists have paid particular attention to these materials, and their commercialization began from those years.

Perhaps the main reason for this attention was the problems caused by energy mismanagement and improper use of it. Today, inadequate energy management, especially fossil fuels, has caused many environmental and economic problems. Therefore, the necessity of efficient energy demand as well as development of renewable energies and energy storage systems is highly significant. One of the important topics in this field is the design of special energy storage equipment to other types. Energy storage not only reduces the discrepancy between energy supply and demand but also indirectly improves the performance of energy generation

systems as well as plays a vital role in saving of energy by converting it into other reliable forms. Hence, this matter saves high-quality fuels and reduces energy wastes [1–3].

2. Phase change materials: an overview

Energy storage is one of the important parts of renewable energies. Energy can be stored in several ways such as mechanical (e.g., compressed air, flywheel, etc.), electrical (e.g., double-layer capacitors), electrochemical (e.g., batteries), chemical (e.g., fuels), and thermal energy storages [4].

Among several methods of energy storage, thermal energy storage (TES) is very crucial due to its advantages. TES is accomplished by changing the internal energy of materials, such as sensible heat, chemical heat, latent heat, or a combination of them.

In sensible heat storage (SHS) systems, heat can be stored by increasing the temperature of a material. Hence, this system exploits both the temperature changes and the heat capacity of the material to store energy. The amount of heat stored in this system depends on the specific heat, temperature differences, and amount of material; thus it requires a large amount of materials, whereas Latent heat storage (LHS) is generally based on the amount of heat absorbed or released during the phase transformation of a material. Lastly, In the chemical heat storage (CHS), heat is stored by enthalpy change of a chemical reaction.

Among the aforementioned heat storage systems, the LHS is particularly noteworthy. One of the special reasons is its ability to store large amount of energy at an isothermal process [5–7].

2.1 Phase change materials as thermal energy storage

Any high-performance LHS system should contain at least one of the following terms:

- Appropriate PCM with optimum melting temperature range

- Desirable and sufficient surface area proportional to the amount of heat exchange

- Optimal capacity compatible with PCM

Phase change materials perform energy storage in LHS method. In this case, a material during the phase change absorbs thermal energy from surrounding to change its state, and in the reverse process, the stored energy is released to the surrounding. PCMs initially behave likewise to other conventional materials as the temperature increases, but energy is absorbed when the material receives heat at higher temperatures and close to the phase transformation. Unlike conventional materials, in PCMs absorption or release of thermal energy is performed at a constant temperature. A PCM normally absorbs and releases thermal energy 5–14 times more than other storage materials such as water or rock [8, 9].

PCMs can store thermal energy in one of the following phase transformation methods: solid-solid, solid-liquid, solid-gas, and liquid-gas. In the solid-solid phase change, a certain solid material absorbs heat by changing a crystalline, semicrystalline, or amorphous structure to another solid structure and vice versa [10]. This type of phase change, usually called phase transitions, generally has less latent heat

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and smaller volume change comparing to the other types. Recently, this type of PCM has been used in nonvolatile memories [11].

Solid-liquid phase change is a common type of commercial PCMs. This type of PCM absorbs thermal energy to change its crystalline molecular arrangement to a disordered one when the temperature reaches the melting point. Unlike solid-solid, solid-liquid PCMs contain higher latent heat and sensible volumetric change. Solid-gas and liquid-gas phase changes contain higher latent heat, but their phase changes are associated with large volumetric changes, which cause many problems in TES systems [8]. Although the latent heat of solid-liquid is less than liquid-gas, their volumetric change is much lower (about 10% or less). Therefore, employing PCMs based on solid-liquid phase change in TES systems would be more economically feasible.

The overall classification of energy storage systems as well as phase change materials is given in **Figure 1**.
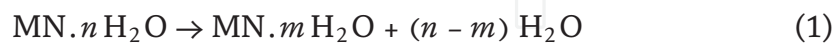
2.2 Classification of phase change materials

As mentioned in the previous section, despite the high thermal energy absorption capacity, PCMs in liquid-gas and solid-gas transitions have extremely high volume changes. On the other hand, solid-solid PCMs also have a lower thermal energy storage capacity. Therefore, the abovementioned PCMs, with the exception of specific cases, have not received much attention to commercialization. Currently, the most common type of transition that has been mass-marketed is solid-liquid PCMs. The classification of phase change materials is schematically given in **Figure 1**. Solid-liquid PCMs are generally classified as three general organics, inorganic, and eutectics [12, 13]. However, in some references they are classified into two major organics and inorganics.

2.2.1 Inorganic PCMs

Inorganic PCMs mainly have high capacity for thermal energy storage (about twice as much as organic PCMs) as well as have higher thermal conductivity. They are often classified as salt hydrates and metals.

Salt hydrates are the most important group of inorganic PCMs, which is widely employed for the latent heat energy storage systems. Salt hydrates are described as a mixture of inorganic salts and water (AB × nH$_2$O). The phase change in salt hydrates actually involves the loss of all or plenty of their water, which is roughly equivalent to the thermodynamic process of melting in other materials.

$$\mathrm{MN}.n\,\mathrm{H_2O} \rightarrow \mathrm{MN}.m\,\mathrm{H_2O} + (n-m)\,\mathrm{H_2O} \tag{1}$$

$$\mathrm{MN}.n\,\mathrm{H_2O} \rightarrow \mathrm{MN} + n\,\mathrm{H_2O} \tag{2}$$

At the phase transition, the hydrate crystals are subdivided into anhydrous (or less aqueous) salt and water. Although salt hydrates have several advantages, some deficiencies make restrictions in their application. One of these problems is incongruent melting behavior of salt hydrates. In this problem the released water from dehydration process is not sufficient for the complete dissolution of the salts. In this case, the salts precipitate and as a result phase separation occurs. In order to prevent this problem, an additional material such as thickener agent is added to salt hydrates. Another major problem with salt hydrates is the supercooling phenomenon. In this phenomenon, when crystallization process occurs, the nucleus
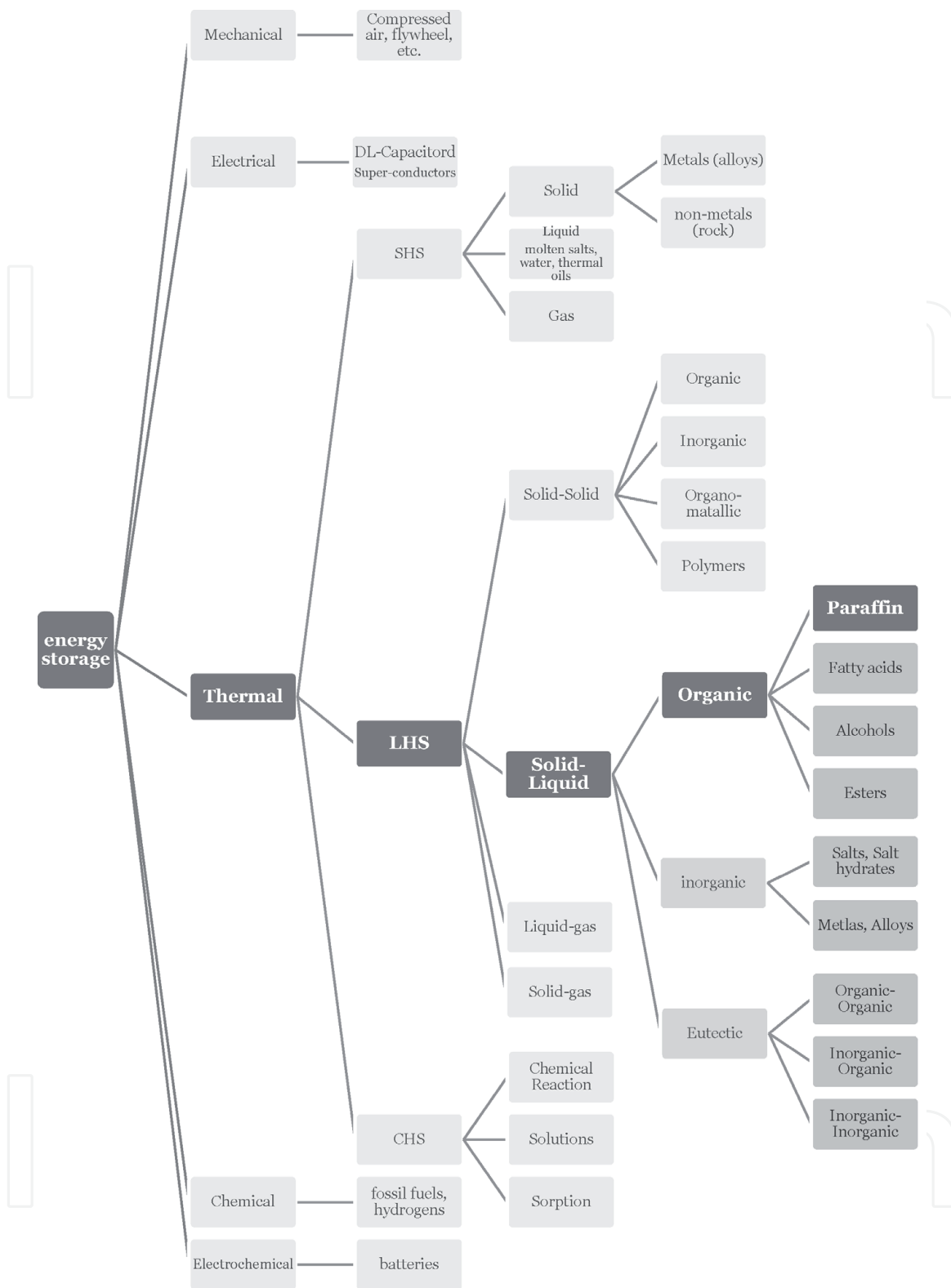
Figure 1.
Overview of energy storage and classification of phase change materials.

formation is delayed; therefore, even at temperatures below freezing, the material remains liquid [7, 11, 14].

Overall, the most attractive properties of salt hydrate are (i) high alloy latent temperature, (ii) relatively high thermal conductivity (almost two to five times more than paraffin), and (iii) small volume changes in melting. They are also very low emitting and toxic, adaptable to plastic packaging, and cheap enough to use [15].

Metals are another part of the inorganic PCMs. Perhaps the most prominent advantages of metals are their high thermal conductivity and high mechanical

properties. Metals are available over a wide range of melting temperatures. They are also used as high-temperature PCMs.

Some metals such as indium, cesium, gallium, etc. are used for low-temperature PCMs, while others such as Zn, Mg, Al, etc. are used for high temperatures. Some metal alloys with high melting points (in the range of 400–1000°C) have been used for extremely high temperature systems. These metal alloys as high-temperature PCMs can be used in the field of solar power systems [16, 17]. They can also be used in industries that require temperature regulation in furnaces or reactors with high operating temperatures.

2.2.2 Organic PCMs

Perhaps the most important fragment is the organic PCMs. Organic PCMs show no change in performance or structure (e.g., phase separation) over numerous phase change cycles. In addition, supercooling phenomena cannot be observed in organic PCMs. The classification of organic PCMs is unique. This division is mainly based on their application contexts. In general, they are classified into two major paraffin and non-paraffin sections.

Paraffins are the most common PCMs. Since this book is about paraffin, to avoid duplication, this section will briefly discuss the chemistry (structure and properties) of paraffin, but their ability as phase change materials will be reviewed in detail.

Non-paraffinic organic PCMs are known to be the most widely used families. In addition to their different properties compared to paraffins, they have very similar properties to each other. Researchers have used various types of ether, fatty acid, alcohol, and glycol as thermal energy storage materials. These materials are generally flammable and less resistant to oxidation [18–20].

Although non-paraffin organic PCMs have high latent heat capacity, they have weaknesses such as flammability, low thermal conductivity, low combustion temperatures, and transient toxicity. The most important non-paraffinic PCMs are fatty acids, glycols, polyalcohols, and sugar alcohols.

Fatty acids $[CH_3(CH_2)_{2n}COOH]$ also have high latent heat. They can be used in combination with paraffin. Fatty acids exhibit high stability to deformation and phase separations for many cycles and also crystallize without supercooling. Their main disadvantages are their costs. They are 2–2.5 times more expensive than technical grade paraffins. Unlike paraffins, fatty acids are of animal or plant origin. Their properties are similar to those of paraffins, but the melting process is slower. On the other hand, they are moderately corrosive as well as generally odorous [21].

2.2.3 Eutectics

A eutectic contains at least two types of phase change materials. Eutectics have exceptional properties. In eutectics, the melting-solidification temperatures are generally lower than the constituents and do not separate into the components through the phase change. Therefore, phase separation and supercooling phenomena are not observed in these materials.

Eutectics typically have a high thermal cycle than salt hydrates. Inorganic-inorganic eutectics are the most common type of them. However, in recent studies, organic-inorganic and organic-organic varieties have received more attention. The major problem of eutectics is their commercialization. Their cost is usually two to three times higher than commercial PCMs [22, 23].

Some of the above PCMs and their thermal properties, which are competitive with paraffins in terms of latent heat capacity, are summarized in **Table 1**.

Type of PCMs		Materials	Melting point (°C)	Latent heat (kJ/kg)	Density[*] (kg/m^3)	Thermal conductivity (W/mK)[**]	Ref.
Inorganic salt hydrates		LiClO$_3$·3H$_2$O	8	253	1720		[24, 25]
		K$_2$HPO$_4$·6H$_2$O	14	109			[24]
		Mn(NO$_3$)$_2$·6H$_2$O	25.8	126	1600		[14, 25]
		CaCl$_2$·6H$_2$O	29.8	191	1802	1.08	[24, 25]
		Na$_2$CO$_3$·10H$_2$O	32–34	246–267			[14, 24]
		Na$_2$SO$_4$·10H$_2$O	32.4	248, 254	1490	0.544	[14, 26]
		Na$_2$HPO$_4$·12H$_2$O	34–35	280	1522	0.514	[15, 26]
		FeCl$_3$·6H$_2$O	36–37	200, 226	1820		[25, 26]
		Na$_2$S$_2$O$_3$·5H$_2$O	48–49	200, 220	1600	1.46	[15, 26]
		CH$_3$COONa·3H$_2$O	58	226, 265	1450	1.97	[15, 26]
Non-paraffinic organic PCMs	Fatty acids	Formic acid	8.3	247	1220	—	[1, 25]
		n-Octanoic acid	16	149	910	0.148	[21, 27]
		Lauric acid	43.6	184.4	867		[21, 25]
		Palmitic acid	61.3	198	989	0.162	[21, 27]
		Stearic acid	66.8	259	965	0.172	[21, 25]
	Polyalcohols	Glycerin	18	199	1250	0.285	[1, 25]
		PEG E600	22	127.2	1126	0.189	[27]
		PEG E6000	66	190	1212		[27]
		Xylitol	95	236	1520	0.40	[28]
		Erythritol	119	338	1361	0.38	[28]
	Others	2-Pentadecanone	39	241			[1, 25]
		4-Heptadekanon	41	197			[1, 25]
		D-Lactic acid	52–54	126, 185	1220		[1, 25]

Type of PCMs		Materials	Melting point (°C)	Latent heat (kJ/kg)	Density* (kg/m^3)	Thermal conductivity (W/mK)**	Ref.
Eutectics	O-O, O-I, I-I ***	$CaCl_2 \cdot 6H_2O$ + $MgCl_2 \cdot 6H_2O$	25	127	1590		[27]
		$Mg(NO_3)_2 \cdot 6H_2O$ + $MgCl_2 \cdot 6H_2O$	59	144	1630	0.51	[27]
		Trimethylolethane + urea	29.8	218			[21]
		$CH_3COONa \cdot 3H_2O$ + Urea (60:40)	31	226			[27]
	Metals	Mg-Zn (72:28)	342	155	2850	67	[16, 17]
		Al-Mg-Zn (60:34:6)	450	329	2380		[16, 17]
		Al-Cu (82:18)	550	318	3170		[16, 17]
		Al-Si (87.8:12.2)	580	499	2620		[16, 17]

*At 20°C.
**Just above melting point (liquid phase).
***Inorganic-inorganic (I-I), organic-inorganic (O-I), and organic-organic (O-O).

Table 1.
Thermophysical properties of some common PCMs with high latent heat.

3. Paraffin-based phase change materials

Paraffin is usually a mixture of straight-chain *n*-alkanes with the general formula CH_3-$(CH_2)_n$-CH_3. However, in some cases, paraffin is used as another name for alkanes. Gulfam R. et al. in their article have classified paraffins based on the number of carbon atoms as well as their physical states. According to this classification, at room temperature, 1–4 numbers of carbons refer to pure alkanes in a gas

Materials	Melting point (°C)	Latent heat (kJ/kg)	Density* (kg/m³)	Thermal conductivity** (W/mK)
n-Tetradecane (C$_{14}$)	6	228–230	763	0.14
n-Pentadecane (C$_{15}$)	10	205	770	0.2
n-Hexadecane (C$_{16}$)	18	237	770	0.2
n-Heptadecane (C$_{17}$)	22	213	760	0145
n-Octadecane (C$_{18}$)	28	245	865	0.148
n-Nonadecane (C$_{19}$)	32	222	830	0.22
n-Eicosane (C$_{20}$)	37	246		
n-Henicosane (C$_{21}$)	40	200, 213	778	
n-Docosane (C$_{22}$)	44.5	249	880	0.2
n-Tricosane (C$_{23}$)	47.5	232		
n-Tetracosane (C$_{24}$)	52	255		
n-Pentacosane (C$_{25}$)	54	238		
n-Hexacosane (C$_{26}$)	56.5	256		
n-Heptacosane (C$_{27}$)	59	236		
n-Octacosane (C$_{28}$)	64.5	253		
n-Nonacosane (C$_{29}$)	65	240		
n-Triacontane (C$_{30}$)	66	251		
n-Hentriacontane (C$_{31}$)	67	242		
n-Dotriacontane (C$_{32}$)	69	170		
n-Triatriacontane (C$_{33}$)	71	268	880	0.2
Paraffin C$_{16}$-C$_{18}$	20–22	152		
Paraffin C$_{13}$-C$_{24}$	22–24	189	900	0.21
RT 35 HC	35	240	880	0.2
Paraffin C$_{16}$-C$_{28}$	42–44	189	910	
Paraffin C$_{20}$-C$_{33}$	48–50	189	912	
Paraffin C$_{22}$-C$_{45}$	58–60	189	920	0.2
Paraffin C$_{21}$-C$_{50}$	66–68	189	930	
RT 70 HC	69–71	260	880	0.2
Paraffin natural wax 811	82–86	85		0.72 (solid)
Paraffin natural wax 106	101–108	80		0.65 (solid)

*At 20°C.
**Just above melting point (liquid phase).

Table 2.
Thermophysical properties of n-paraffins and commercial paraffinic PCMs [1, 24, 25].

phase, 5–17 carbons are liquid paraffins, and more than 17 is known as solid waxes. These waxy solids refer to a mixture of saturated hydrocarbons such as linear, iso, high branched, and cycloalkanes [29]. Generally, paraffin-based PCMs are known as waxy solid paraffins. Commercial paraffins contain mixture of isomers, and therefore, they have a range of melting temperatures.

Paraffins typically have high latent heat capacity. If the length of the chain increases, the melting ranges of waxes also increase, while the latent heat capacity of melting is not subject to any particular order (**Table 2**).

In general, paraffin waxes are safe, reliable, inexpensive, and non-irritating substances, relatively obtained in a wide range of temperatures. As far as economic issues are concerned, most technical grade waxes can be used as PCMs in latent heat storage systems. From the chemical point of view, paraffin waxes are inactive and stable. They exhibit moderate volume changes (10–20%) during melting but have low vapor pressure.

The paraffin-based PCMs usually have high stability for very long crystallization-melting cycles. **Table 2** illustrates the thermal properties of some paraffin waxes.

Besides the favorable properties, paraffins also show some undesirable properties such as low thermal conductivity, low melting temperatures, and moderate-high flammability. Some of these disadvantages especially thermal conductivity and flammability can be partially eliminated with the help of additives or paraffin composites.

4. Methods for using paraffin-based PCMs (PPCMs)

Measures must be taken to make the solid-liquid PCMs usable. For this purpose, there are several methods for stabilizing the shapes of paraffinic PCMs. Two main methods of them are discussed below.

4.1 Encapsulation of PPCMs

Encapsulation is generally a worthy method to protect and prevent leakage of PCMs in the liquid state. The capsules consist of two parts, the shell and the core. The core part contains PCMs, whereas the shell part is usually composed of polymeric materials with improved mechanical and thermal properties. The shell part plays the role of protection, heat transfer, and sometimes preventing the release of toxic materials into the environment. In these cases, the shell must have appropriate thermal conductivity. Polymeric shells are also commonly used in encapsulating PPCMs. The choice of core part depends on its application field. The encapsulation of PPCMs is classified into three major parts: bulk or macroencapsulation, microencapsulation, and nano-encapsulation.

Macroencapsulation is one of the simplest ways to encapsulate paraffins. This method has a lower cost than other methods. These products are used in transportation, buildings, solar energy storage systems, and heat exchangers. Sometimes metals are also used as shell materials [30].

In order to increase the efficiency of heat transfer in these types of capsules, either the size of the capsules should be appropriately selected or suitable modifiers should be used. In general, the smaller the diameter of spherical capsules or cylinders, the better the heat transfer. In some cases, metal foams are used to improve the heat transfer properties of paraffin. Aluminum and copper open-cell foams are among the most studied, whereas, in other cases metal oxides, metals and graphite are used [30, 31].

There are various forms of macroencapsulation, such as ball shape, spherical shape, cylindrical, flat sheets, tubular, etc. [31]. Cylindrical tubes are one of the famous forms of macroencapsulated PPCMs. This type of encapsulation is most commonly used in buildings or in solar energy storage systems.

Most of the research carried out on macroencapsulated PPCMs has been focused on improving their thermal conductivity. In one of these studies, different metal oxide nanoparticles such as aluminum oxide, titanium oxide, silicon oxide, and zinc oxide were used to improve the thermal conductivity of paraffin. The results show that titanium oxide performs better under the same conditions than the other oxides [32]. In a similar study, copper oxide nanoparticles were used to improve thermal conductivity and performance of paraffin in solar energy storage systems [33]. In some studies, graphite flakes and expanded graphite have also been used as improving agent for heat conductivity [31].

Hong et al. have used polyethylene terephthalate pipes as a shell for paraffin. In this macroencapsulated system, introduced as cylinder modules, float stone has been added to paraffin as an enhancer of thermal conductivity. In this study, the effect of various parameters such as pipe diameter on heat transfer is investigated, and the results of experimental section are compared with modeling [34].

D. Etansova et al. studied numerical computation and heat transfer modeling of paraffin-embedded stainless steel macroencapsulates for use in solar energy storage systems. In this study, the effect of geometric size and shape on heat transfer was investigated [35].

Microencapsulation of PCMs is another suitable way to improve efficiency and increase thermal conductivity. The size of the microencapsulates usually ranges from 1 μm to 1 mm. Microencapsulation of paraffins is a relatively difficult process, but it performs better than macroencapsulates. This is due to increased contact surface area, shorter discharge and loading times, and improved thermal conductivity. Different materials are used for the shell part of the microencapsulates.

In general, there are two major physical and chemical methods for microencapsulation. The most important physical methods are fluidized bed, spray dryer, centrifuge extruder, and similar processes. However, chemical methods are often based on polymerization. The most important techniques include in situ suspension and emulsion polymerization, interfacial condensation polymerization, and sol-gel method. The latter is sometimes known as the physicochemical method [12, 29].

In the suspension or emulsion polymerization method, the insoluble paraffin is first emulsified or suspended in a polar medium, which is predominantly aqueous phase, by means of high-speed stirring. Surfactants are used to stabilize the particles. Then, lipophilic monomers are added to the medium, and the conditions are prepared for polymerization. This polymer, which is insoluble in both aqueous and paraffin phases, is formed on the outer surface of paraffin particles and finally, after polymerization, encapsulates the paraffin as a shell. The size of these capsules depends on the size of emulsion or suspension of paraffin droplets. Sometimes certain additives are added to the medium to improve some of the polymer properties. For instance, in some studies, polyvinyl alcohol (PVA) has been added to the medium with methyl-methacrylate monomer, which is known as one of the most important shell materials. As a result, paraffin has been encapsulated by PVA modified polymethyl methacrylate (PMMA). Adding this modifier forms a smooth surface of the microencapsulates [36, 37].

In the interfacial method, soluble monomers in the organic phase with other monomers in the aqueous phase at the droplet interface form a polymer that precipitates on the outer layer of the organic phase.

The sol-gel method is a multi-step procedure. In this method, firstly, an organosilicon compound such as tetraethoxysilane (TEOS) is hydrolyzed in an

acidic medium at low pH. The prepared homogenous solution is known as the sol part. Then, the paraffin emulsion is prepared in an aqueous medium and stabilized by special emulsifiers. Actually, these emulsifiers are the first layer of the shell. Subsequently, the sol solution is slowly added to the aqueous phase containing paraffin. The silicon compounds containing OH groups (silanols) form hydrogen bonding with polar side of emulsifiers, and finally the condensation process is carried out on the first layer interface. As a result, paraffin microencapsulates with an inorganic material that is often silica. Silica is one of the significant materials used as a shell for micro and nano-encapsulation. Silica has high thermal conductivity and on the other hand has better mechanical properties than some polymers [38–41].

As mentioned, most of the materials used to microencapsulation are polymers. The main polymers used as shell materials are polymethyl methacrylate [42], polystyrene [43], urea-formaldehyde [44], urea-melamine-formaldehyde [45], polyaniline [46], etc. However, in many cases, these polymers are used in modified form. For example, polymethyl methacrylate modified with polyvinyl alcohol or with other methacrylates [36, 37], polystyrene copolymers [47], and melamine modified-formaldehyde with methanol [48] can be considered. **Table 3** shows the most common polymers used as shell materials.

In addition to the aforementioned microencapsulation approaches, which mainly form polymeric materials as shells, other materials have been also recommended. For example, Singh and colleagues have used silver metal as a shell for paraffin microencapsulates. They first emulsified paraffin into small particles in water and then converted silver salts to metallic silver via an in situ reduction reaction. The average particle size of 329 μm has been reported, and the thermal properties of paraffin have been investigated using DSC and TGA. This type of metal shell microencapsulates has been suggested for use in microelectronics heat management systems [49].

There are several techniques to study the properties of micro and nano-encapsulates. In all studies, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) have been used to determine the thermal properties of PPCMs, such as enthalpy of fusion, melting temperature, weight loss, degradation, etc. Various methods such as XRD, FTIR, and ^{12}C NMR have been used to study the structure and chemical composition of PPCMs. The morphology and diameters of the microcapsules have often been studied by scanning electron microscopy (SEM) and particle size analyzer.

The latter technique is used to study the influence of different variables on the diameter of the microcapsules. One of these variables is the effect of stirring speed on emulsification of paraffin. The results of some studies show that higher stirring speed of emulsification process leads to decrease of the mean size of paraffin droplets [48].

Along with studies on the type of microcapsules, many studies have been conducted to improve thermal conductivity and mechanical properties of microencapsulates. Part of these studies has been dedicated to the effect of graphene and graphene oxide on the improvement of thermal conductivity [51]. L. Zhang et al. investigated the effect of graphene oxide on improving the mechanical properties and leakage protection as well as improving the thermal conductivity of melamine-formaldehyde as shell materials of PPCM microencapsulates [52]. In another part of studies, metals and metal oxides have been used. For example, 10 and 20 wt% of nanomagnetite (Fe_3O_4) with particle size from 40 to 75 nm increase the thermal conductivity by 48 and 60%, respectively [53]. Also, addition of TiO_2 and Al_2O_3 nanoparticles in a mass fraction of 5% with respect to PPCM at the size range of 30–60 nm increases the thermal conductivity by 40 and 65%, respectively [54].

Core material PPCM	Shell material	Encapsulation method	Particle size (µm)	Recommended application	Ref
n-Nonadecane	Polymethyl methacrylate	Emulsion	~ 8	Smart building and textiles	[42]
n-Heptadecane	Polystyrene	Emulsion	<2	General fields	[43]
Commercial paraffin wax	Polystyrene-co-PMMA	Suspension	~ 20		[50]
Commercial RT21	PMMA	Suspension	20–40		[36]
Commercial RT21	PMMA modified with PVA	Emulsion	15	Building	[37]
Commercial paraffin wax	Polyaniline	Emulsion	<1		[46]
Commercial paraffin wax	Urea-formaldehyde	In situ	~ 20		[44]
n-Octadecane, n-nonadecane	Urea-melamine-formaldehyde	In situ	0.3-0.6		[45]
Commercial paraffin wax	Methanol-melamine-formaldehyde	In situ	10–30	Building	[48]
Commercial paraffin wax	Silica	Sol-gel	4–10	Textile	[38]
Commercial paraffin wax	Silica	Sol-gel	0.2–0.5		[39]
n-Octadecane	Silica	Sol-gel	7–16		[40]
n-Pentadecane	Silica	Sol-gel	4–8		[41]

Table 3.
Common materials for microencapsulation of PPCMs.

Nano-encapsulation of PPCM is very similar to the microencapsulation process. However, these types of encapsulation specific techniques, such as ultrasonic, are used to adjust the size of the paraffin droplets to less than 1 micron. In the next step, using the chemical methods mentioned in the microencapsulation method, the shell formation is performed. The most common method for nano-encapsulation is the emulsion polymerization method. However, although limited, interfacial and sol-gel methods have also been reported.

4.2 Shape-stable PPCMs

In recent years, research on polymeric matrix-based shape-stable PCMs has gained great importance. Among these types of phase change materials, the paraffin-polymer composite is particularly attractive. The combination of paraffin and polymers as new PCMs with a unique controllable structure can be widely used. This compound remains solid at paraffin melting point and even above without any softening, which is why this type of PCM is called shape-stable. These materials are well formed and have high-energy absorption capacity; hence they can be widely used as stable PCMs with specific properties. On the other hand, some problems such as high cost and difficulty of encapsulating processes could be resolved. Despite these advantages, some common disadvantages such as low thermal stability, low thermal conductivity, and relatively high flammability can restrict their application, particularly in building materials. For this reason, further studies

are required to eliminate these disadvantages and improve the properties of these materials. A large part of research is relevant to increase or improve their thermal conductivity, flame retardation, and thermophysical and mechanical properties. Suitable additives are proposed to improve these properties [55, 56].

In some articles, a simple method involves mixing-melting of polyethylene and paraffin, consequently cooling the composite, or using a simple twin extruder to prepare a shape-stable PCM has been reported [57, 58]. When this compound contains sufficient polymer, a homogeneous mixture remains solid at temperatures above the melting point of paraffin and below the polymer melting point. During the preparation of these composites, no chemical reaction or chemical bonds are formed between the polymers and paraffin; therefore these types of compounds are considered as physical mixtures. Shape-stable PPCMs can be used in all previously described areas. Due to the thermoplastic properties of these composites, it is possible to melt and crystalize them for many cycle numbers. Shape-stable PPCMs have several advantages over other PCMs. They are also nontoxic and do not require high-energy consumption during production process.

Inaba and Tu [59] developed a new type of shape-stable PPCM and determined their thermophysical properties. These materials can be used without encapsulation. Feldman et al. [60] prepared plates of shape-stable PCM and determined their high thermal energy storage capacity when used in small chambers. In this type of polymer-based plates, fatty acids are used as PCMs that absorb or releases large amounts of heat during melting and solidification, without altering the composition of the shape-stable PCM. The same researchers determined the role of polymer-PCM sheets in stabilizing the shape and size of the plates when PCM was liquefied. The composition of paraffin and high-density polyethylene (HDPE) has been studied by Lee and Choi [61] and has been introduced as a shape-stable energy storage material. In this study, the amount of energy stored by the mentioned composites is also studied. They also studied the morphology of the high-density polyethylene crystal lattice (HDPE) and its effect on paraffin through scanning electron microscopy and optical microscopy (OM) analysis. On the other hand, they also reported of high thermal energy storage capacity of the prepared paraffin/HDPE-based shape-stable PCMs. Hong and Xin-Shi [62] synthesized polyethylene-paraffin as a shape-stable PCM and characterized its morphology and structure by scanning electron microscopy and its latent heat of melting by differential scanning calorimetry. In this study, a composition consisting of 75% paraffin as a cheap, effective, easy-to-prepare, low-temperature shape-stable PPCM is recommended. In another study, Xiao et al. [63] prepared a shape-stable PCM based on the composition of paraffin with a thermoplastic elastomer (styrene butadiene rubber) and determined its thermal properties. The obtained results show that the stable mixture has the phase changing property and the amount of latent heat of melting stored in this compound is estimated to be 80% of pure paraffin. In another part of this study, the thermal conductivity of PCMs was significantly increased by using graphite.

Despite the above benefits, some disadvantages of shape-stable PPCMs are also reported. One of the major problems is the softening and paraffin leakage phenomenon at elevated temperatures. Seiler partly resolved this problem by adding a different ratio of silica and copolymers to the polyethylene-paraffin composition [64]. Another problem is the low thermal conductivity of the polyethylene-paraffin compound. A lot of research has been conducted to increase this property. A. Sari [65] prepared two types of paraffin with different melting temperatures (42–44°C and 56–58°C) and combined each with HDPE as phase modifier. By addition of 3% expanded graphite, the thermal conductivity of composites increased by 14 and 24%, respectively. Zhang et al. [66] developed new PCMS based on graphite

and paraffin with high thermal energy storage capacity and high thermal conductivity. Zhang and Ding et al. [67] have used various additives such as diatomite, Wollastonite, organic modified bentonite, calcium carbonate, and graphite to improve the thermal conductivity of shape-stable PCMs.

It should be noted that metal particles and metal oxides due to their higher thermal conductivity are widely used to improve this property of PCMs. One of the materials that has received more attention in recent years is alumina. Aluminum oxide nanoparticles were added to paraffin to increase its thermal conductivity in both liquid and solid states [57, 68]. This compound coupled with its high thermal conductivity is cheaper and more abundant than other metal oxides.

Another problem with shape-stable PPCMs is their flammability. The effect of various additives has been studied by scientists to eliminate this problem. One of the most effective of these substances is halogenated compounds, but they cause environmental pollution and also release toxic compounds while burning. Researchers have used hybrid and environmentally friendly materials to enhance the durability of flame retardant materials. They studied the effect of clay nanoparticles and organo-modified montmorillonite. Adding these materials not only increases their resistance to burning but also increases their mechanical and thermal properties [69–71]. In another study, Y. Cai et al. added paraffin, HDPE, and graphite, then added ammonium polyphosphate and zinc borate separately, and studied their resistance to burning. The results show that the addition of ammonium polyphosphate decreases flammability, while zinc borate increases the flammability risk [72]. One of the most interesting and harmless fire retardant compounds is metal hydroxides, especially aluminum hydroxide, magnesium hydroxide, or their combination [73–75].

Some researchers have used other advanced materials as supporting materials to prepare shape-stable PPCMs instead of using the polymer matrix [76–78]. Rawi et al. used acid-treated multi-walled carbon nanotubes (A-CNT). They reported that adding 5% by weight A-CNT to paraffin decreases 25% of the latent heat while increasing heat conductivity up to 84% [79]. Y. Wan et al. used pinecone biochar as the supporting matrix for PCMs. They prepared shape-stable PCM materials at different ratios and studied the leakage behavior. The optimal ratio is suggested as 60% of the PCM. For the above ratio, no PCM leakage was observed after the melting temperature. The results showed that the thermal conductivity of the same ratio shape-stable PCM increased by 44% compared to the pure PCM [80].

5. Criteria for selection of PCMs and application fields of PPCMs

PCMs are available in a wide range of desired temperature ranges. Obviously, a PCM may not have all the properties required to store heat energy as an ideal material. Therefore, it would be more appropriate to use these materials in combination with either other PCMs or various additives to achieve the required features. However, as latent heat storage materials, while using PCMs, the thermodynamic, kinetic, and chemical properties as well as the economic and availability issues of them must be taken into account. Employed PCMs must have the optimum phase change temperature. On the other hand, the higher the latent heat of the material, the lower its physical size. High thermal conductivity also helps to save and release energy. From the physical and kinetic point of view, the phase stability of PCMs during melting and crystallization contributes to optimum thermal energy storage. Their high density also enables high storage at smaller material sizes. During phase change, smaller volume changes and lower vapor pressures are appropriate for continuous applications.

H. Nazir et al. in their review article [12] have explained the criteria for selection of PCMs as a pyramid. In this pyramid, at the bottom, known as the fundamentals, there are several items such as cost, regularity compliance, and safety. In the next section, the thermophysical properties such as energy storage capacity and runtime are discussed. In the upper section, reliability and operating environment consist of degradation, cycle life, shelf life, and thermal limits are reflected. Finally, at the top section of pyramid, user perception and convenience are located. These criteria help us to find a proper PCM for certain application fields.

These criteria may also be extended to paraffinic PCMs. Nowadays, paraffinic PCMs (PPCMs) are widely used as thermal energy storage materials, including solar energy storage systems, food industries, medical fields, electrical equipment protection, vehicles, buildings, automotive industries, etc. [24, 29, 81–85].

Generally, application fields of PPCMs can be considered in two main sections: thermal protection and energy storage purposes. The major difference between these two areas of application is in thermal conductivity of the PPCMs.

Protection and transportation of temperature-sensitive materials is one the mentioned area. Sometimes a certain temperature is required to transport sensitive medicines, medical equipment, food, etc. In all cases, using of PPCMs would be appropriate as they can regulate and stabilize the temperature over a given range. Similarly, in sensitive electrical equipment, these materials are also essential to prevent the maximum operating temperature. On the other hand, they can be used to prevent possible engine damage at high temperatures [86, 87].

One of the studies related to these issues is the use of paraffin containing heavy alkanes to protect electronic devices against overheating. In this study, paraffin has been used as a protective coating for the resistor chip, and its effect on cooling of the devices has been investigated. Experimental results show that paraffin coating increases the relative duration of overheating by 50 to 150% over the temperature range of 110–140°C [88]. In another study, a mixture of paraffin and polypropylene has been used as an overheating protector in solar thermal collectors [89].

However, *energy storage purposes* are the most important part of PPCM application. In general, PCMs act as passive elements and therefore do not require any additional energy source. Most studies on the application of energy storage properties of PPCMs have been confined to buildings, textiles, and solar systems. In the following, building applications will be further attended.

One of the main drawbacks of lightweight building materials is their low thermal storage capacity, which results in extensive temperature fluctuations as a result of intense heating and cooling. Therefore, PPCMs have been used in buildings due to their ability to regulate and stabilize indoor temperatures at higher or lower outdoor temperatures [90].

Generally, PPCMs in buildings are used as thermal energy storage at daytime peak temperature, and they released the stored energy at night when temperatures are low. The result of this application is to set the comfort condition for a circadian period. This application minimizes the amount of energy consumed for cooling during the day and warming up at night.

In contrast, in order to stabilize the ambient conditions at low temperatures, some special PCMs are also used in air conditioner systems. In this case, cool air is stored during the night and released into the warm hours of the day.

Y. Cui et al. [91] in a review article categorized PPCM application methods based on their location of use such as PCMs in walls, floor heating systems, ceiling boards, air-based solar heating systems, free cooling systems (with ventilation systems), and PCM shutter (in windows). Both types of encapsulation and shape-stable PPCMs could be used in all of the above classification of building applications. Sometimes these materials can be added directly to concrete, gypsum, etc. [90, 92–95].

In order to increase the performance of PPCMs in this application field, great deals of studies have also been done on improving their thermal conductivity. On the other hand, extensive research into safety issues has been done to reduce the flammability of PPCMs by adding flame retardants to these materials.

Overall, these studies cover the importance of using PPCMs in heating and cooling as well as indicate the general characteristics, advantages, and disadvantages of these materials used for thermal storage in buildings.

6. Conclusion

It is clear that at this time, where renewable energy is particularly important, the use of PPCMs is on the rise. As it has been mentioned, PPCMs have many application fields due to their advantages. For example, they can be used in the construction, pharmaceutical and medical industries, textiles, automobiles, solar power systems, transportation, thermal batteries, heat exchangers, and so on.

This chapter of the book has attempted to focus more on how to use paraffins. For this reason, two methods, namely, encapsulation and shape-constant, have been widely discussed. In addition, improving their weak properties such as thermal conductivity and flammability has also been studied. Depending on the benefits of paraffins, new applications are suggested every day. Extensive studies are underway on other new applications in recent years.

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